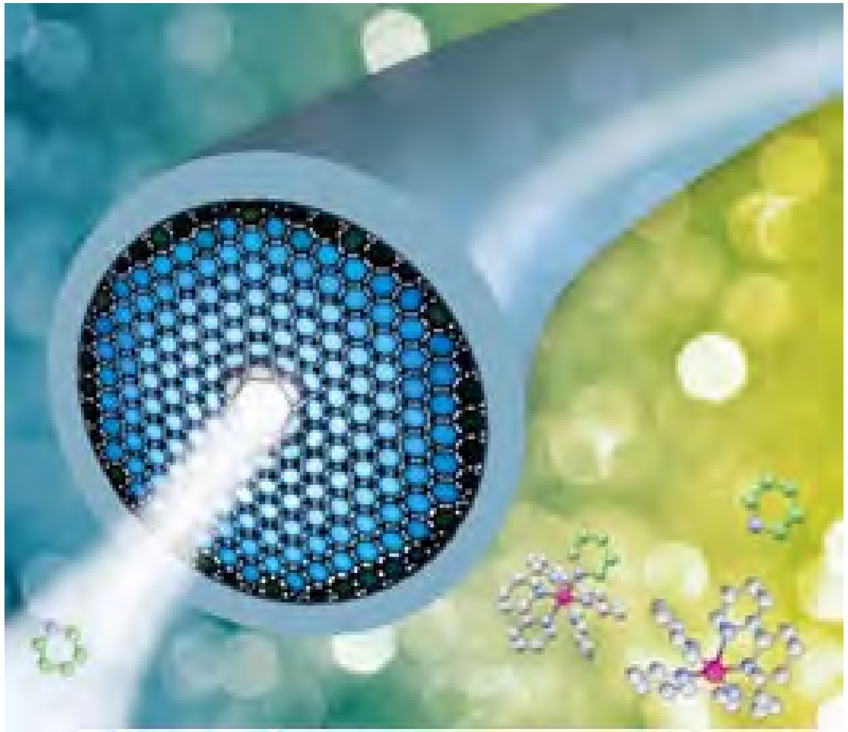
UNIVERSITY OF CAMBRIDGE

Department of Physics
Optofluidics Group

Hollow-core optical fibres as optofluidic microreactors



Tijmen Euser

NanoPhotonics Centre

Cavendish Laboratory

University of Cambridge

Optica Fiber Modeling and Fabrication Technical Group webinar

June 9th 2023

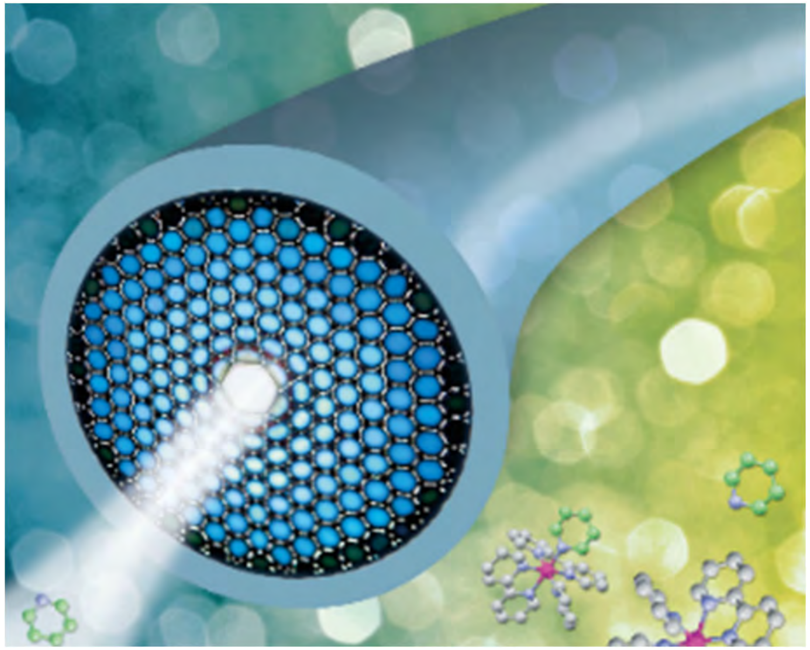
EPSRC Engineering and Physical Sciences Research Council
Isaac Newton Trust
LEVERHULME TRUST
Körber-STIFTUNG Forum für Impulse
THE WINTON PROGRAMME FOR THE Physics of Sustainability
Maxwell Centre

Motivation

We use hollow waveguides to enhance light-matter interactions in: microscale chemistry, biosensing, optical manipulation

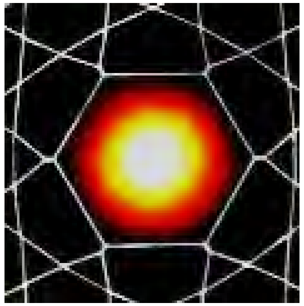
photonic crystal fibre is ideal because:

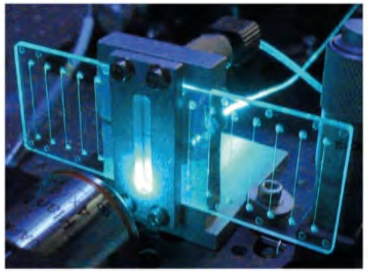
- well-defined optical modes
- tightly confined light
- long interaction lengths
- small sample volumes (nL/cm)

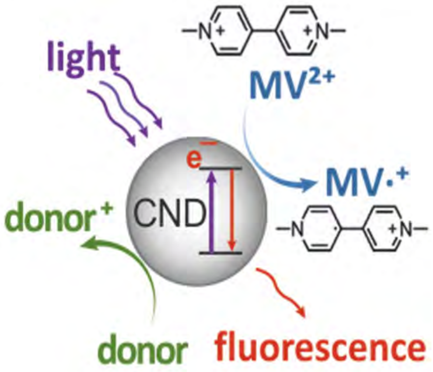


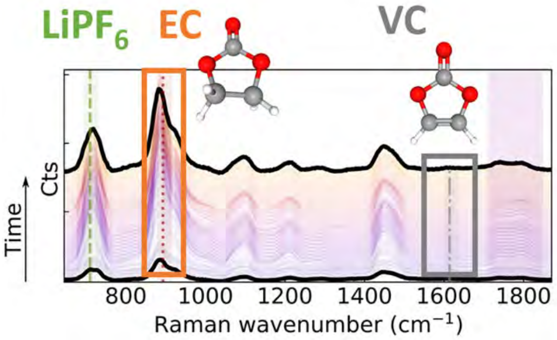
Outline

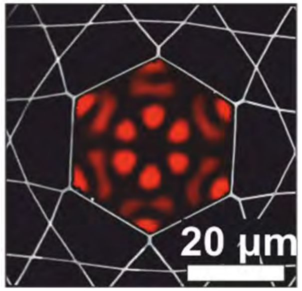
- photonic crystal fibre
- optofluidic microreactors
- (photo)catalysis in PCF
- HC-PCF Raman probes
- higher-order modes





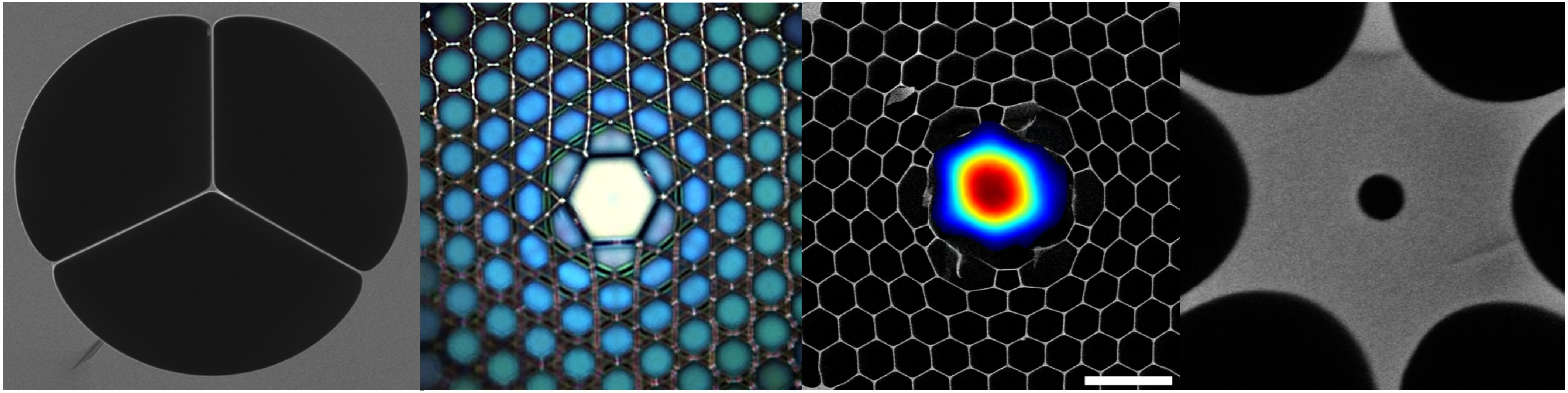






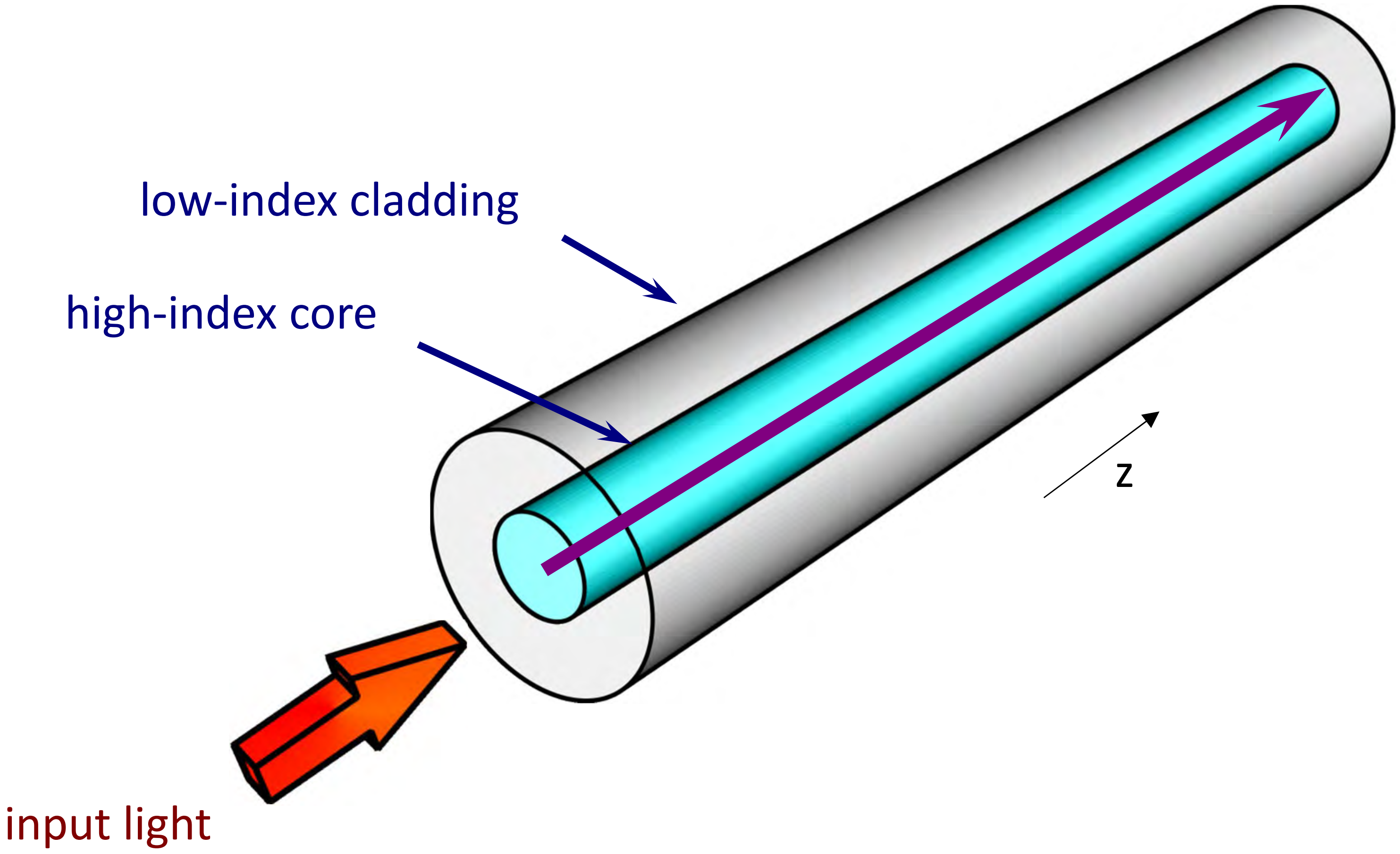
https://www.np.phy.cam.ac.uk/research-themes/optofluidics te287@cam.ac.uk

photonic crystal fibre



Standard optical fibre

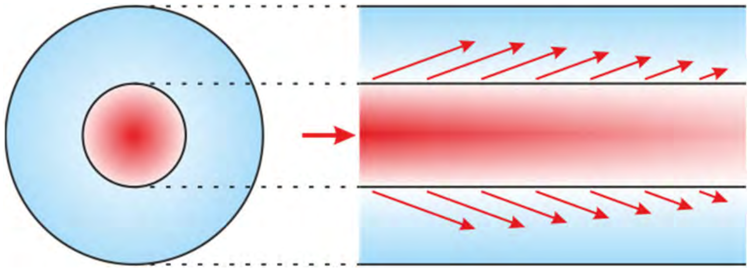
light guided by total internal reflection:
“perfect mirror”



typical diameter 125 μm

How to guide light in a hollow core?

hollow glass capillary ⇒ light leaks out



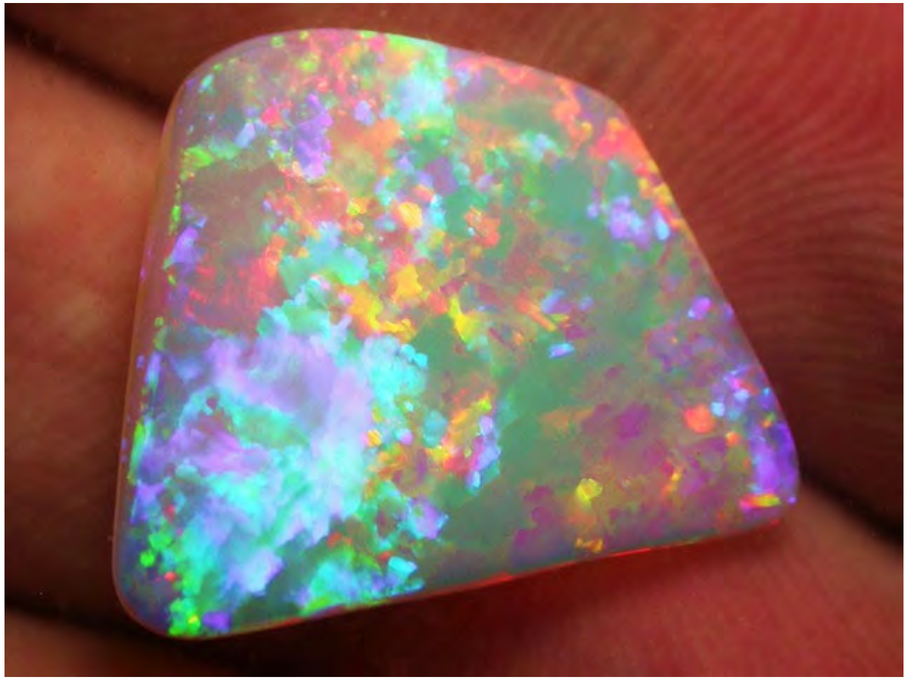
extremely high losses for small diameter capillaries:
>1000 dB/m for a bore radius of 10 µm

We need a mirror to keep the light trapped!

Inspiration from nature: photonic crystal mirrors

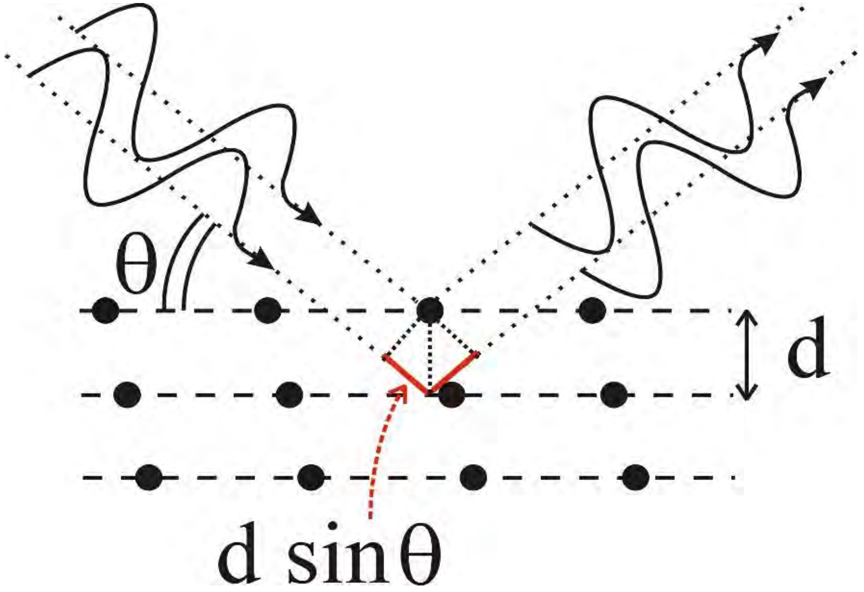
“**crystal**”: ordered dielectric composite

refractive index *n* varies spatially
$\Rightarrow$ light is scattered

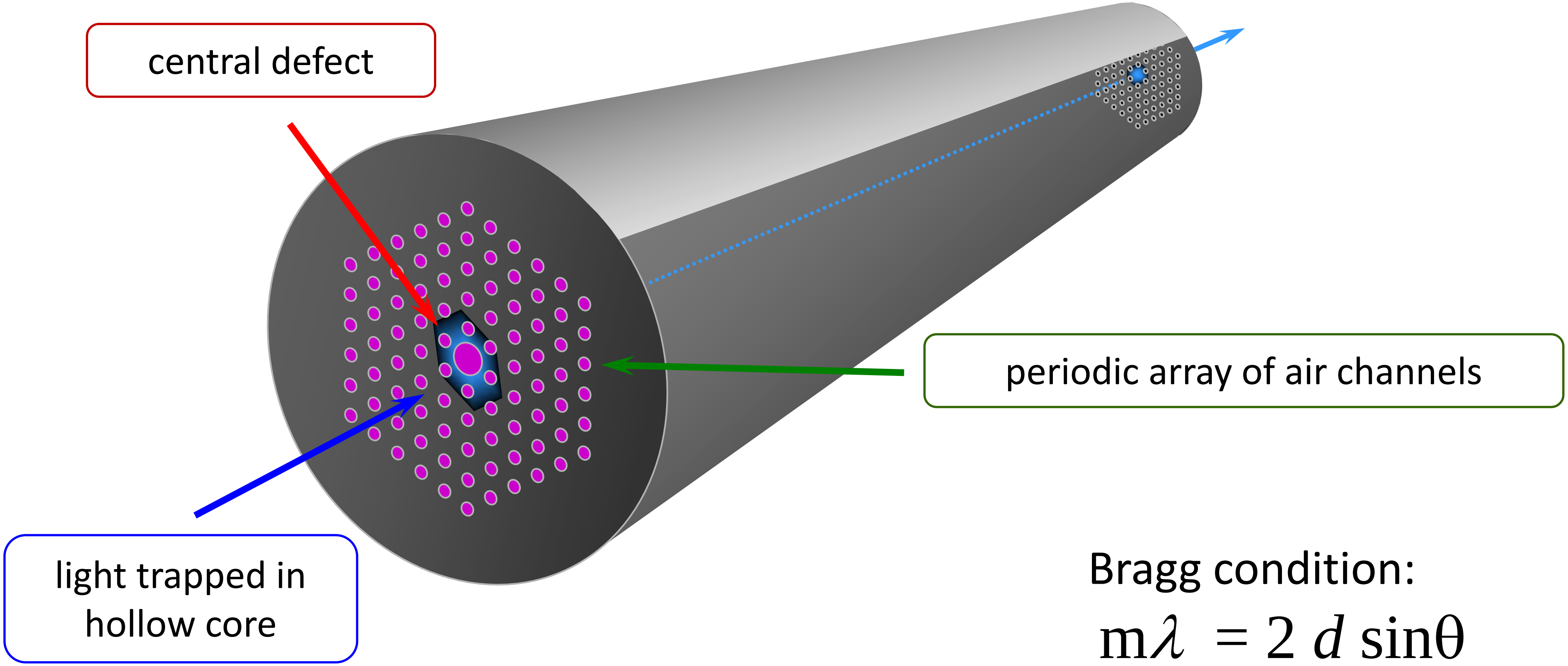


“**photonic**”: $d \approx \lambda$
$\Rightarrow$ scattered light interferes,
Bragg diffraction

Condition: $m\lambda = 2\, d \sin\theta$



Hollow-core photonic crystal fibre (PCF)



central defect

periodic array of air channels

light trapped in
hollow core

typical diameter: 100-200 μm

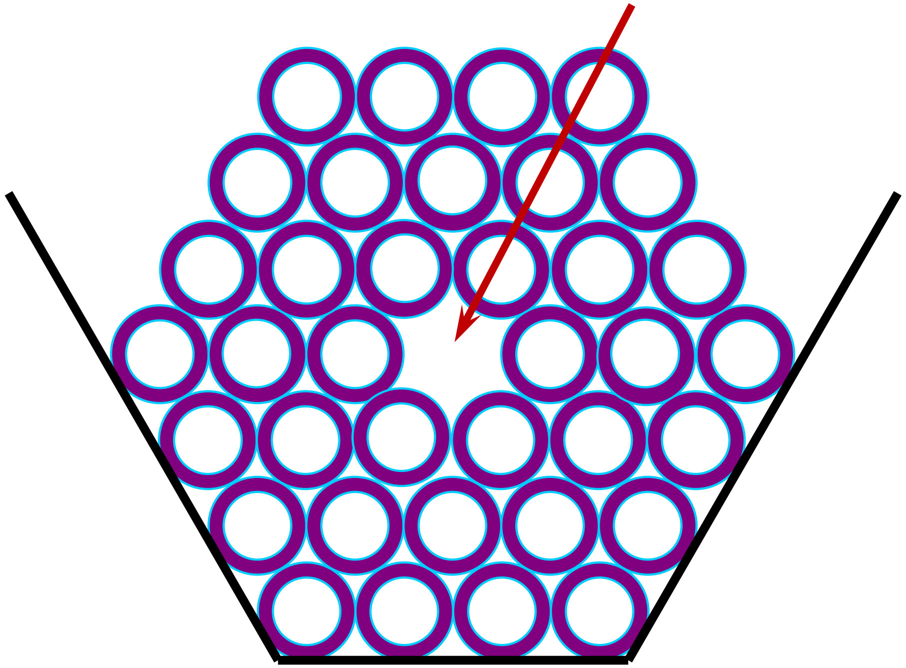
Bragg condition:

$$m\lambda = 2\,d\,\sin\theta$$

R. F. Cregan, *et al.* *Science* **285**, 1537–1539 (1999).
PCF review: P. St.J. Russell, *Science* **299**, 358 (2003).

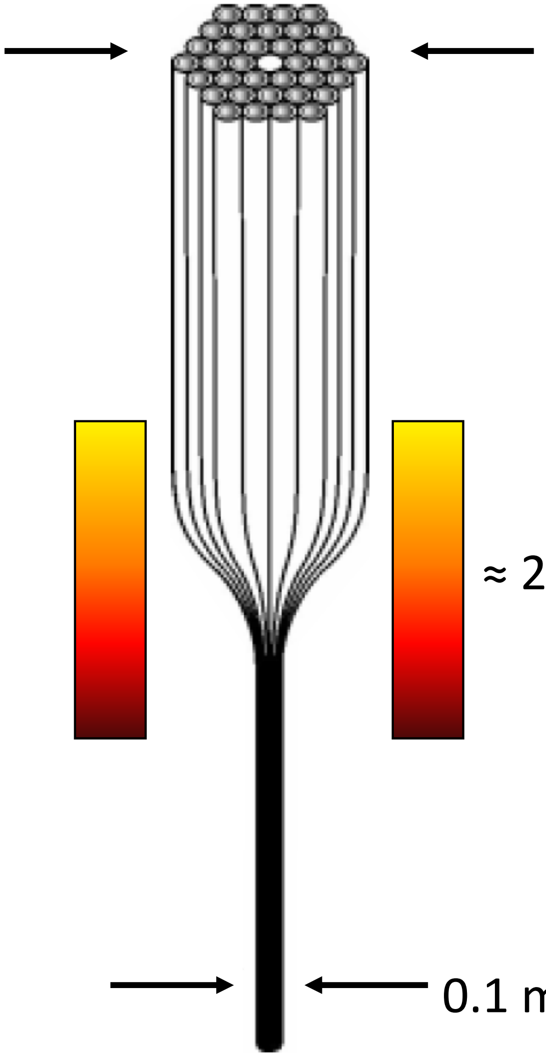
Stack-and-draw process

○ silica capillary (1mm)



low index defect

fabrication



20 mm

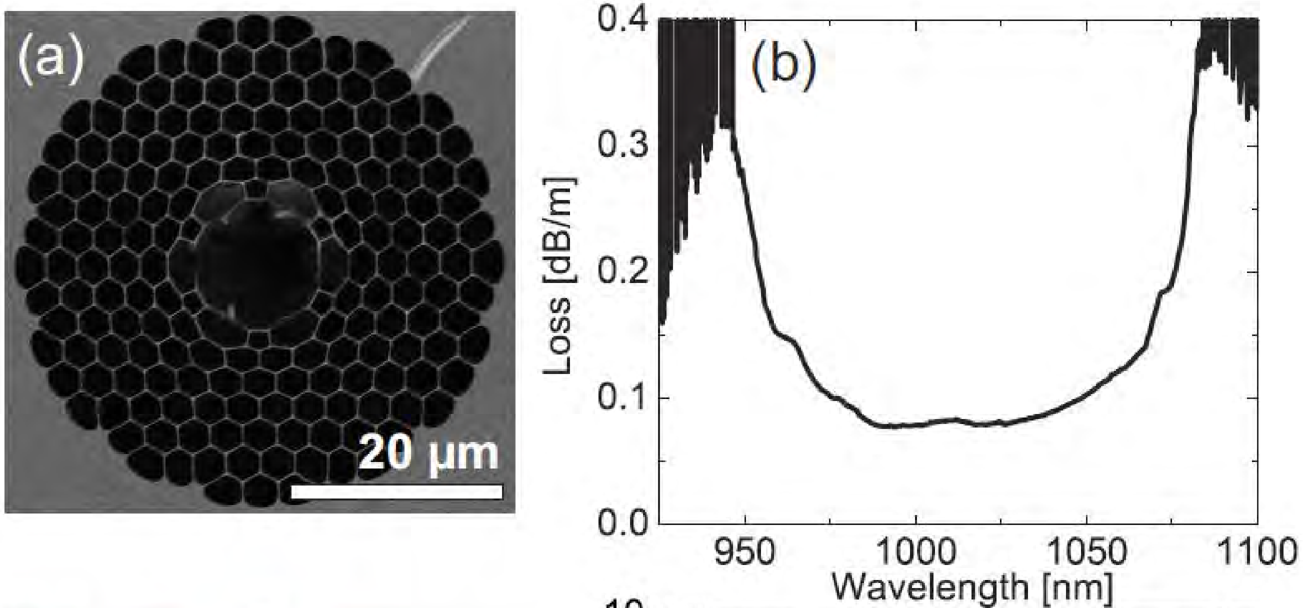
≈ 2000 °C

0.1 mm

Hollow-core photonic crystal fibre

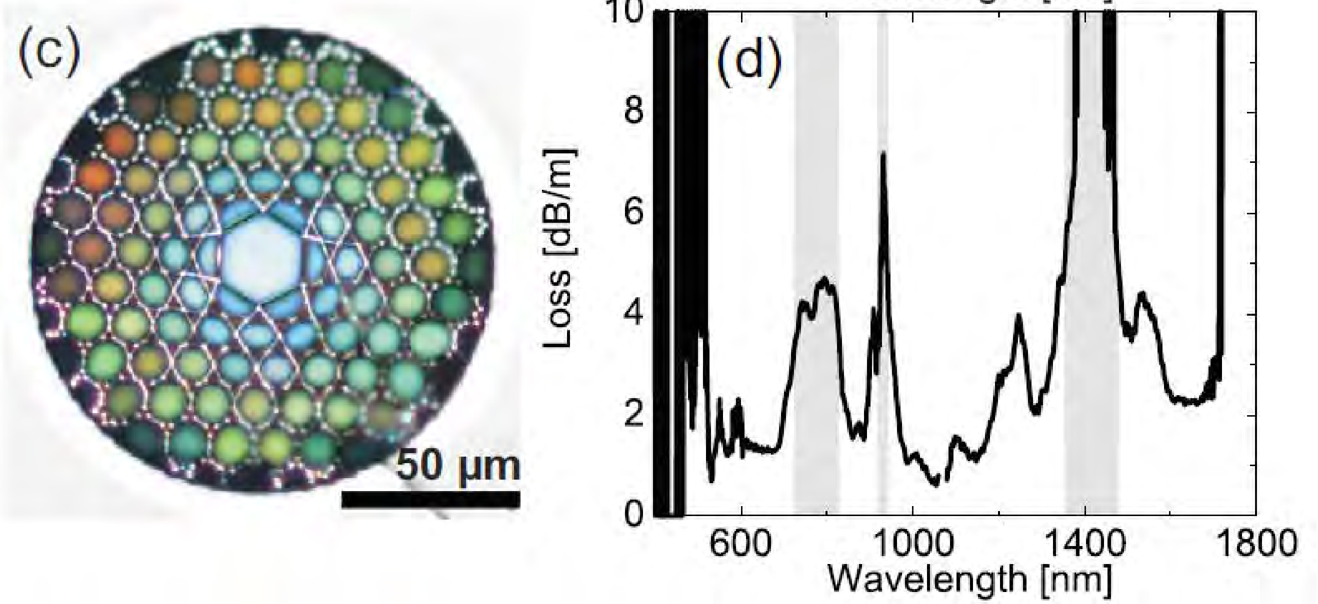
HC bandgap PCF

- small core: ~12 µm
- low losses (~0.1 dB/m)
- narrow transmission window

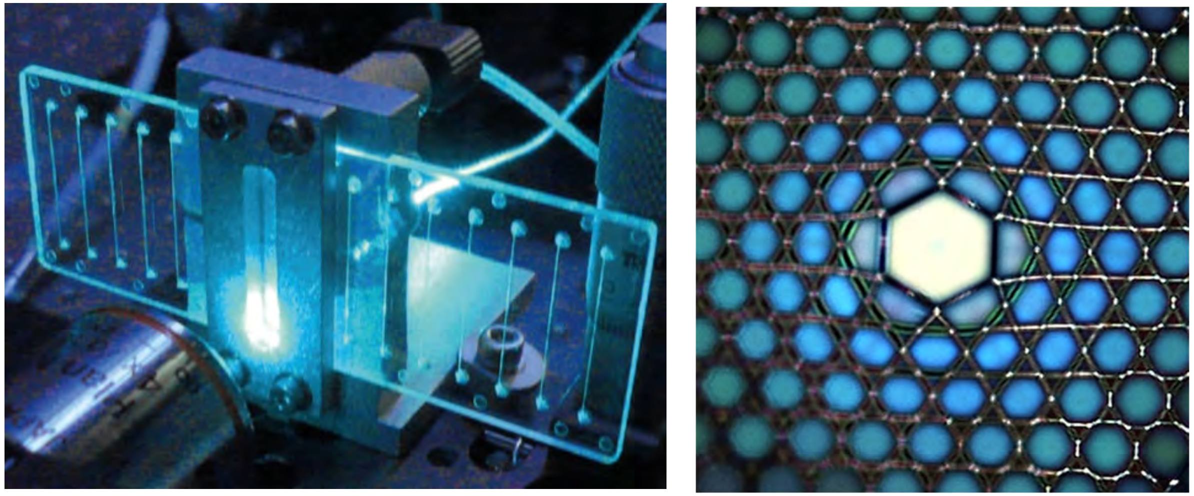


Kagome HC-PCF

- large core: ~23 µm
- higher loss (~1 dB/m)
- broadband guiding



optofluidic HC-PCF microreactors

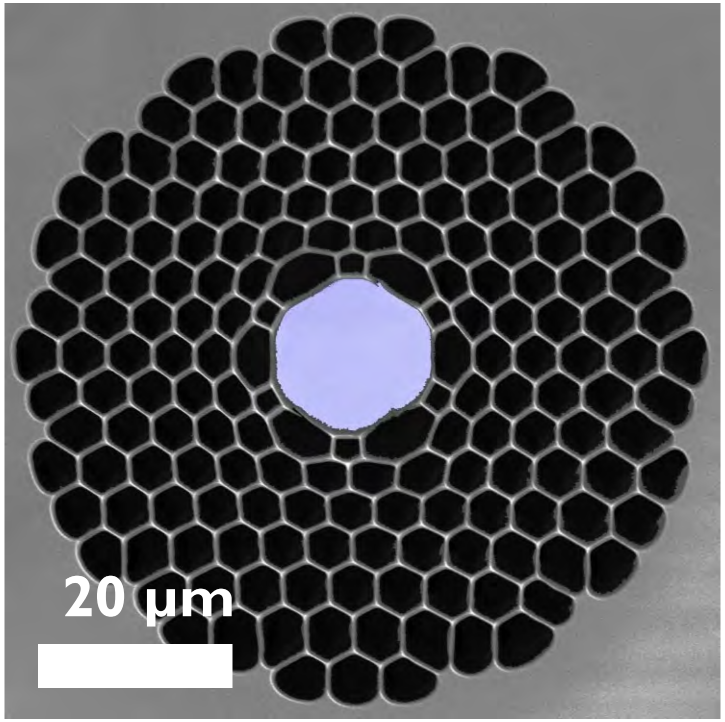


Conventional photochemical reactors

- large sample volumes (100s of ml)
- high power excitation required (>100 Watts)
- offline detection only => very slow optimization processes

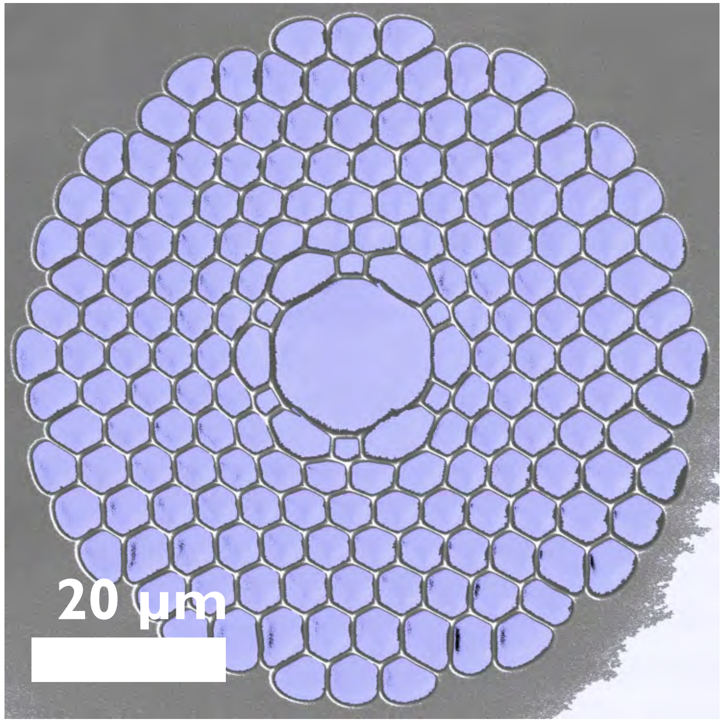
Liquid-filled photonic bandgap fibre

only core filled



- total internal reflection
- highly multimode

core and cladding holes filled



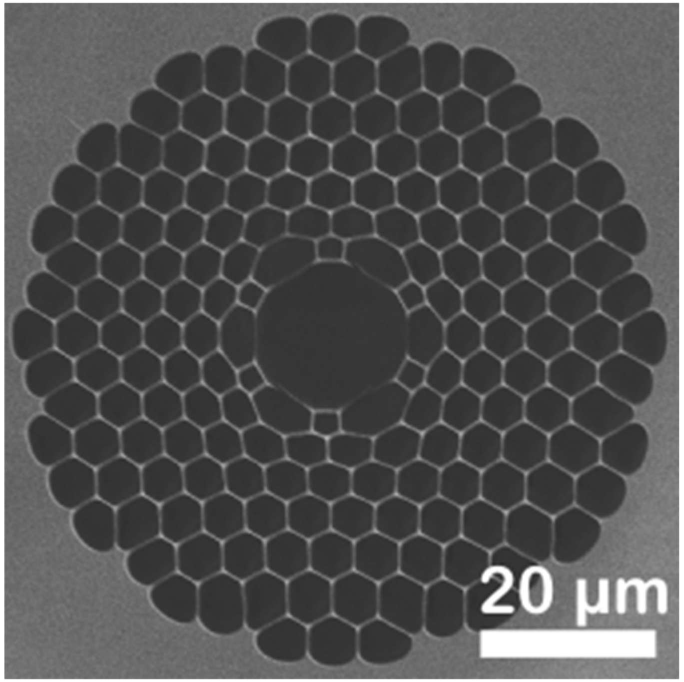
- bandgap guidance
- single-mode

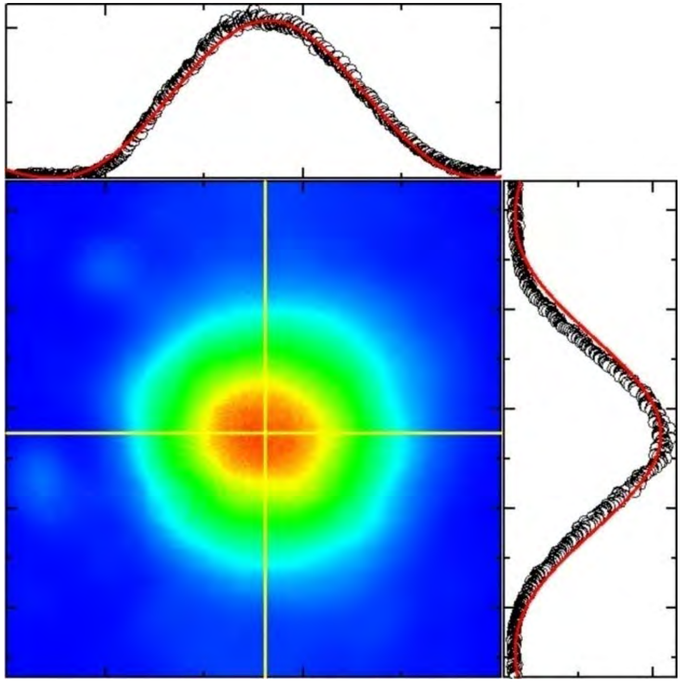
Birks *et al.*, Opt. Express **12**, 69 (2004).
Antonopoulos *et al.*, Opt. Express **14**, 3000 (2006).

Optofluidic photonic bandgap fibre

low loss of 5dB/m (1064 nm) and 90% launch efficiency

well-defined
guided mode
in the liquid core
(D_2O)



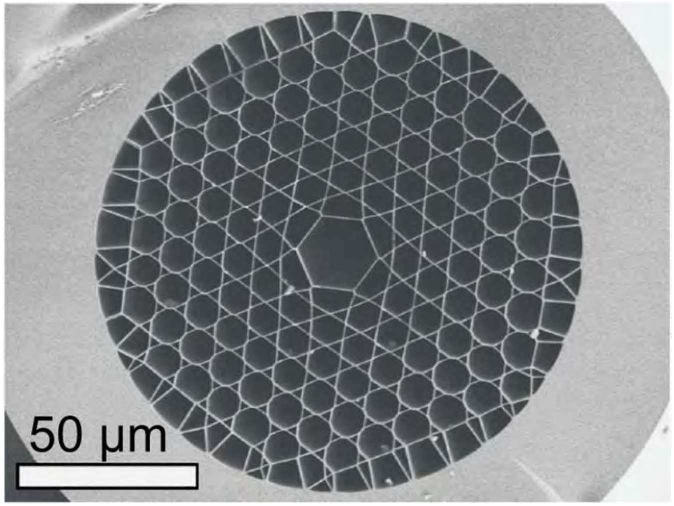


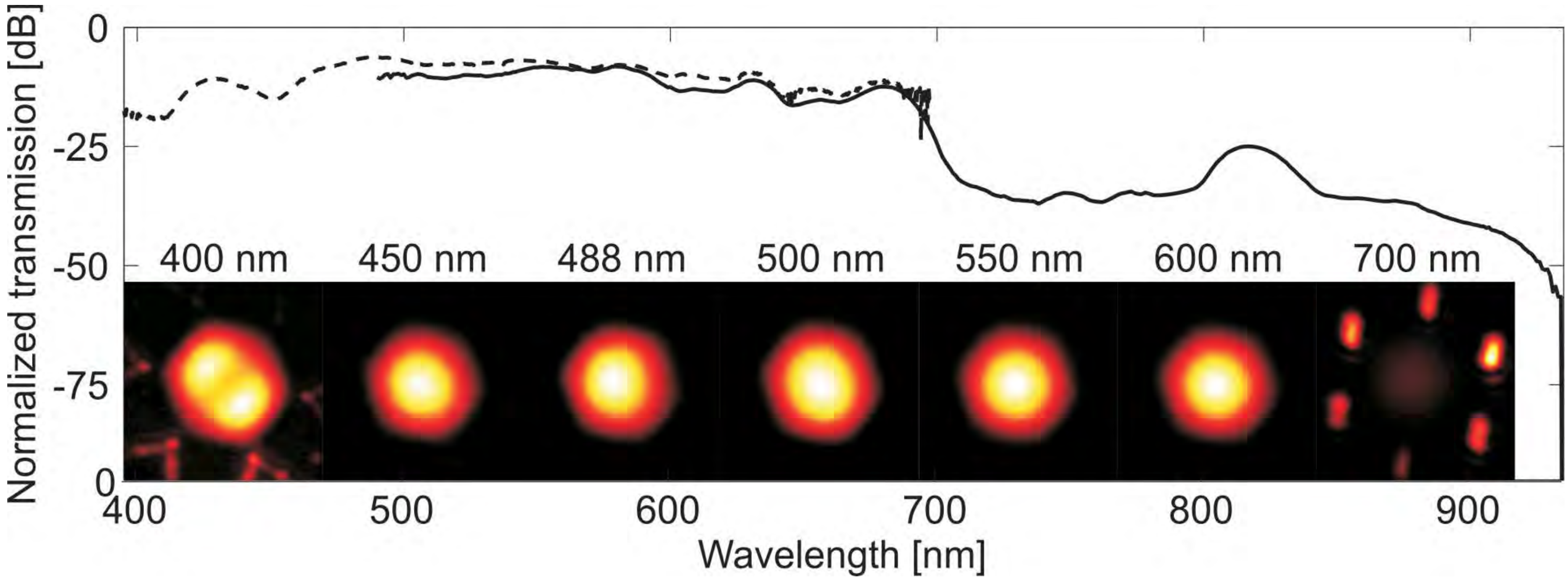
excellent optofluidic waveguide!

Euser *et al.* Opt. Lett. **34**, 3674 (2008).

Optofluidic kagomé hollow-core PCF

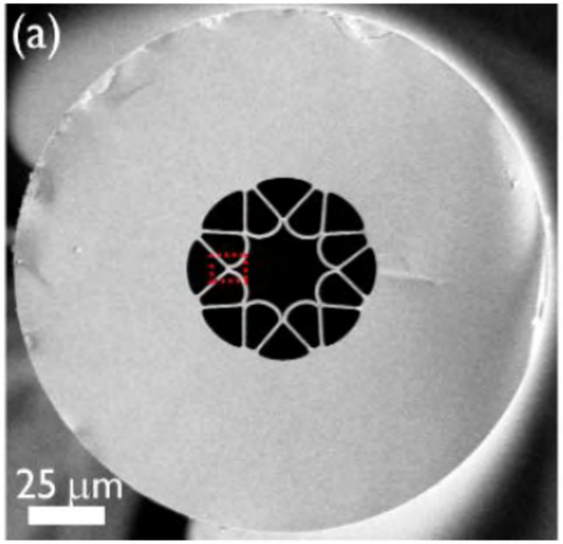
- broadband guiding
  (water-filled: 450-700 nm)
- fundamental mode guidance
- low loss: 5-10 dB/m





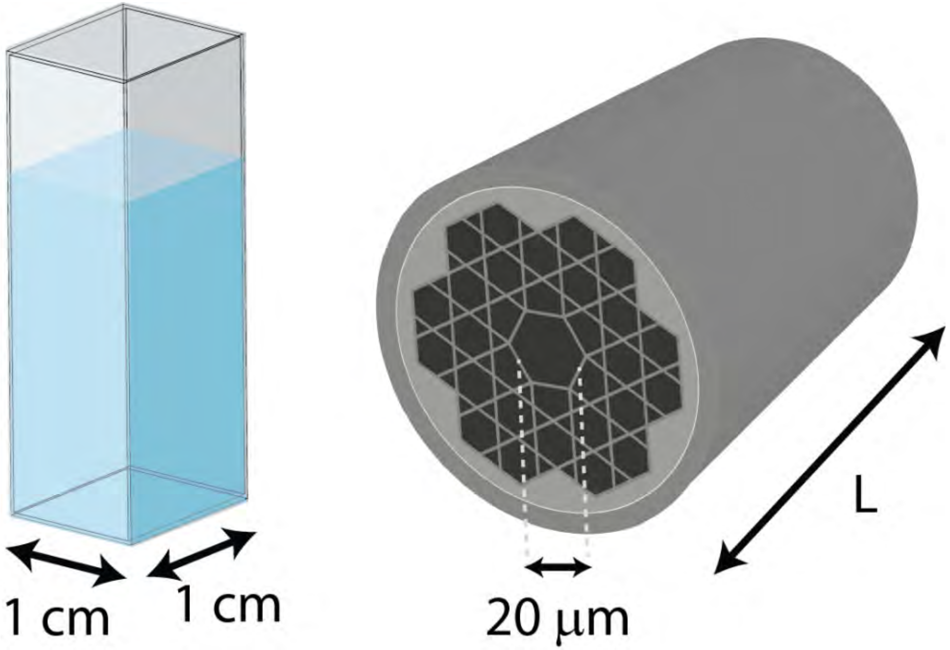
High-index soft glass HC-PCF

- single-ring hollow core fibres [1,2], based on anti-resonant reflection [3]
- high-index SF6 soft glass (n=1.8):
  => can use high-index solvents
- well-defined modes in toluene
  (n= 1.49 at 600 nm) [4]
- monitored photochemical CO-dissociation



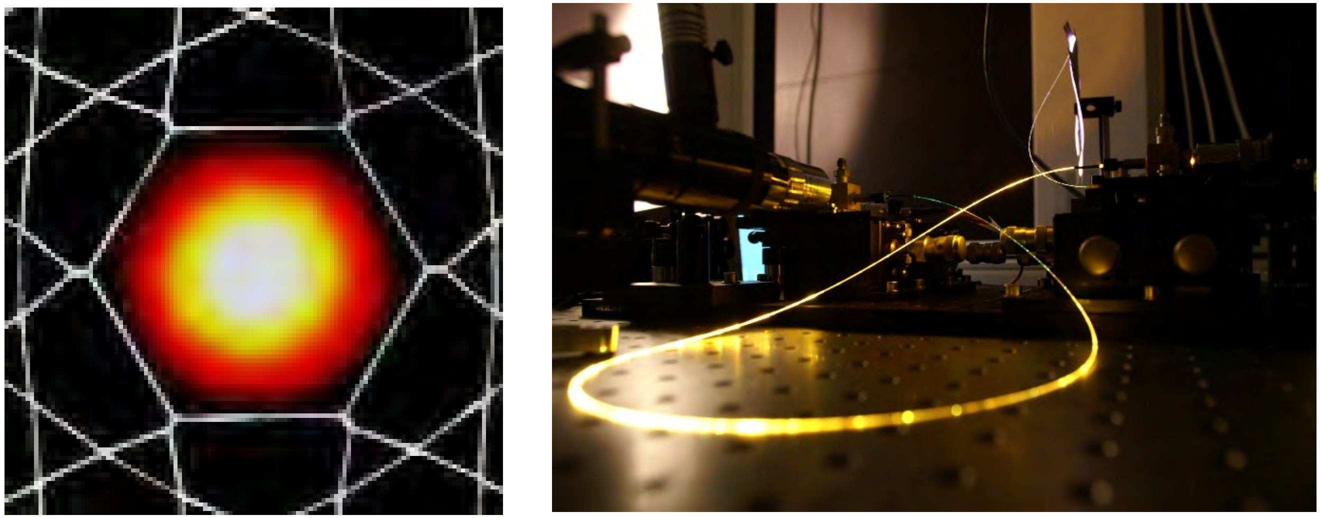
[1] Pyramikov *et al., Opt. Express* **19**, 1441 (2011).
[2] Yu *et al*., IEEE J. Q. Elec. **22**, 4400610 (2015).
[3] Litchinitser *et al., Opt. Express* **11**, 1243 (2003).
[4] A. Cubillas, X. Jiang *et al.*, *Analyst* **142**, 925-929 (2017).

Why use HC-PCF as microreactors?



	Cuvette	Fiber	
Length	1-10 cm	10 cm-1 m	**↑ 10 x**
Volume	3 mL/cm	4 nL/cm	**↓ 750,000 x**
Intensity	1 W/cm^2	3.5×10^5 W/cm^2	**↑ 350,000 x**

Photocatalysis in optofluidic HC-PCF

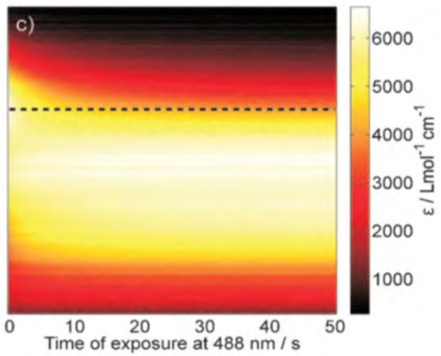


Early photochemistry work in PCF

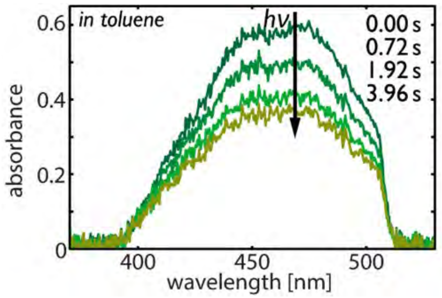
- 100,000 x enhanced photolysis
- photoswitching of azodyes
- heterogeneous catalysis in PCF
- microfluidic flow reactor for rapid screening of photo drugs

mostly proof-of-principle studies

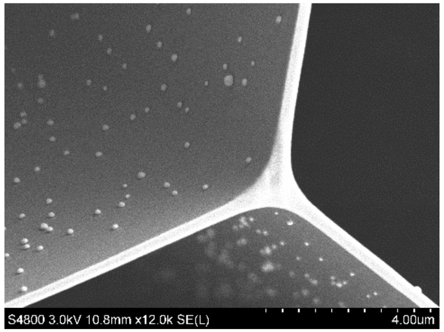
can we also do *new* chemistry?



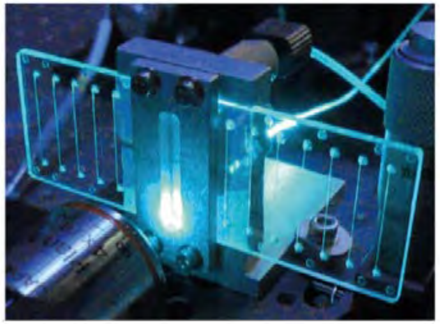
Enhanced photolysis, Chen, ChemEuropJ (2010).



Sub-picomole photo- switching, Williams, Lab Chip. (2012).



Rh heterogeneous catalysis, Cubillas, Adv. Mat. Interf. (2013).



Microfluidic integration Unterkofler, Opt. Lett. (2014) McQuitty, RSC Adv. (2017).

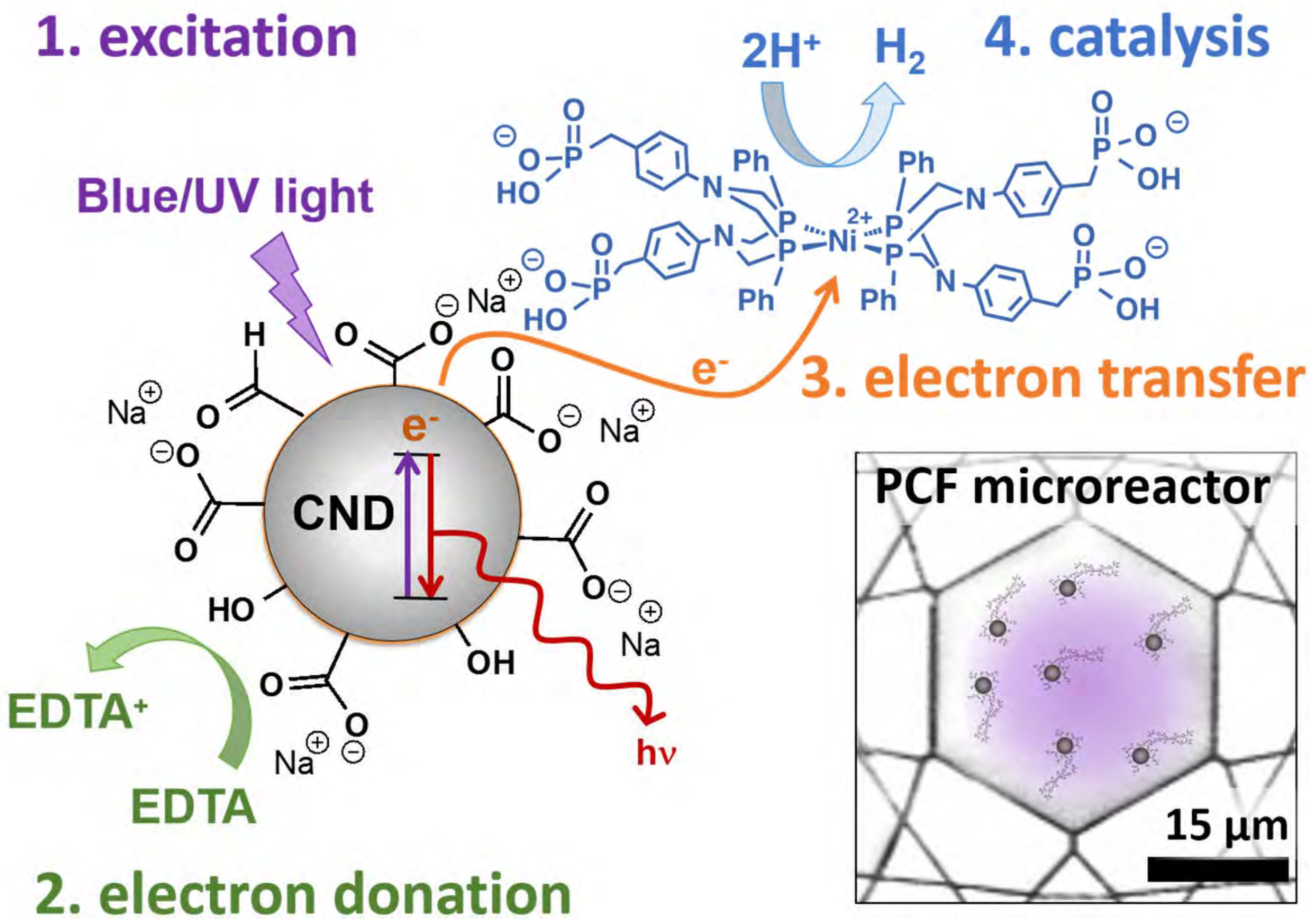
Review: Cubillas *et al.* *Chem. Soc. Rev.* (2013).

Molecular photocatalysis

overall goal: sustainable catalysts for solar fuel generation

- carbon nanodot (CND) light absorbers: non-toxic, cheap, scalable
- Ni- or Co-based molecular catalysts (avoid Pt, Rh)

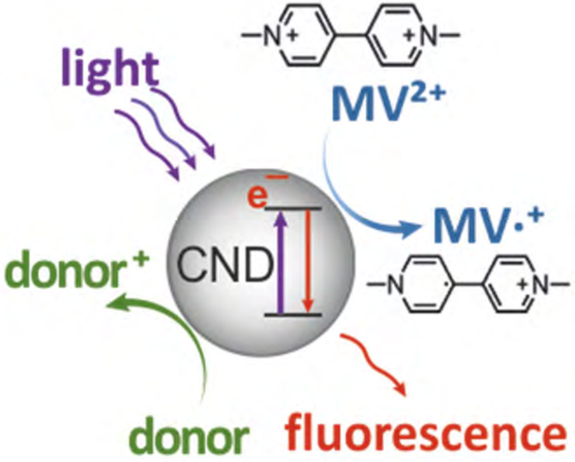
Key issue:
limited mechanistic understanding due to a lack of *in situ* measurements

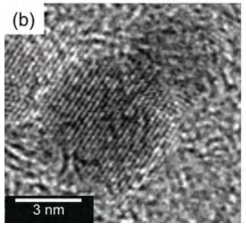


LEVERHULME TRUST

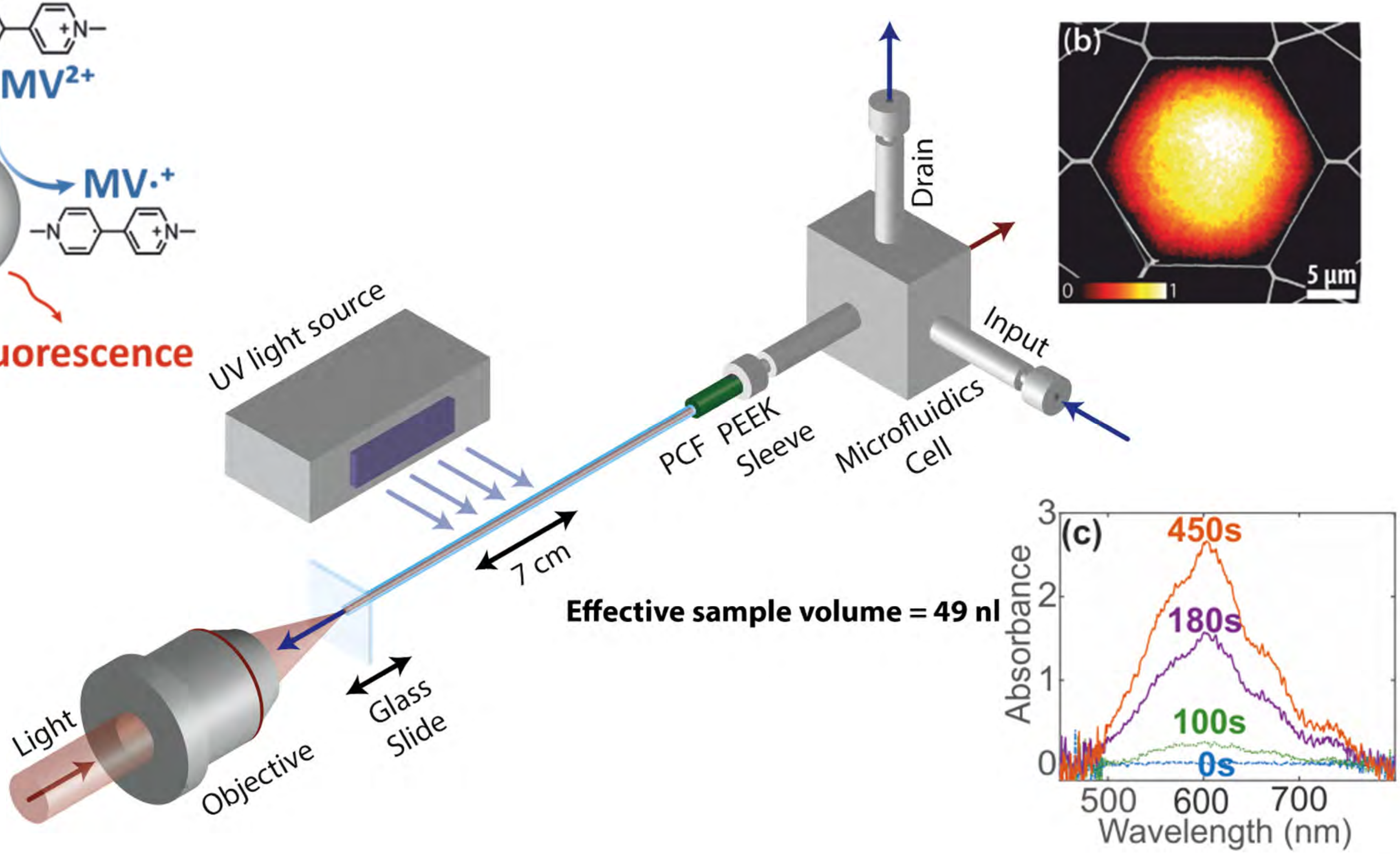
with Erwin Reisner, Cambridge

HC-PCF photocatalysis setup





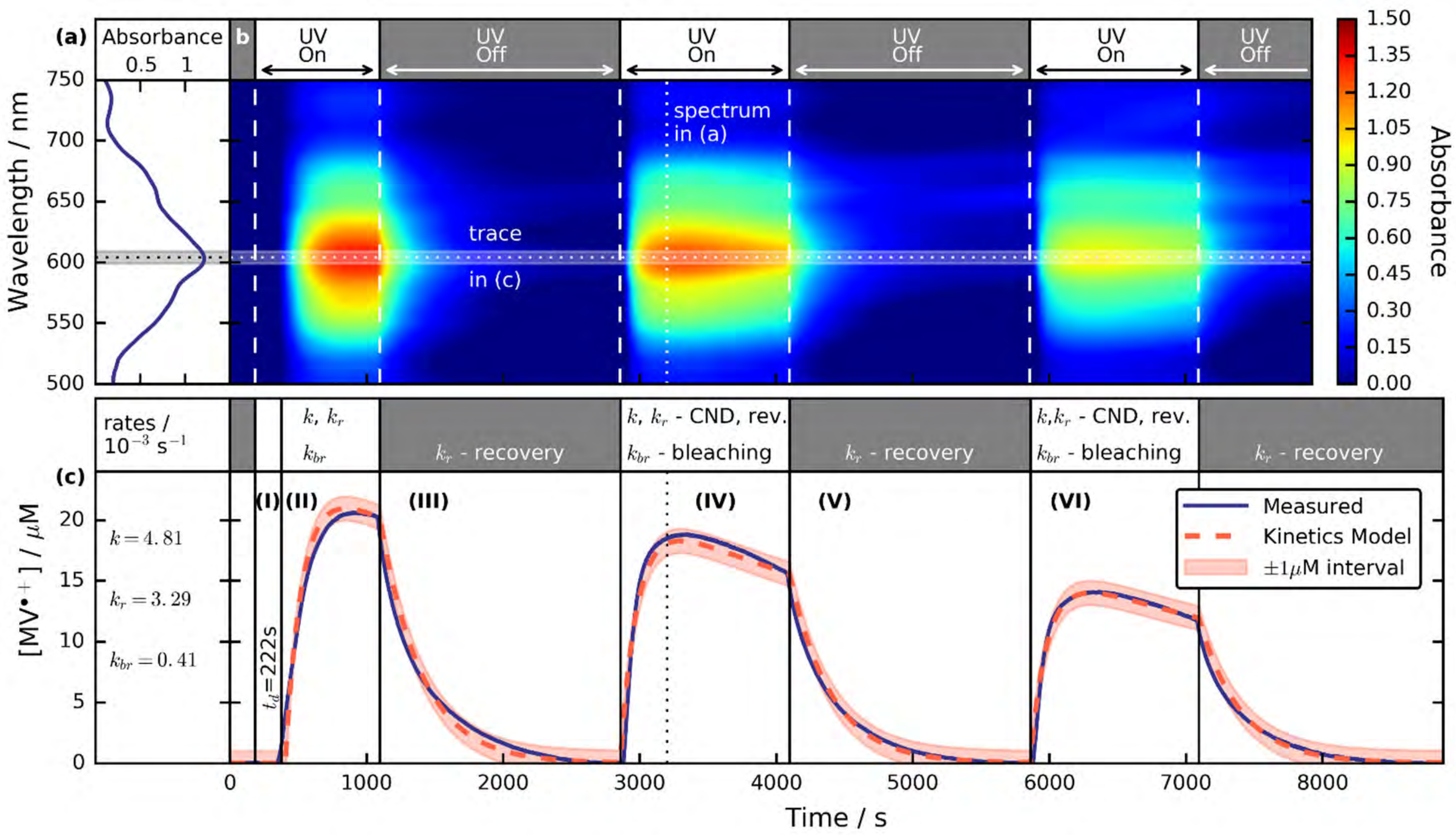
TEM image of CNDs



Effective sample volume = 49 nl

- electron-transfer process between CNDs and catalysts is rate-limiting => we study this process using a methyl viologen (MV) redox dye

Photocatalysis in HC-PCF microreactors

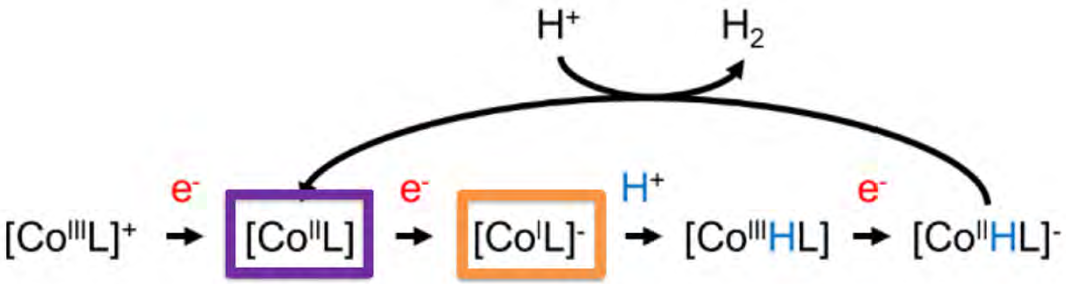


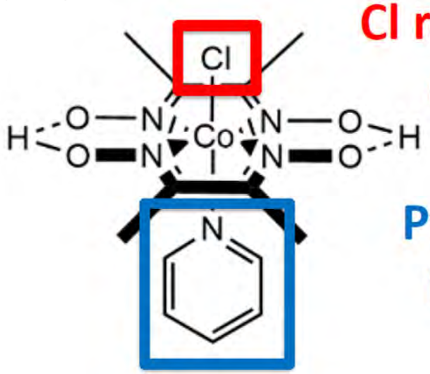
- catalyst screening using very small sample volumes (<40 nL)
- observed unknown CND activation process
- compare UV-Vis absorption time-traces with kinetics modelling

Koehler *et al., Anal. Chem* **93**, 895–901 (2021). https://doi.org/10.1021/acs.analchem.0c03546

Monitoring Cobaloxime photocatalysts

- cobaloxime intermediates involved in H_2 generation via H^+ reduction detected in fibre
- $Ru(bpy)_3^{2+}$ was used in lieu of CNDs.



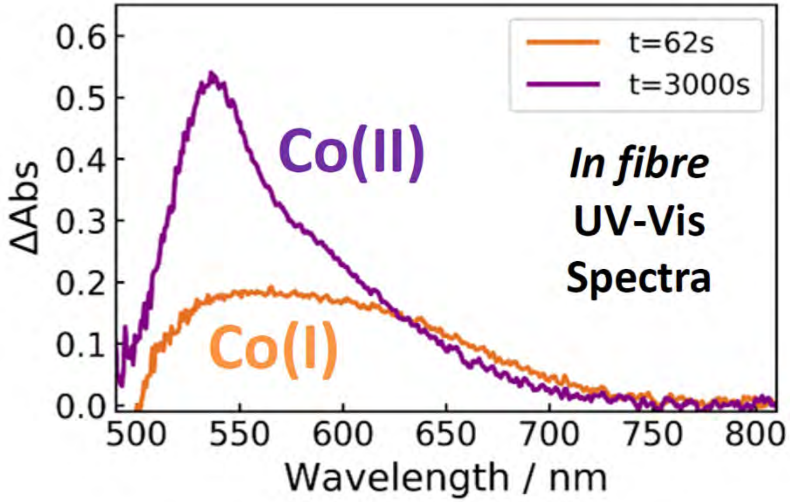


Cl replaced by H_2O during cycle

Pyridine ligand increases H_2 production

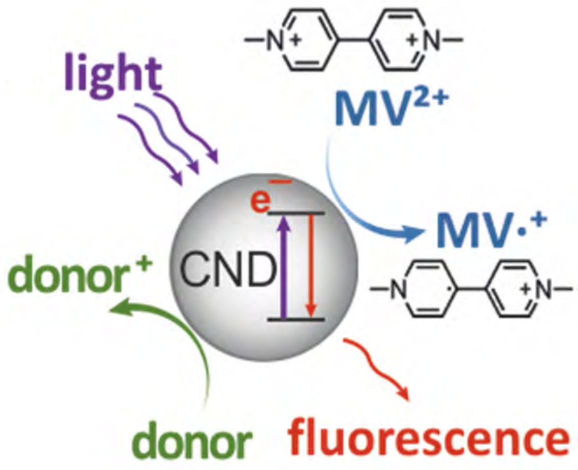
$Co(dmgH)_2pyCl$

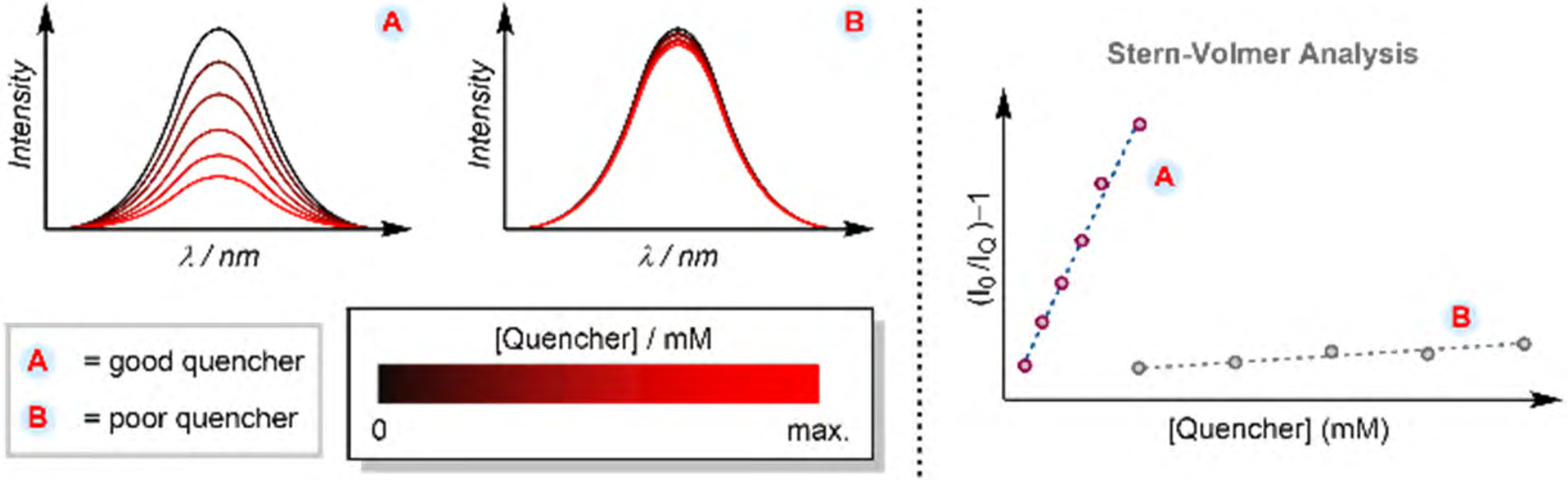
- long pathlength in HC-PCF enables detection of weak absorption peaks
- transient and steady-state observed and assigned with DFT



T. Lawson, A. S. Gentleman *et al., Angew. Chem. Int. Ed (2023).* https://doi.org/10.1002/anie.202214788

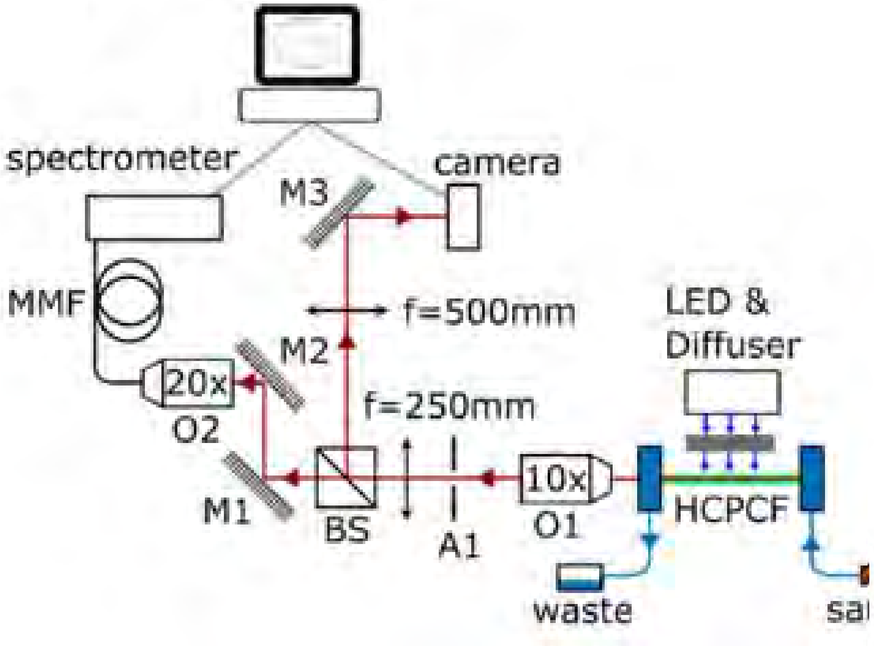
Micro Stern Volmer analysis in hollow-core fibre

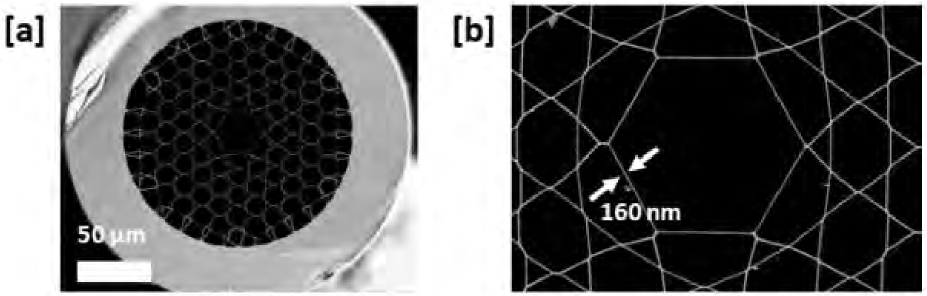


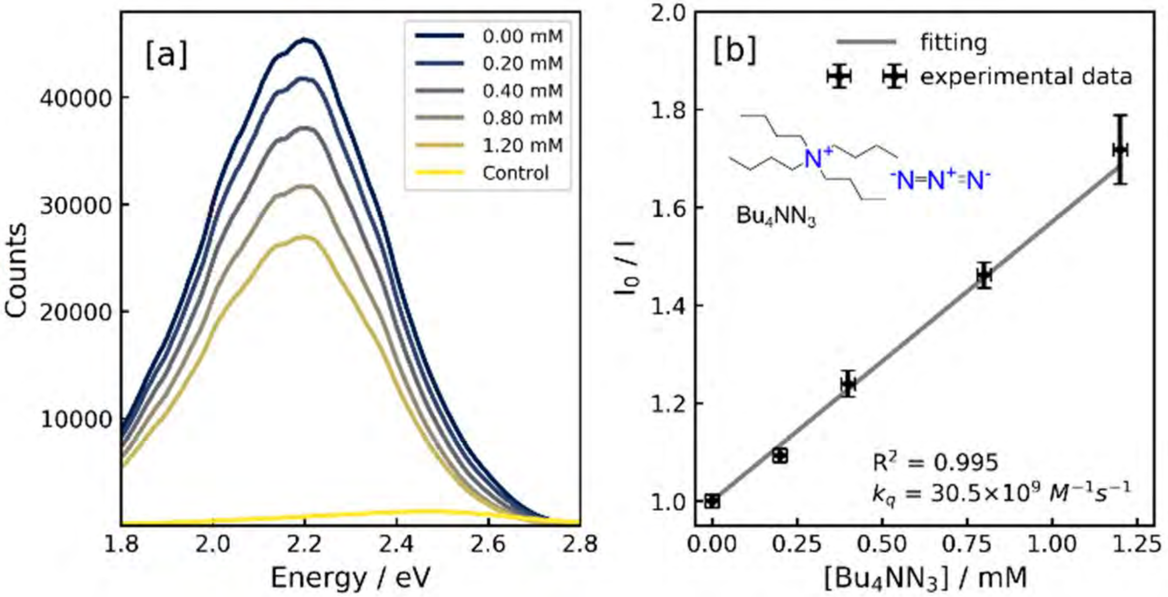


- measure fluorescence to understand photocatalytic pathways?

Micro Stern Volmer analysis in hollow-core fibre







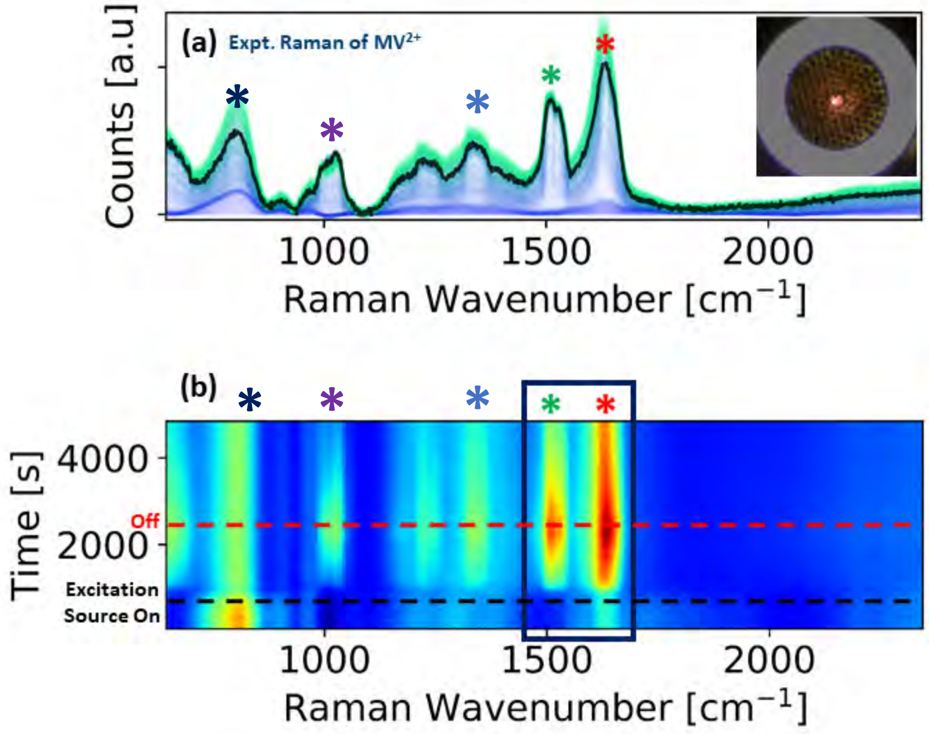
- collection of fluorescence through fibre modes
- obtain quenching coefficients using sub-µL catalyst samples
- demonstrated here with a 4CzIPN photocatalyst

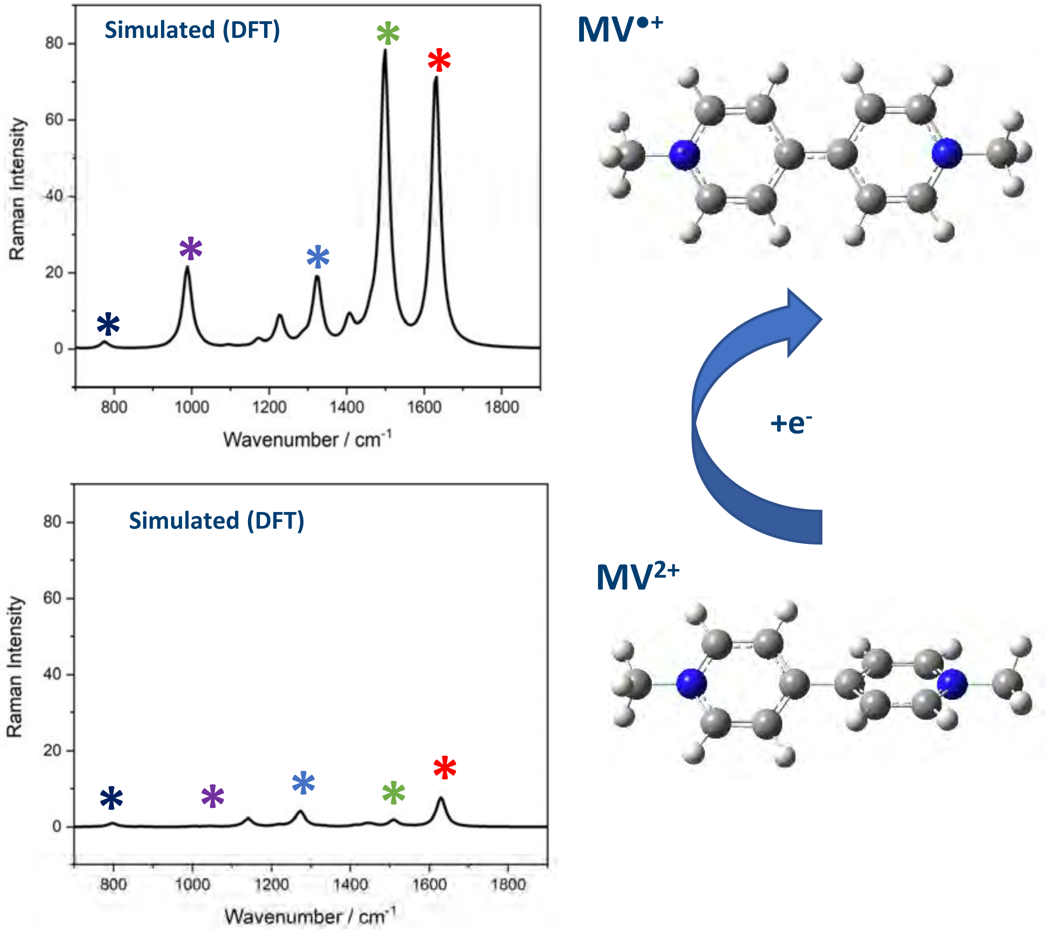
with Alex Cresswell (Bath),
Erwin Reisner (Cambridge)

A. S. Gentleman and T. Lawson *et al.*, *Chem. Science* (2022)
https://doi.org/10.1039/D2CC03996F

In-situ Raman sensing in photocatalysis

- CND driven reduction of MV^{2+} to $MV^{\bullet +}$
- observed clear changes in Raman peaks
- excellent agreement with DFT calculations

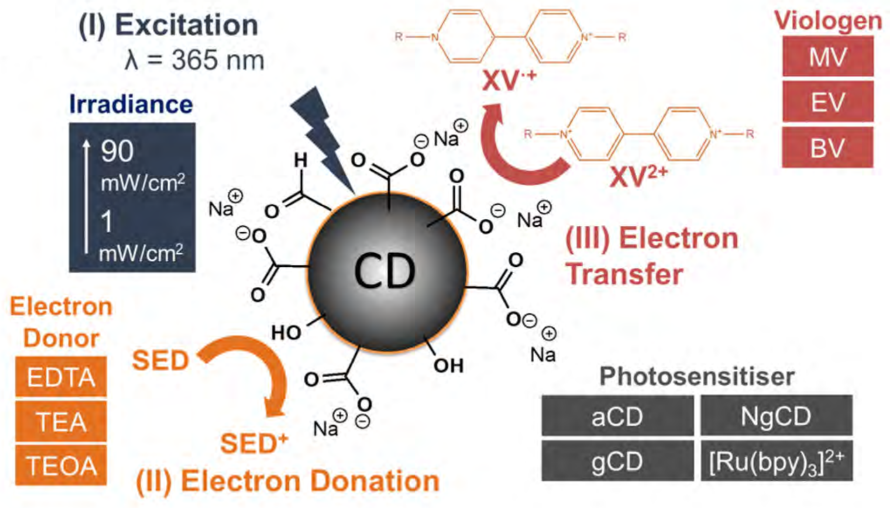




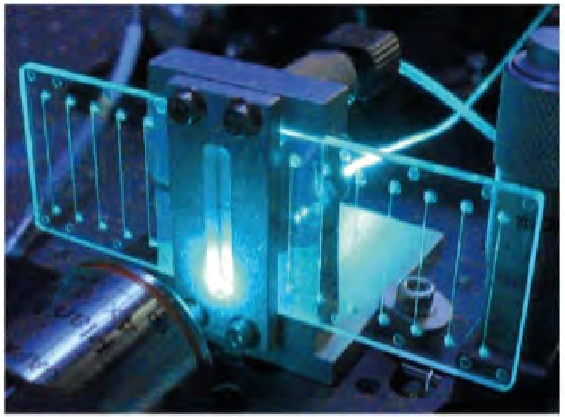
A. S. Gentleman, E. Miele *et al.,* CLEO PR 2020 paper SM4M.8
see also Raman reaction-monitoring work by Schorn *et al.*: *ACS Catal*. 11, 11, 6709–6714 (2021).

Outlook photocatalysis

- optimize reaction conditions for catalysis (CND / electron donor / pH)
- further studies with novel catalysts (CoP, enzymes)
- combine with microfluidic mixing chips for rapid catalyst screening
- monitor with in fibre Raman spectroscopy

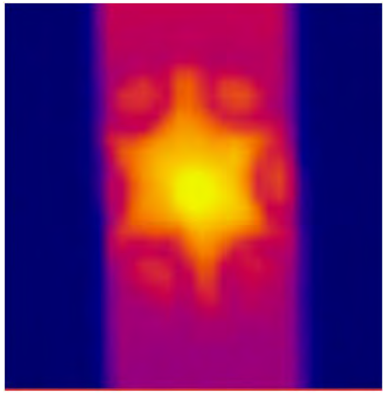


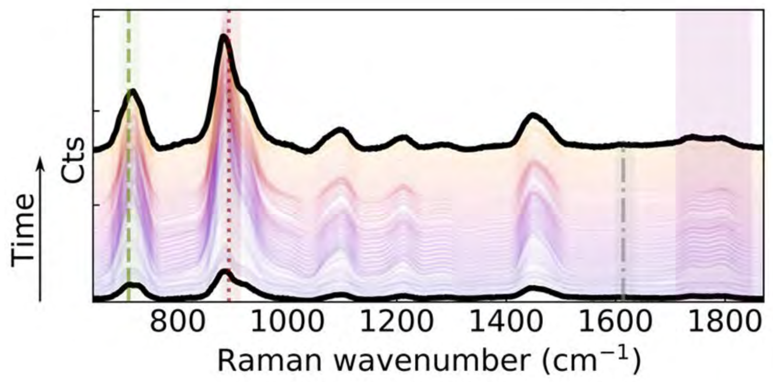
T. Lawson *et al.* (*ACS Catal.*, accepted)



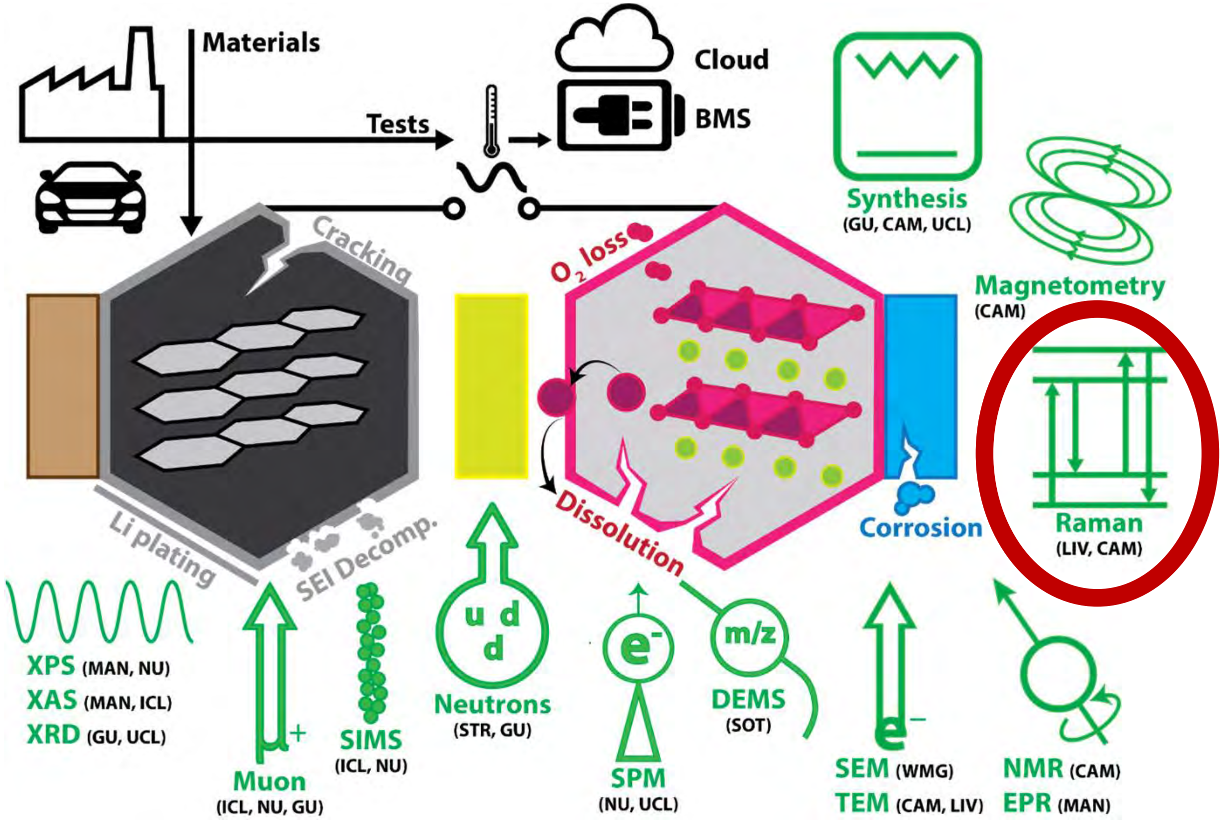
S. Unterkofler *et al.*
(*Opt. Lett.* (2014).)

Raman probes for Li:ion battery chemistry

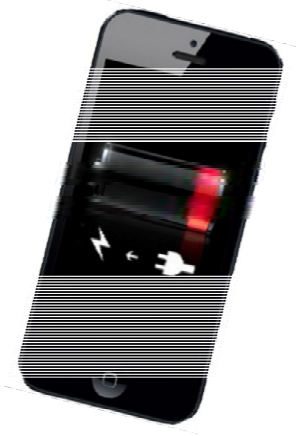




Motivation: understanding battery degradation



Faraday Institution:
UK-wide project to study degradation mechanisms in next-generation Li-ion batteries

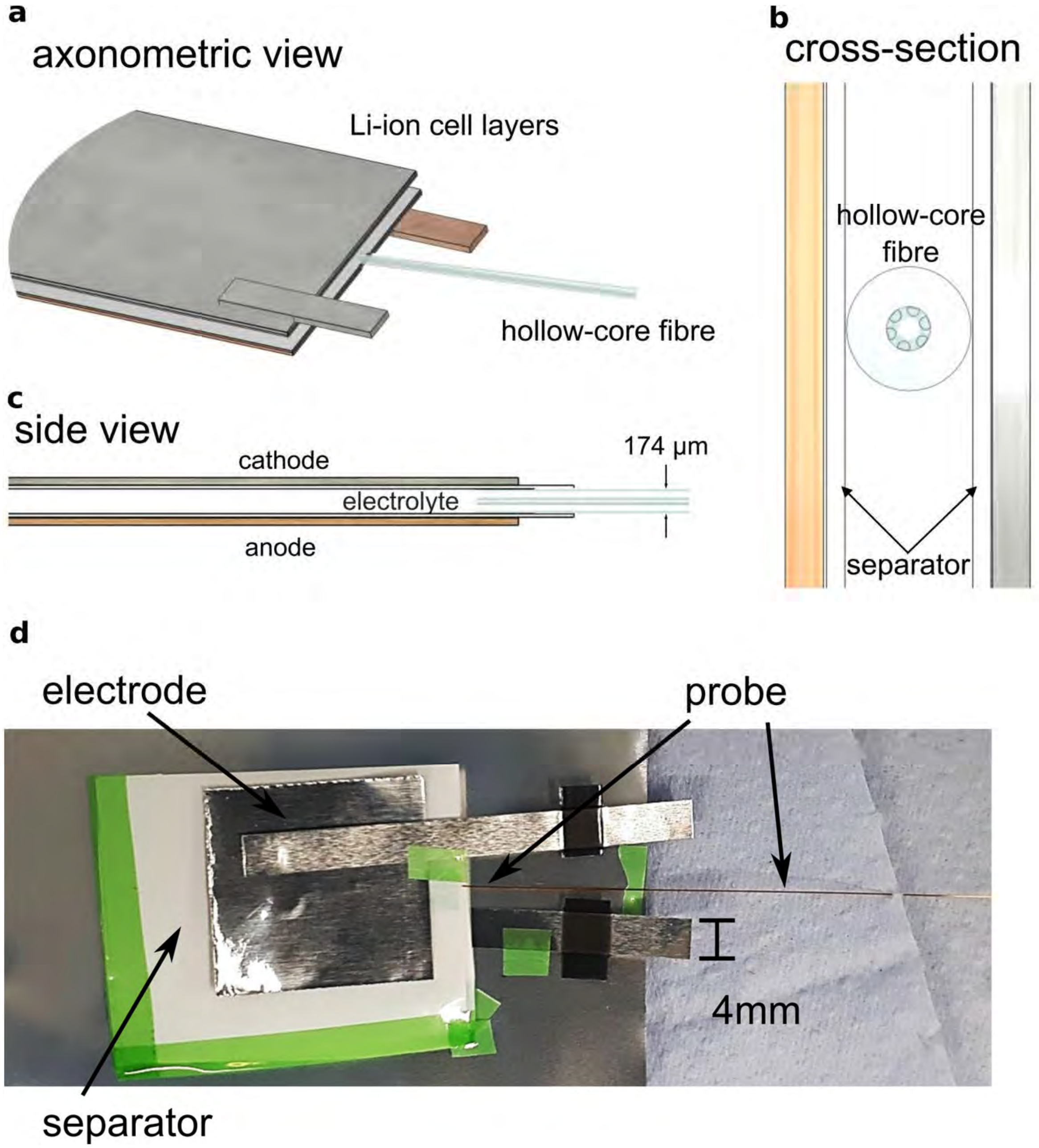


We develop background-free **operando** fibre-coupled **Raman** probes to track changes in the electrolyte chemistry.

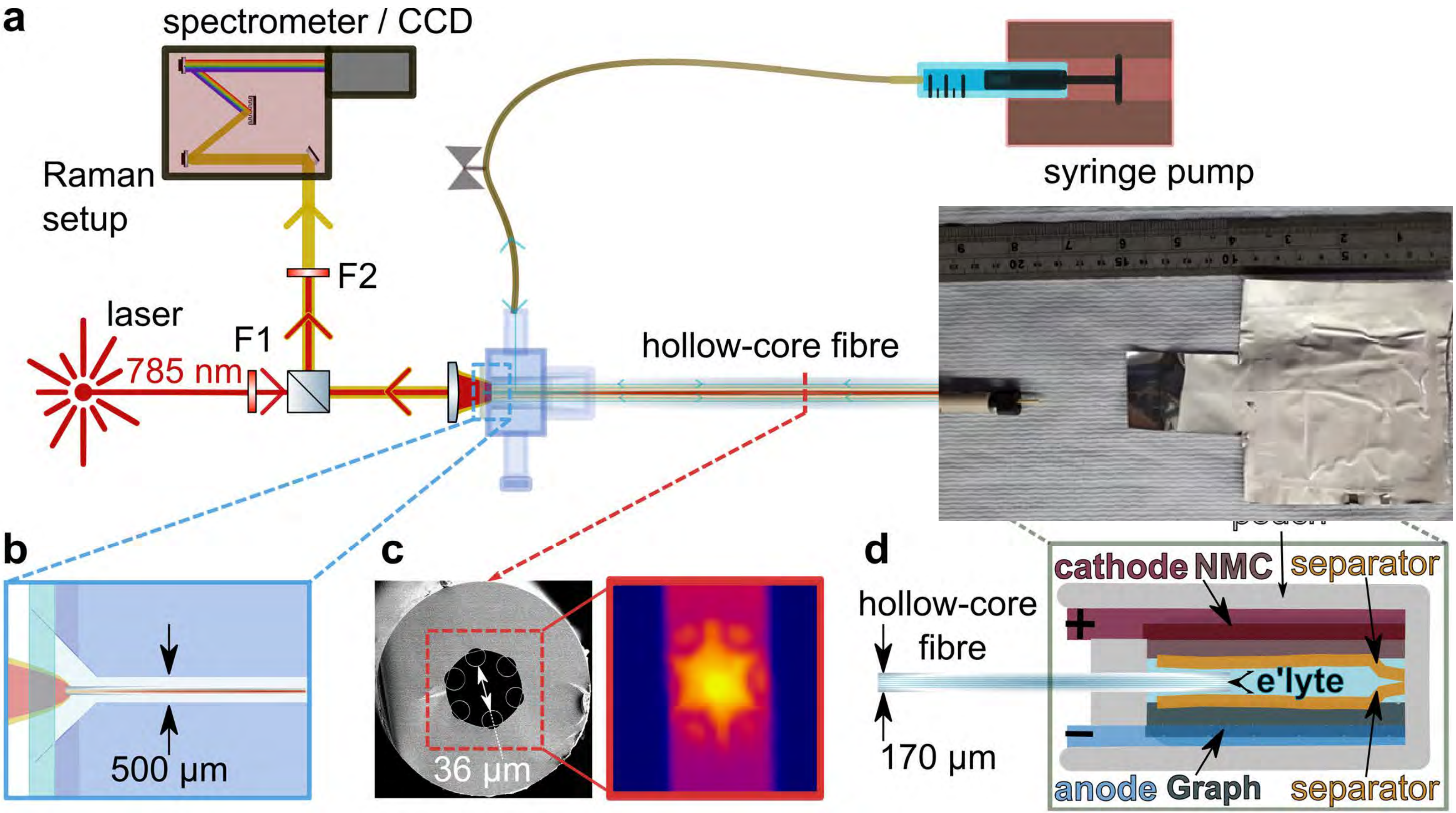
THE FARADAY INSTITUTION
with Clare Grey, Michael de Volder, Jeremy Baumberg

MAX PLANCK INSTITUTE for the science of light
Michael Frosz (Erlangen)

Embedding hollow-core fibre probes in batteries

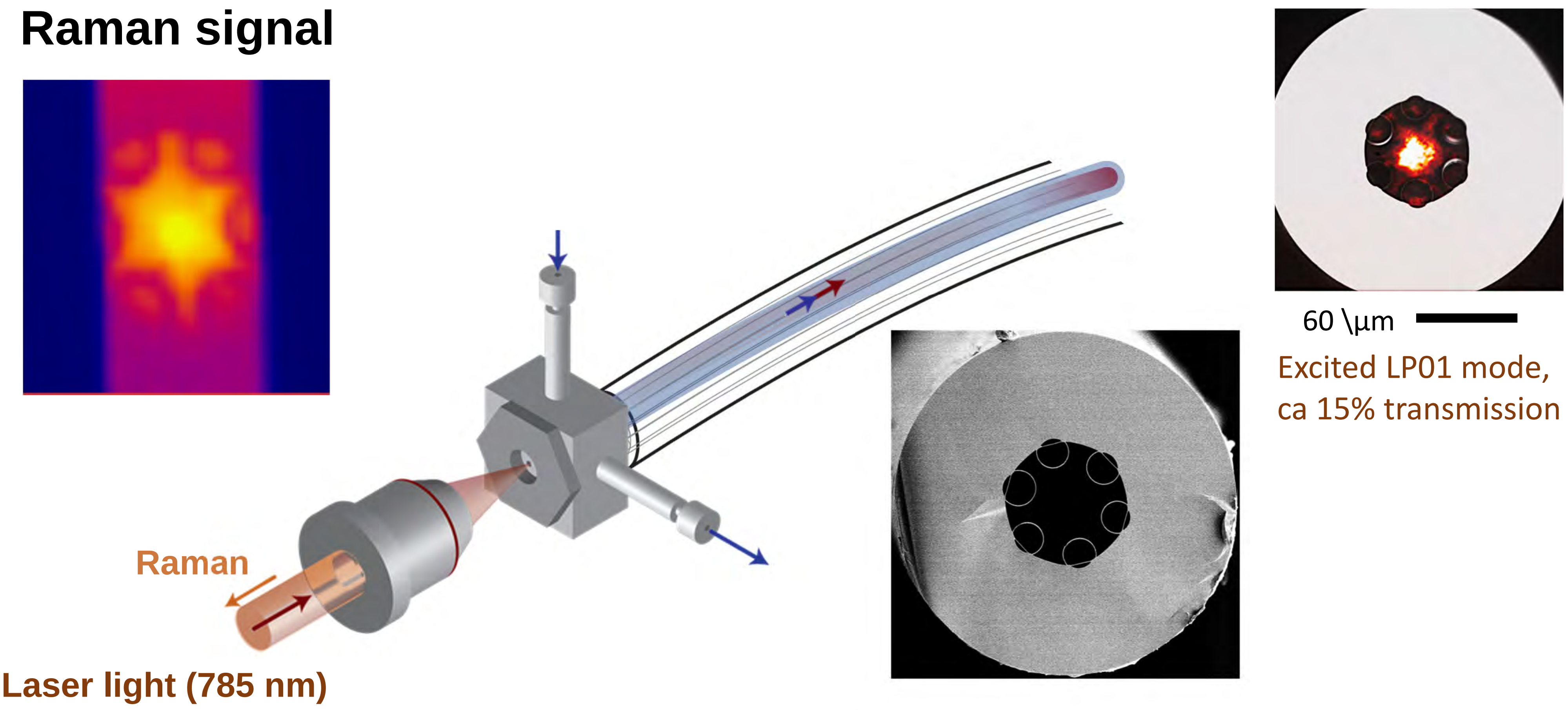


Setup for operando Raman sensing in batteries



E. Miele *et al., Nature Comms* **12**, 1651 (2022). https://doi.org/10.1038/s41467-022-29330-4

Setup for operando Raman sensing in batteries

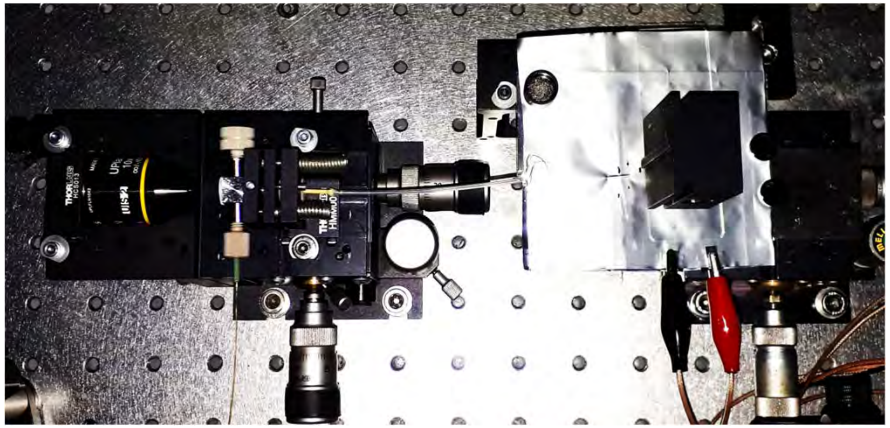


Excited LP01 mode,
ca 15% transmission

- single-ring anti-resonant hollow-core fibre
- sample volume ca 1 µL **LP57** electrolyte: 1.0 M $LiPF_6$ in 3:7 ethylene carbonate (EC): ethyl methyl carbonate (EMC) + 1% vinylene carbonate (VC) additive

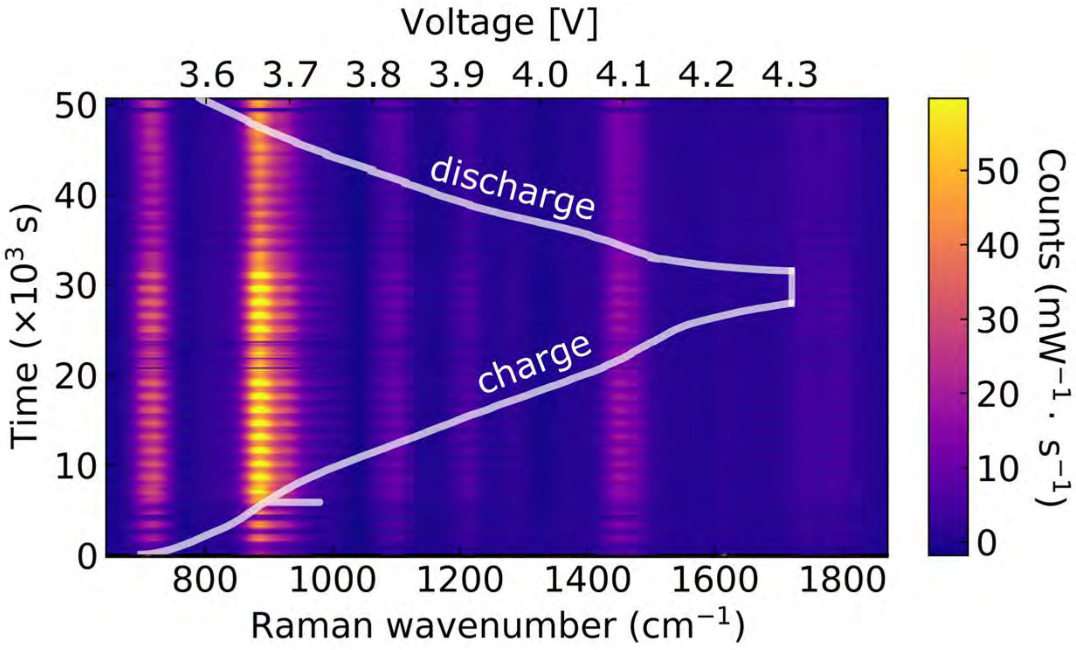
E. Miele *et al.*, *Nature Comms*. **12**, 1651 (2022).

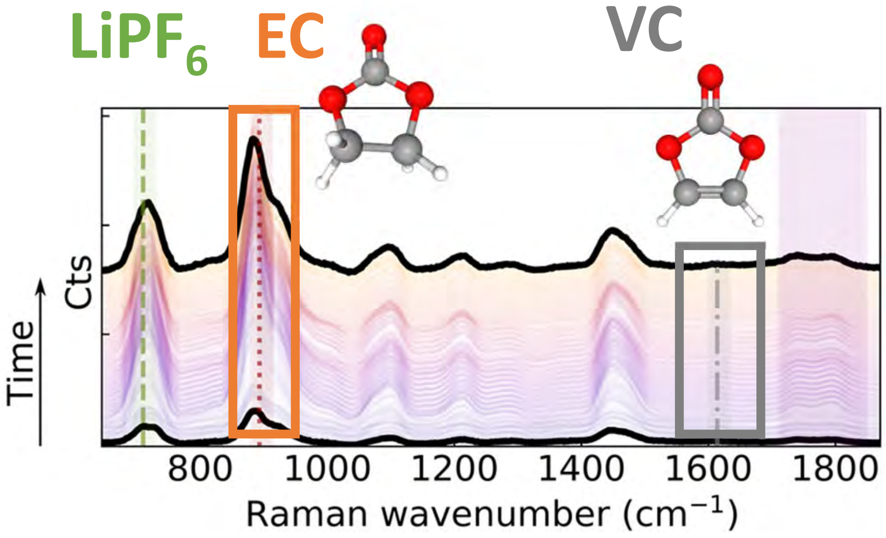
Raman spectra during electrochemical cycle



track Raman lines
of electrolyte components
during electrochemical cycle:

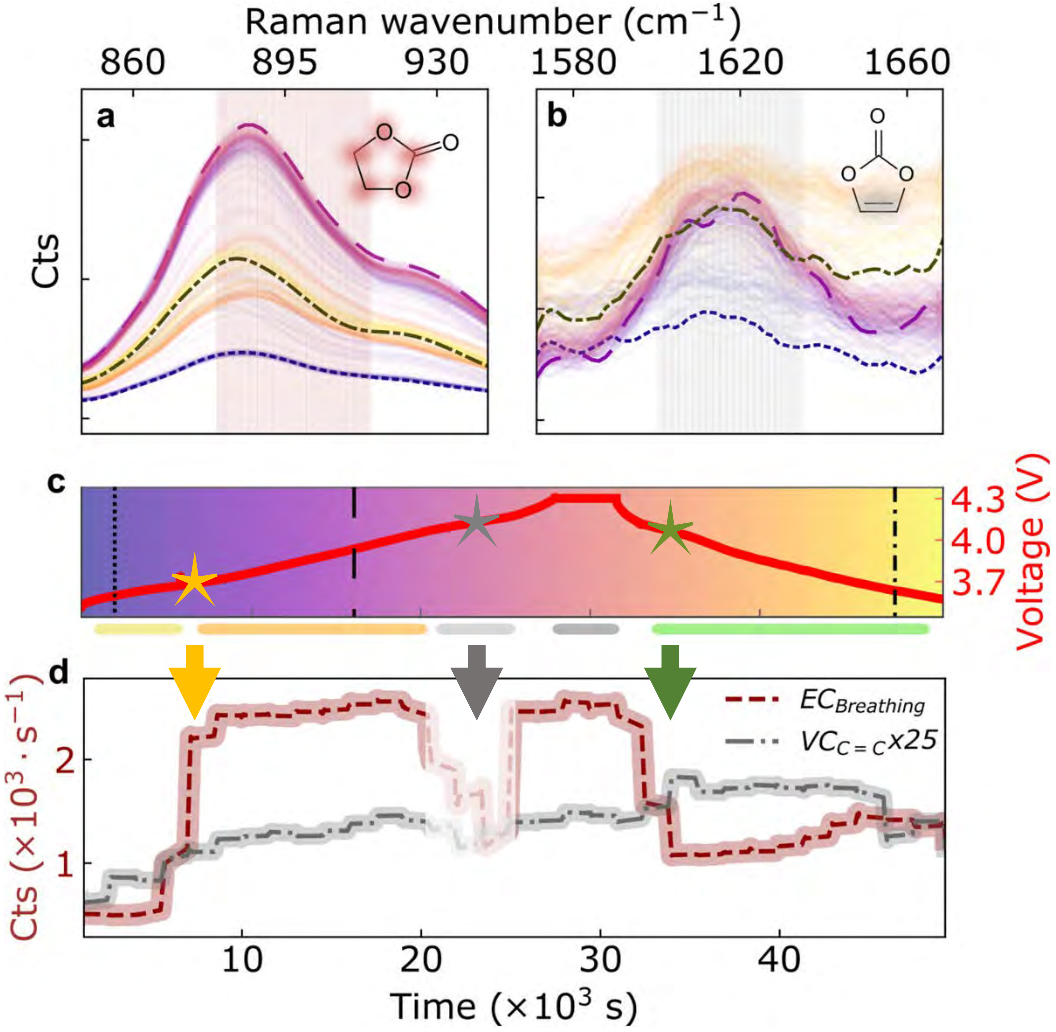
- ethylene carbonate (EC)
- vinylene carbonate (VC)





E. Miele *et al., Nature Comms*. **12**, 1651 (2022).

Raman spectra during electrochemical cycle



Ethylene carbonate Vinylene carbonate

key observations:

- increase in EC mode
  (SEI formation / Li$^+$ intercalation?)
- bubble formation
  (SEI / singlet oxygen formation?)
- increase in vinylene mode
  (cathode electrolyte oxidation?)

- first operando Raman detection in a full-cell battery
- observed creation of vinylene species

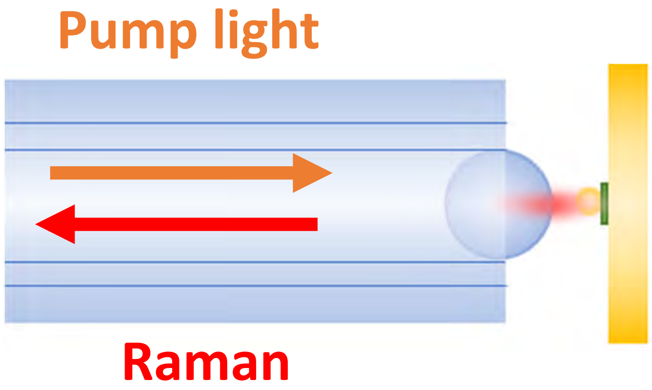
Outlook: battery Raman probes

Electrolyte studies

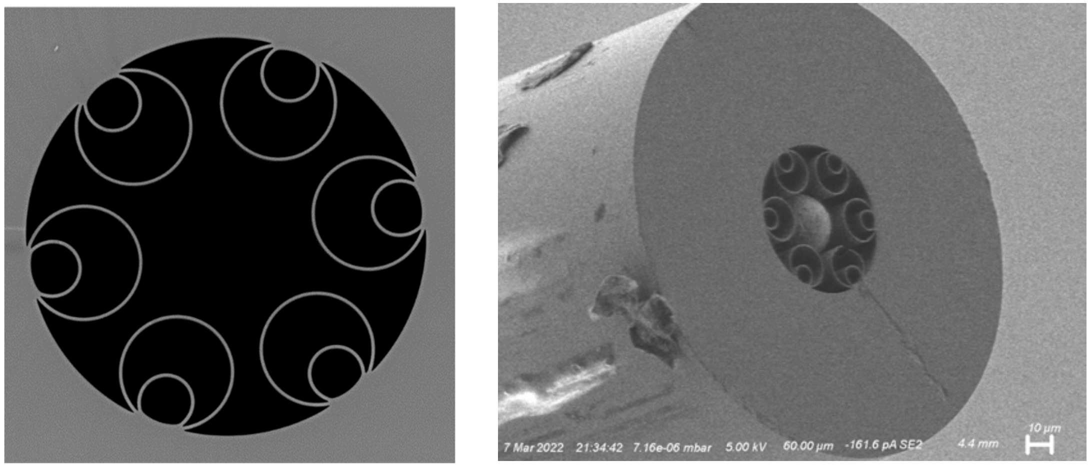
- study degradation mechanism with ‘spiked’ cells (acid, H_2O …)
- combine with FT-IR, NMR, Differential Electrochemical Mass Spec.

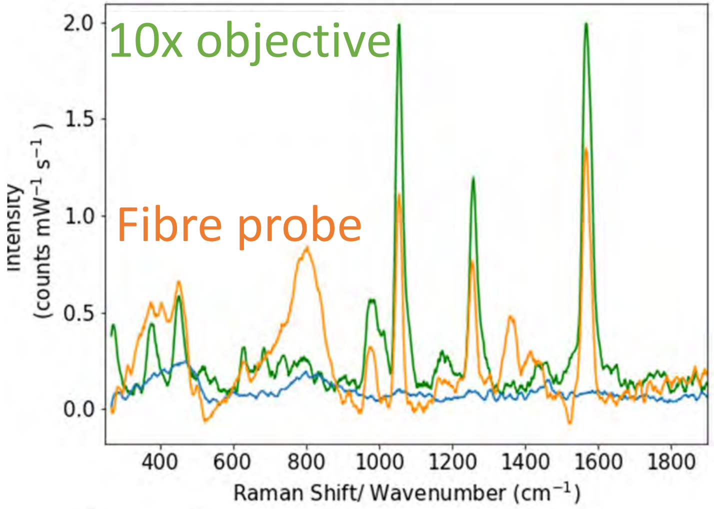
Localized sensing

- embedded high-index glass microlens
- monitor electrode surfaces during cycling



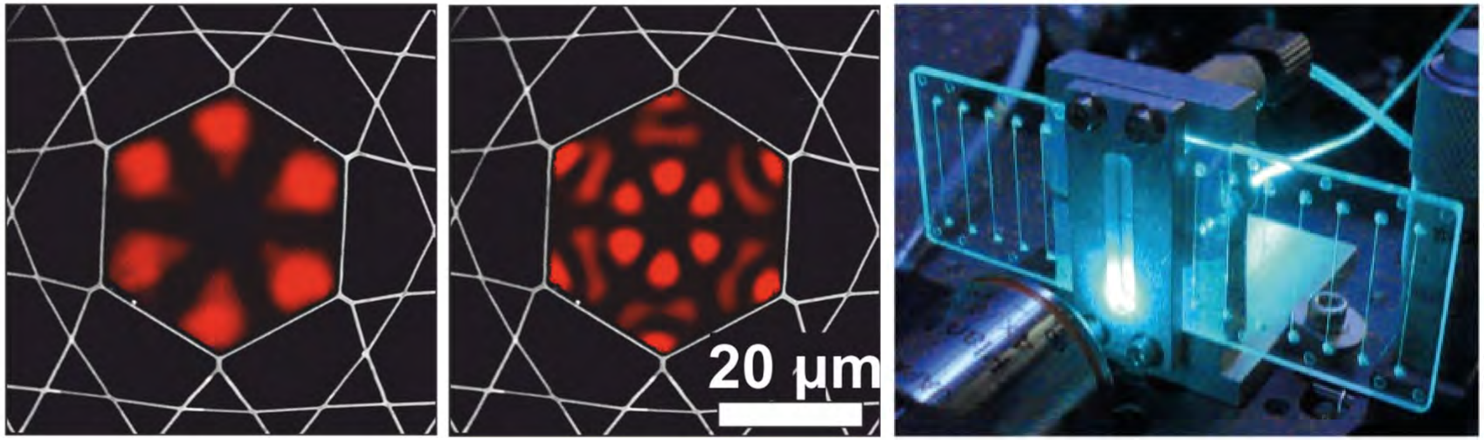
Hollow-core fibre with high-NA micro lens





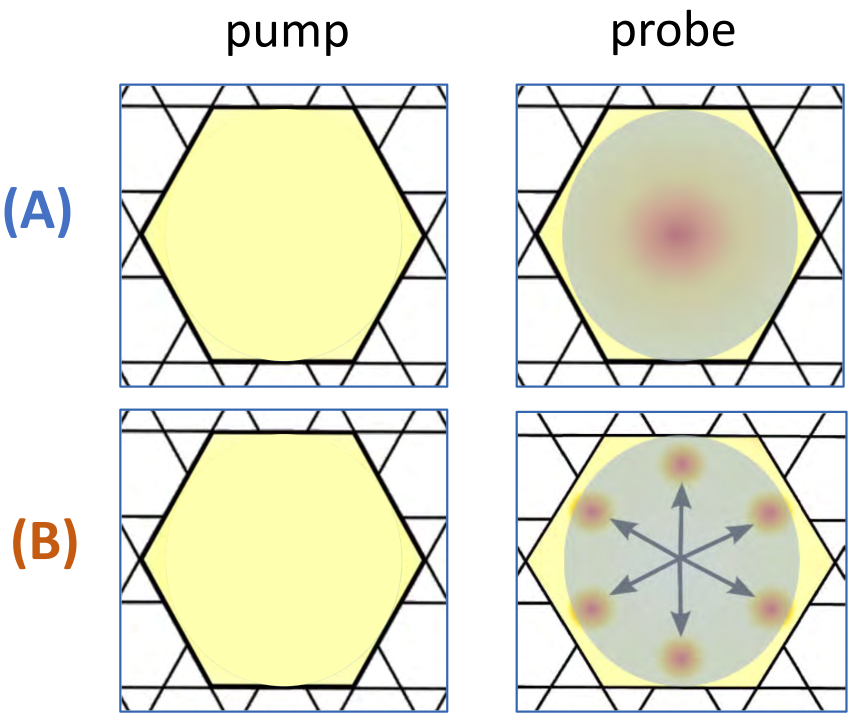
(M. Groom and E. Miele, in preparation)
microlens method similar to: Lombardini *et al. Light: Sc. & Appl.* **7**, 10 (2018)

Higher-order modes in optofluidic HC-PCF



Probing diffusion in optofluidic microreactors

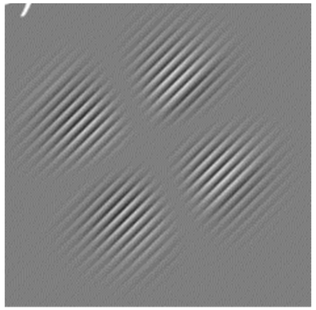
1. probe in **core** and **surface** regions with:
   (A) fundamental mode
   (B) higher-order mode
2. excite reaction in fundamental mode
3. measure diffusion of reaction products

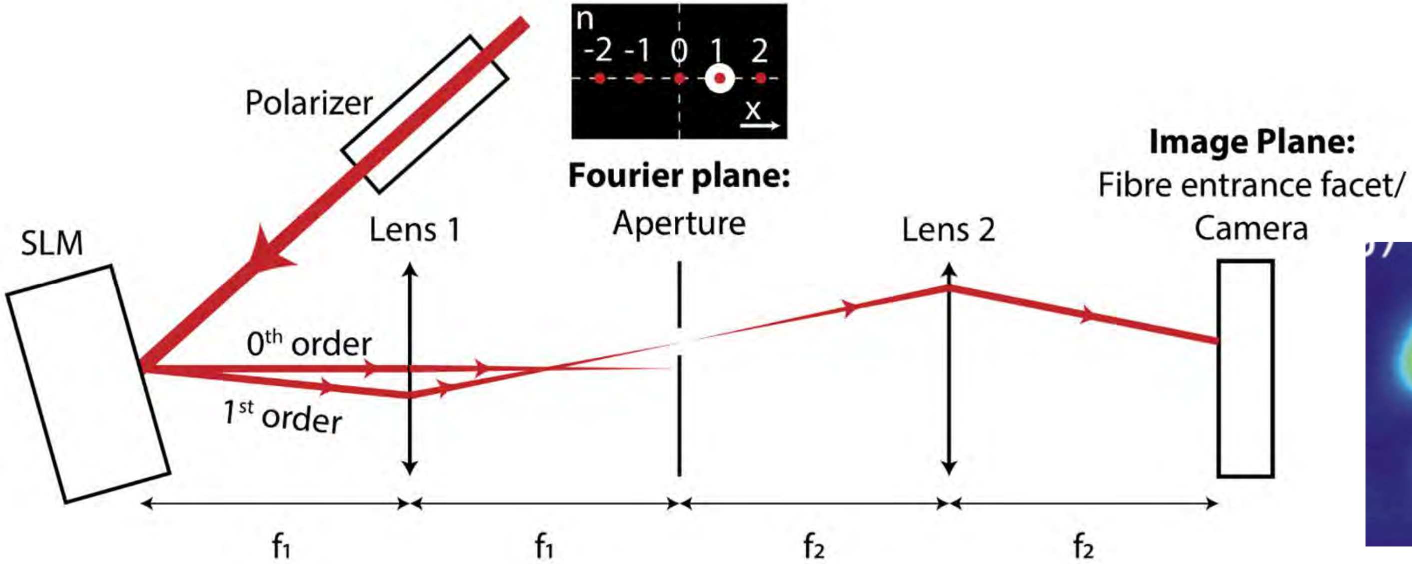


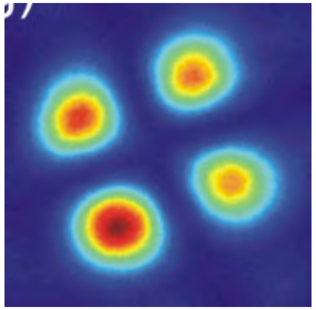
how to controllably excite higher-order modes?

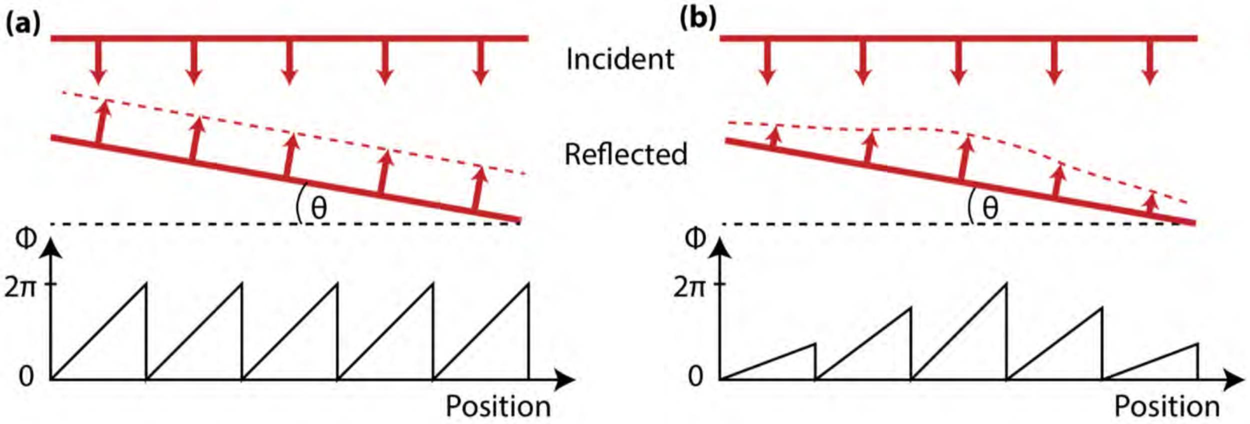
Similar approach in : G. Epple *et al. Opt. Lett* 42, 3271-3274 (2017). https://doi.org/10.1364/OL.42.003271

Spatial light modulation





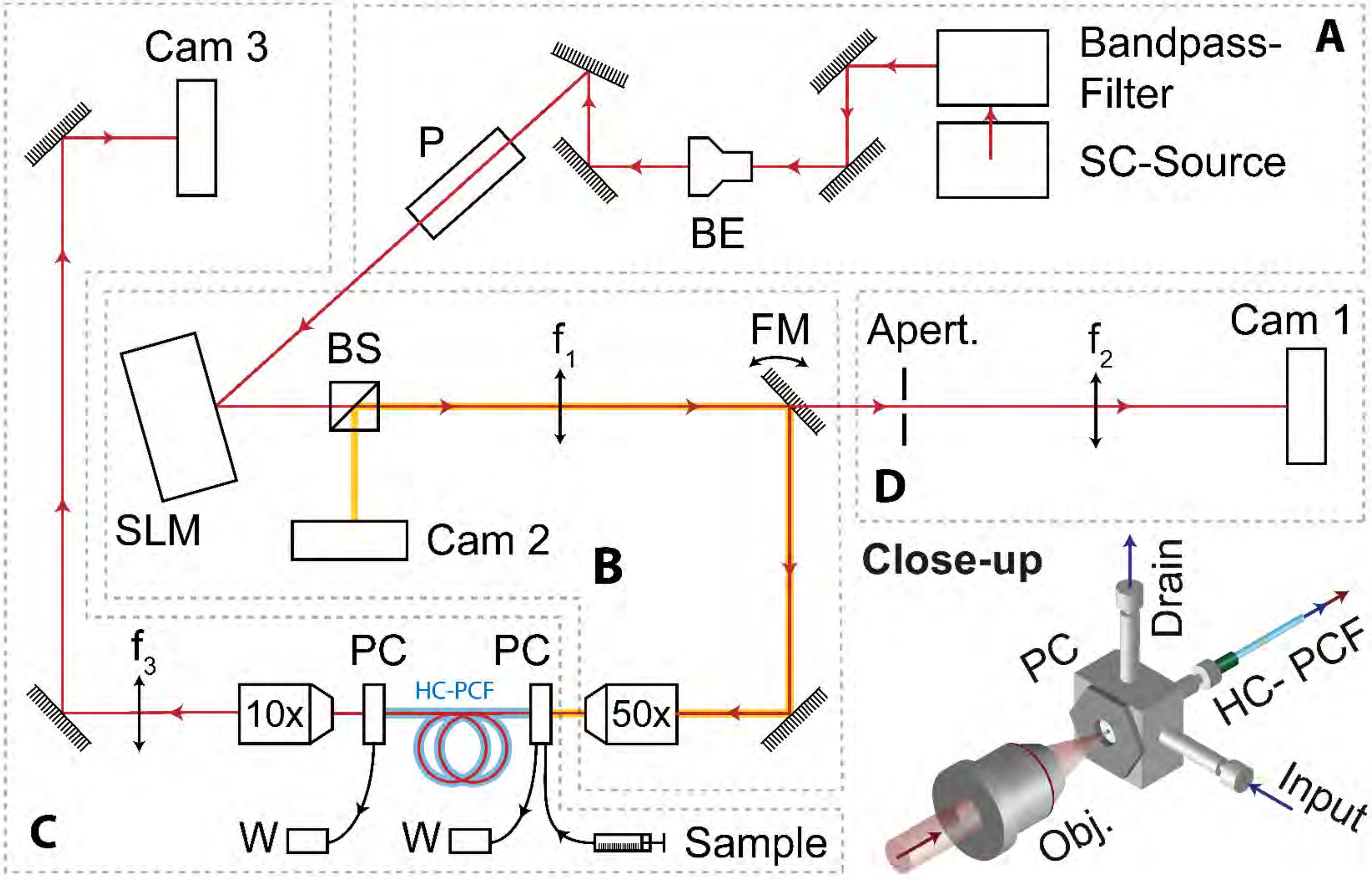




- SLM surface imaged onto fibre end face
- control both phase- and amplitude profile

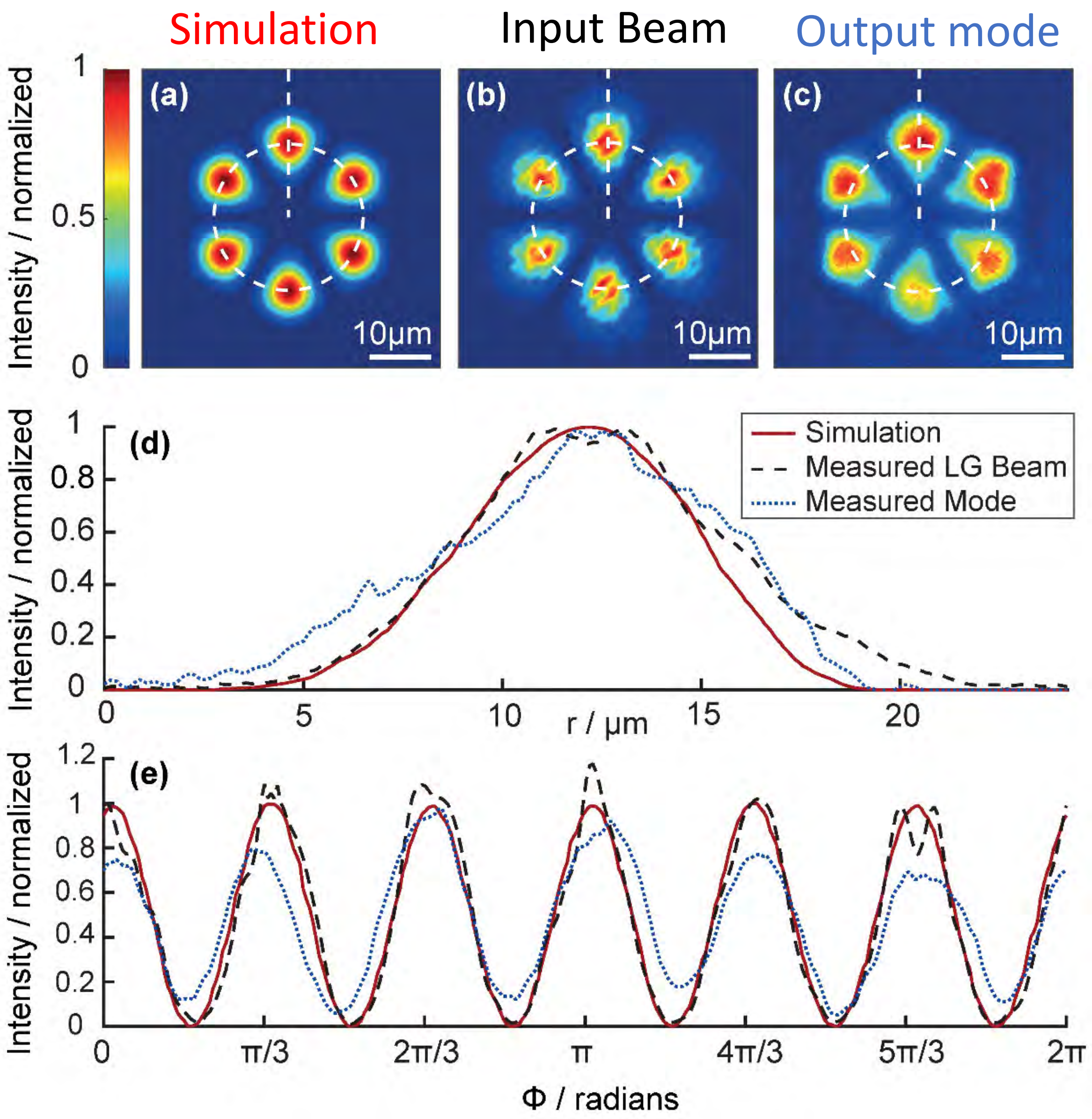
Euser *et al.*, *Opt. Express* **16**, 17972 (2008); Flamm *et al. JLT* **31**, 1023 (2013).

Setup for higher-order mode excitation



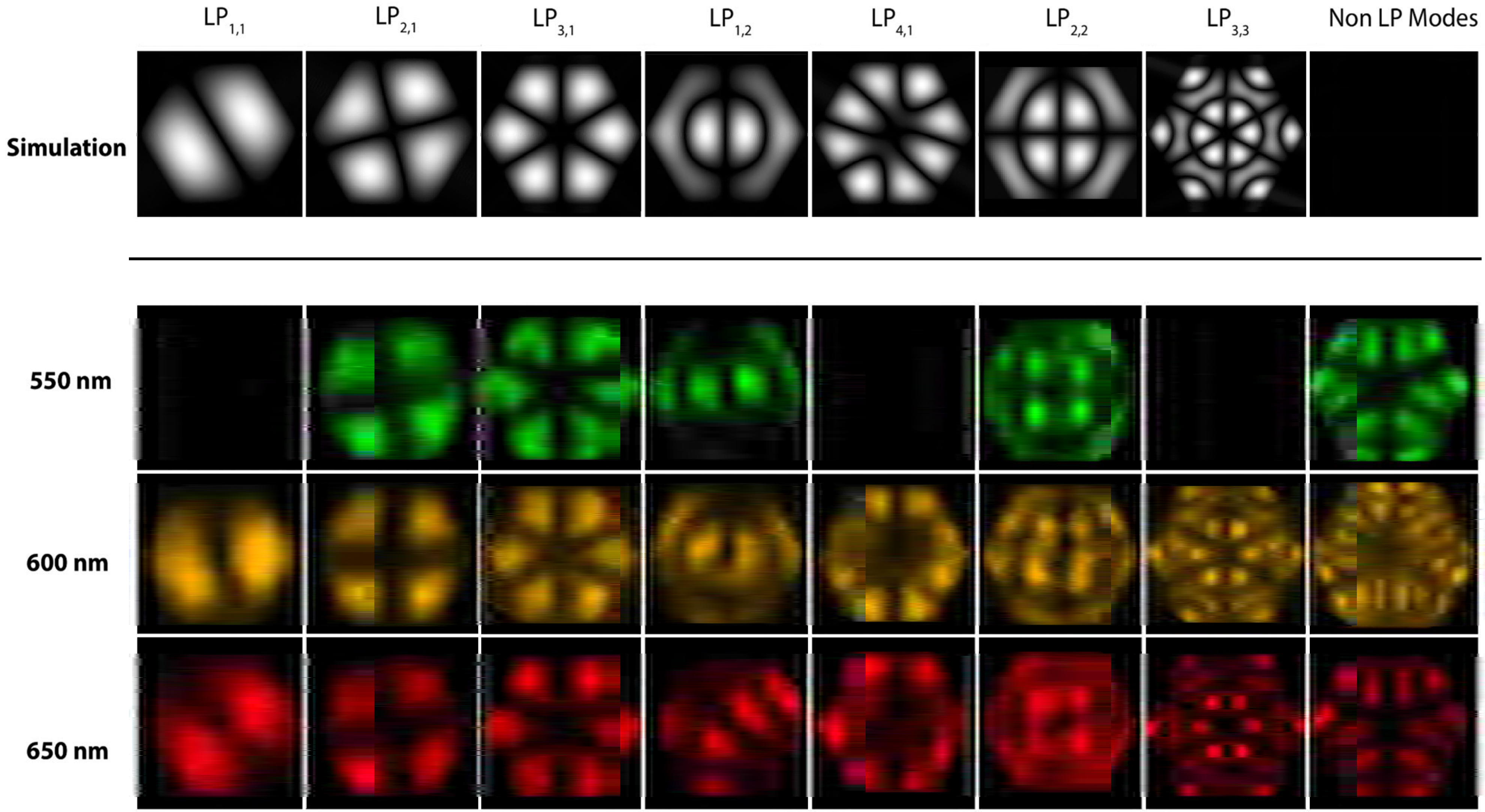
- tunable light source (filtered supercontinuum)

Mode quality in optofluidic kagomé fibre



LP_{31} mode: good agreement between simulation and experiment

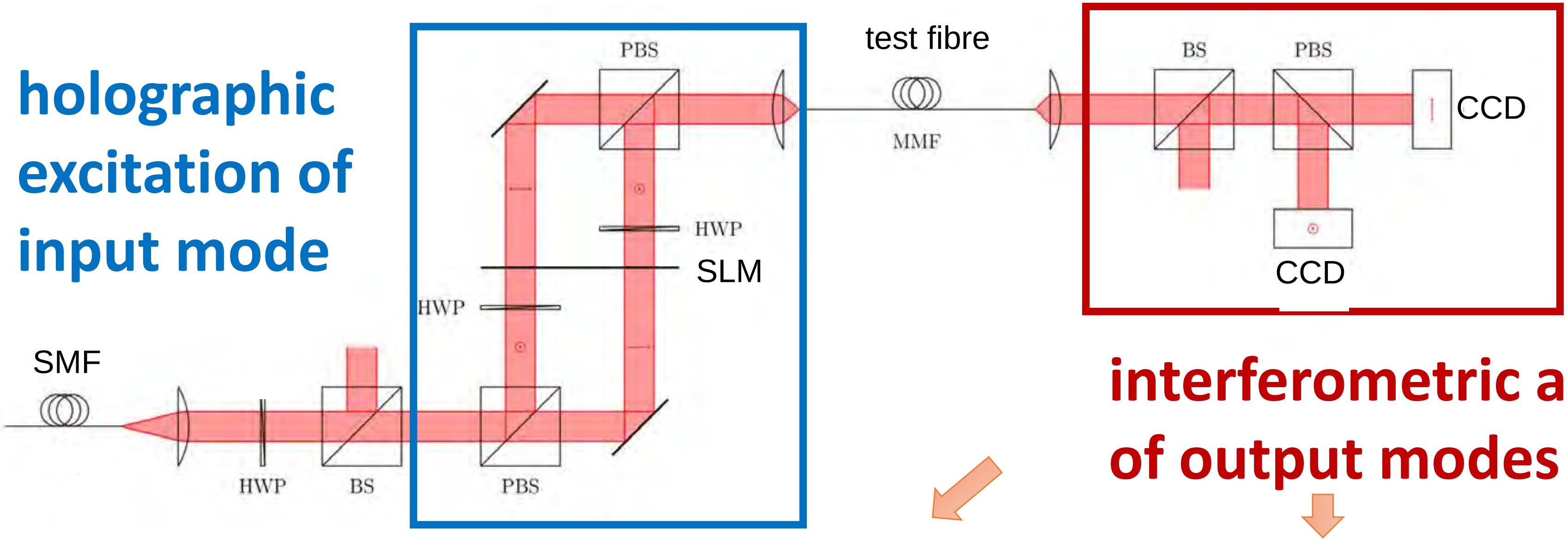
Modes in optofluidic kagomé PCF



- excited modes up to LP_{33} across visible range

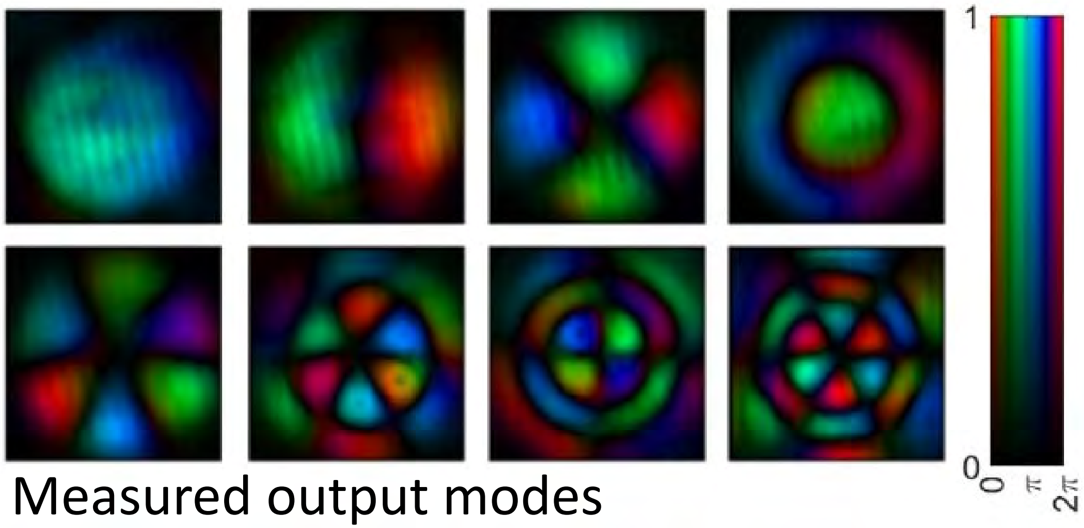
A. Ruskuc *et al.* *Opt. Express* ***26.*** pp. 30245 (2018).

Transmission matrix measurements



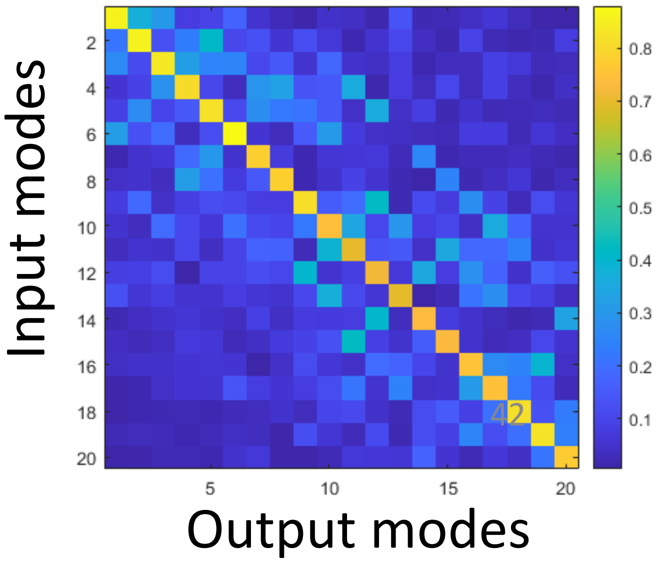
holographic excitation of input mode

interferometric analysis of output modes



Measured output modes

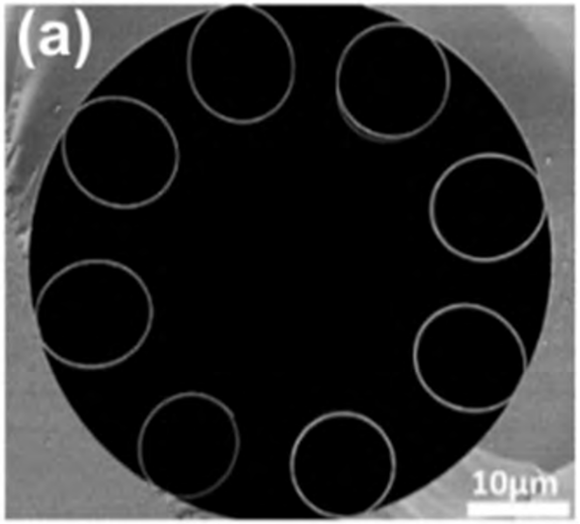
Transmission Matrix

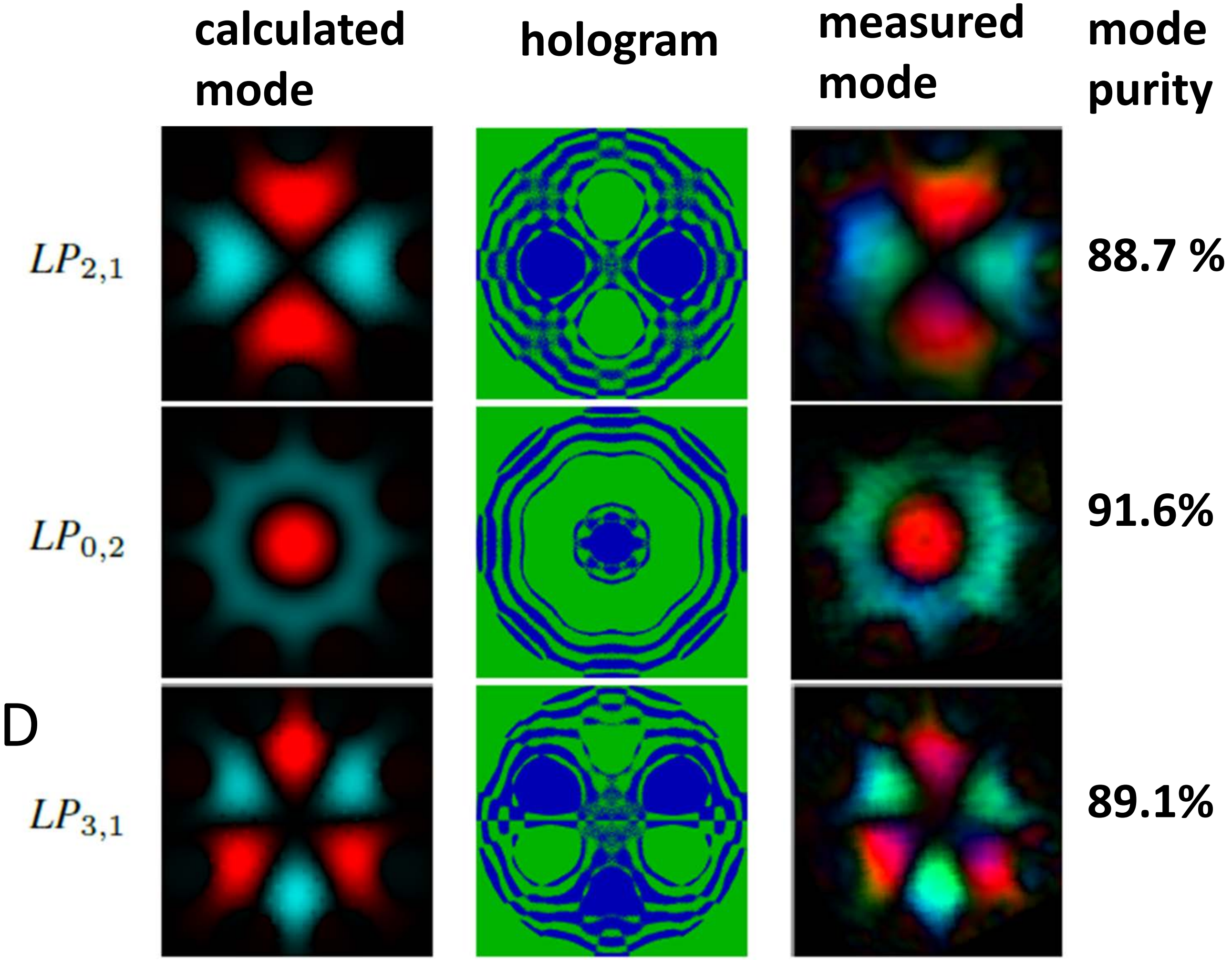


with George Gordon (Nottingham), Tim Wilkinson (Cam)

R. Mouthaan, *PhD Thesis* (2021).

Efficient excitation of high-purity modes



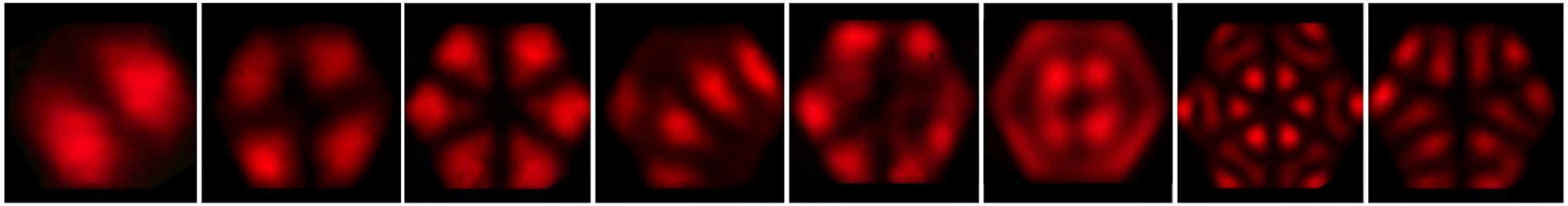


- calculate mode by FDFD
- generate hologram
- measure field by off-axis holography

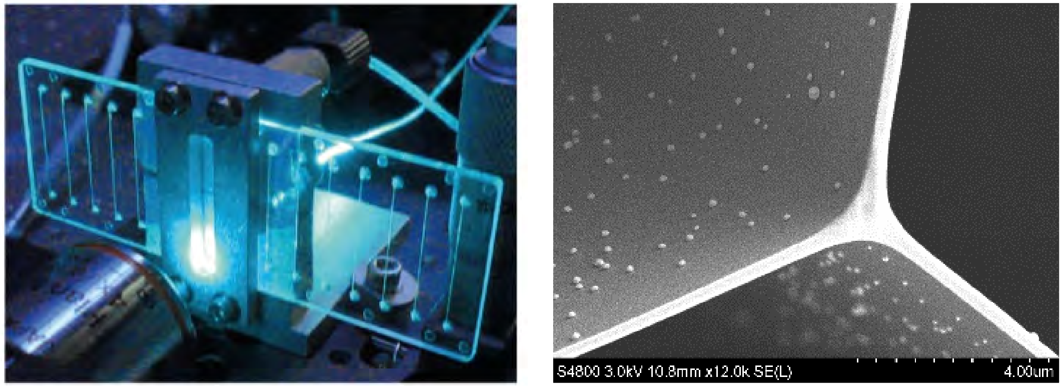
Can obtain pure modes with high launch efficiency

R. Mouthaan *et al.* *J. Lightwave Technol* ***40***, 1150 (2022).

Outlook: mode-based ‘tomography’

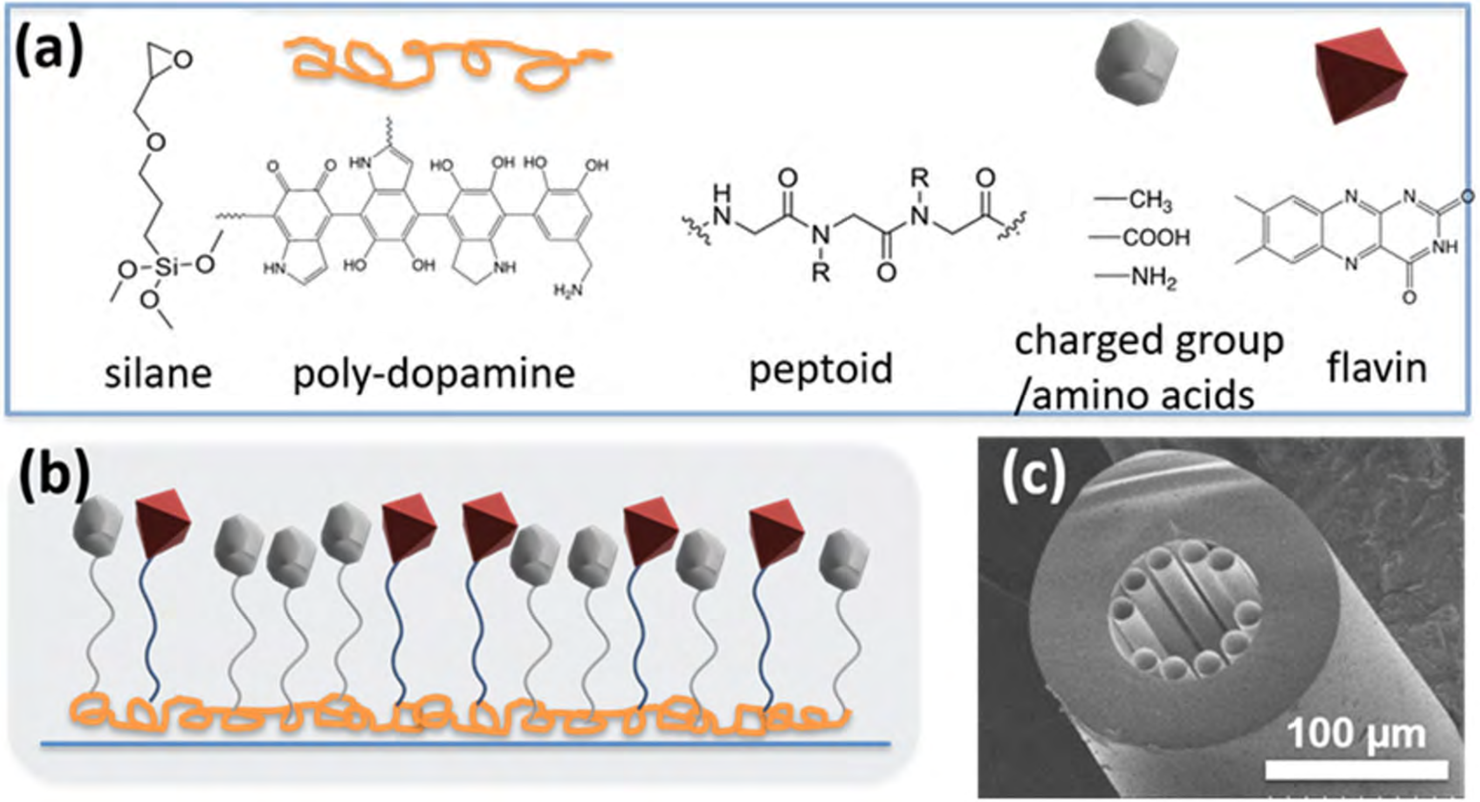


- study catalytic surfaces under reaction conditions
- probe radial concentration profile with higher-order modes
- measure transverse diffusion times



PCF flow reactor, Pt nanoparticles within HC-PCF.

Outlook: functionalize HC-PCF with flavins: enzyme-mimic photocatalysts

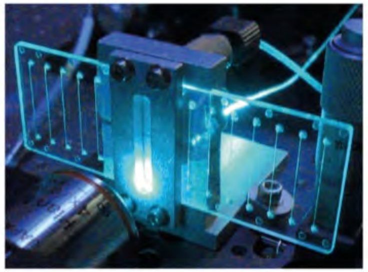


- immobilise Flavins on inner HC-PCF walls
- surface-selective probing with higher-order modes
- study enzyme-functionalized carbon nanodots

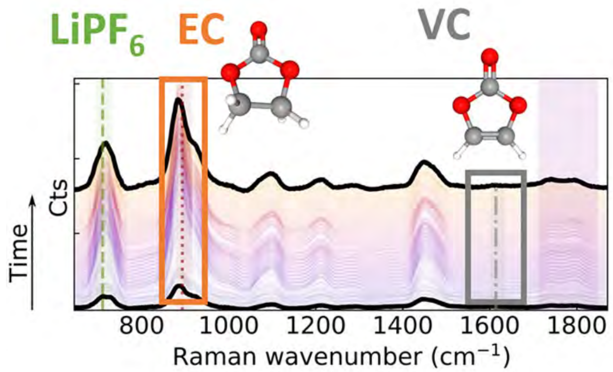
L. Crocker *et al.* , *Nanoscale Horizons* **4** 1318 (2019).

Conclusions

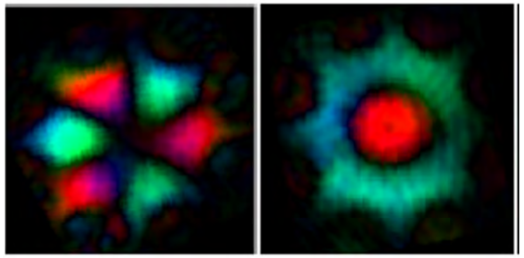
- optofluidic PCF microreactors allow in-situ monitoring of (photo)catalytic processes



- Raman fibre probes can monitor electrolyte chemistry in Li:ion batteries



- higher-order modes enable spatially-resolved sensing



Thank you for your attention!

Matthew Ellis, Jonathan Pinnell, Ashleigh Ruane, TE, Ermanno Miele, Jan Heck, Ruud Jansen

(Megan Groom, Takashi Lawson, Alex Gentleman, Philipp Koehler
Stephen De Bank, Ahmad Azizan)

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Maxwell Centre

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Ahmad Azizan

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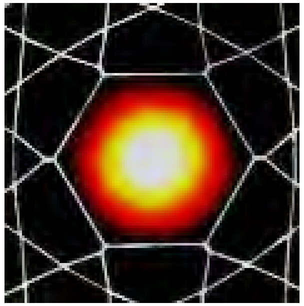
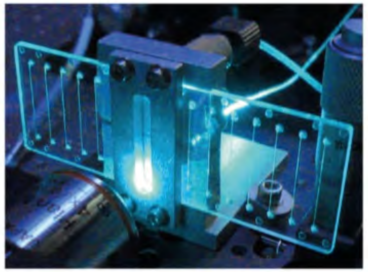
Thank you for your attention!

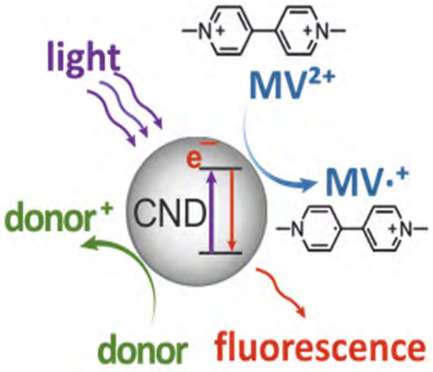
- photonic crystal fibre



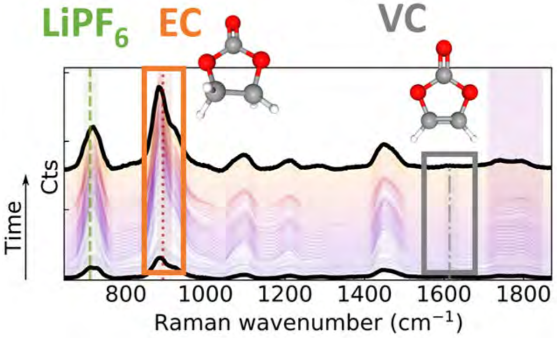
- optofluidic microreactors



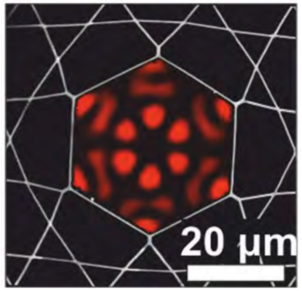
- (photo)catalysis in PCF



- HC-PCF Raman probes



- higher-order modes



https://www.np.phy.cam.ac.uk/research-themes/optofluidics

te287@cam.ac.uk