

Droplet Optics: From Responsive Emulsions to Pathogen Sensors

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1. Pablo Simón-Marqués, Bradley D. Frank, Aleksandr Savateev, Lukas Zeininger, *Adv. Opt. Mater.* 2021

2. Bradley D. Frank, Sara Nagelberg, Agata W. Baryzewska, Pablo Simón-Marqués, Markus Antonietti, Mathias Kolle, and Lukas Zeininger, (in revision)

3. Agata W. Baryzewska, Christian Roth, Peter H. Seeberger, and Lukas Zeininger, (in revision)

MAX PLANCK INSTITUTE
OF COLLOIDS
AND INTERFACES



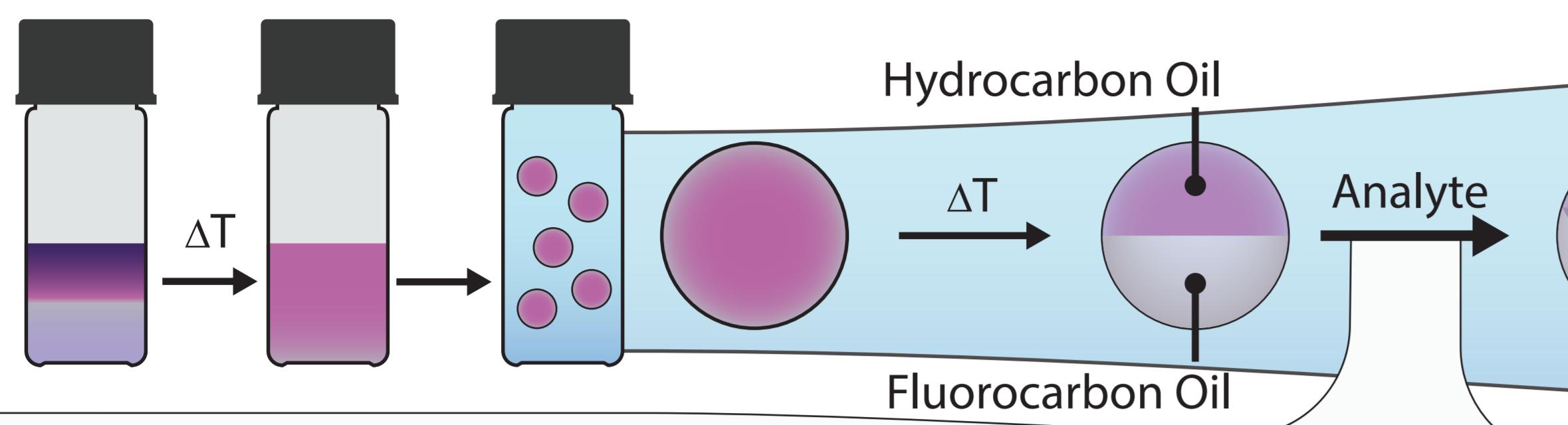
DFG Deutsche Forschungsgemeinschaft

VolkswagenStiftung



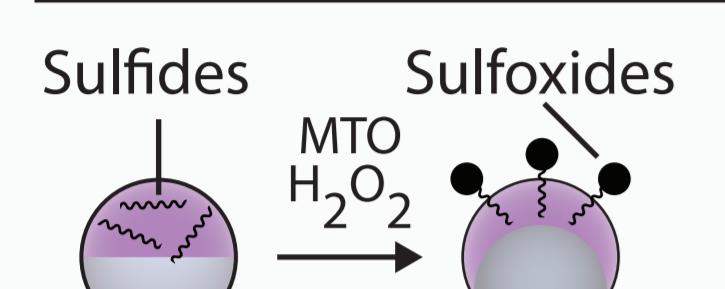
Sensors are stimuli responsive materials. Complex emulsion droplets respond to changes in chemical information as morphological transformation, characteristically.

We explore one pathway for multiplexed, reference-free, and ratiometric measurement of emulsion droplet programmable reconfiguration via concentrating and directing fluorescent light.^{1,2}



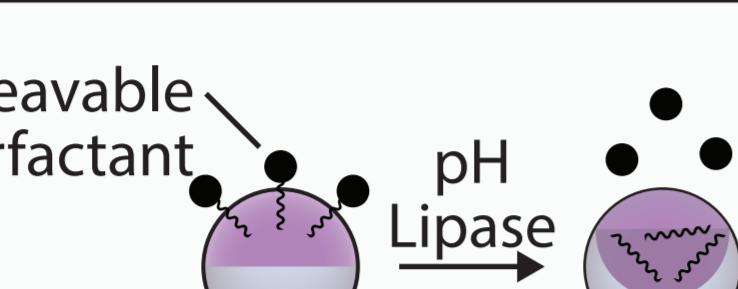
Some existing detection pathways¹

Covalent chemistry



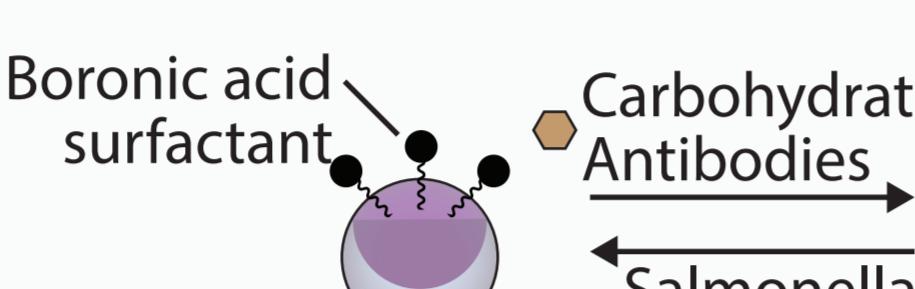
Fong, D., et al., *J. Am. Chem. Soc.* 2021

Enzyme or acid cleavable



Zarzar, L. D., et al., *Nature* 2015
Zarzar, L. D., et al., *PNAS* 2017

Dynamic covalent chemistry

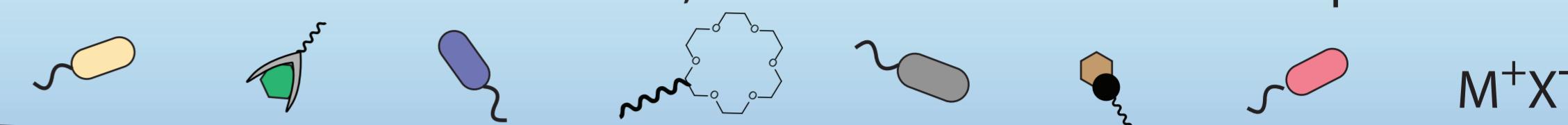


Zeininger, L., et al., *ACS Cent. Sci.*, 2019

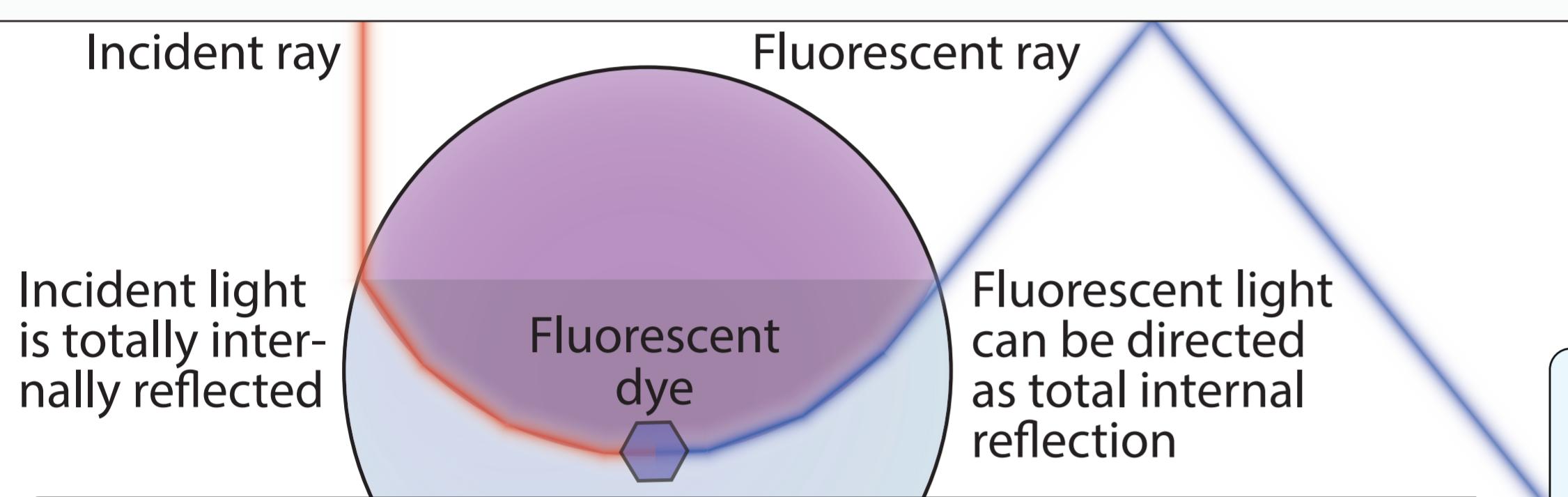
Complex emulsions are simple to prepare with a thermal phase separation approach.

Interfacial programming via chemical orthogonality

The physical response of emulsion droplets is established for a variety of analytes. To establish the transduction of nano-scale chemical events to macro-scale, a facile readout scheme is required.

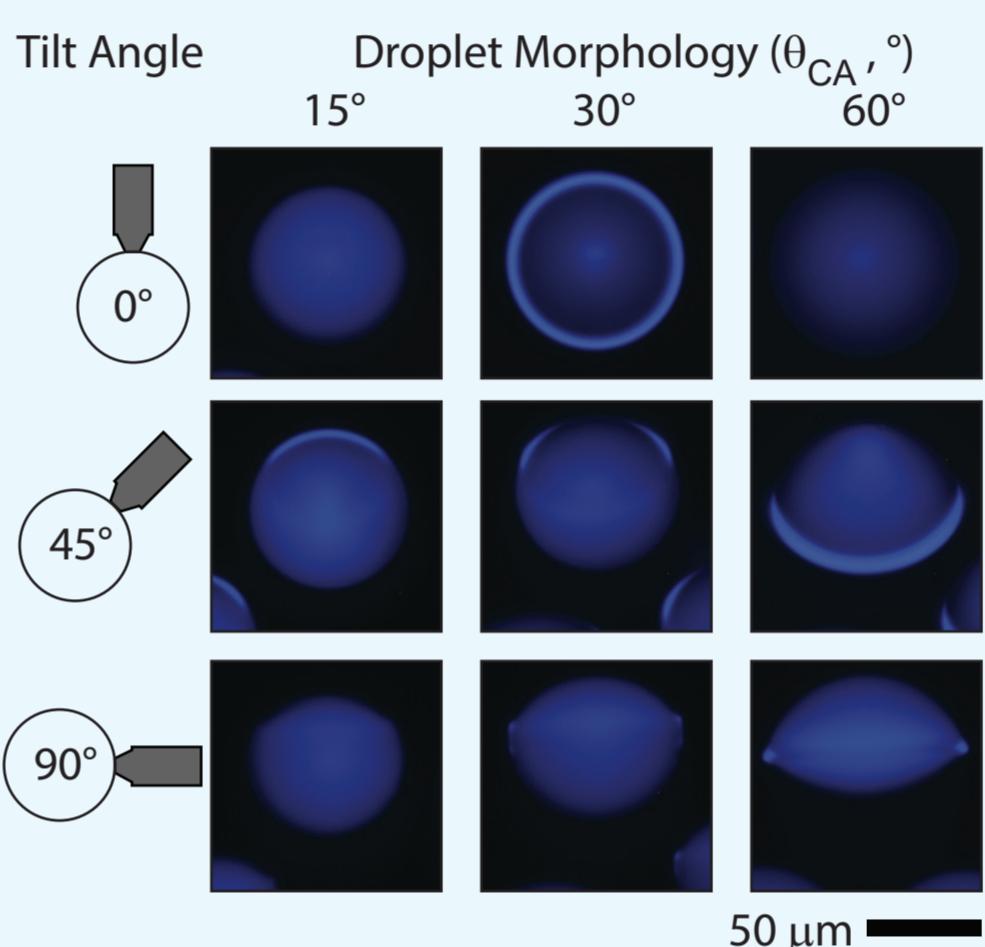
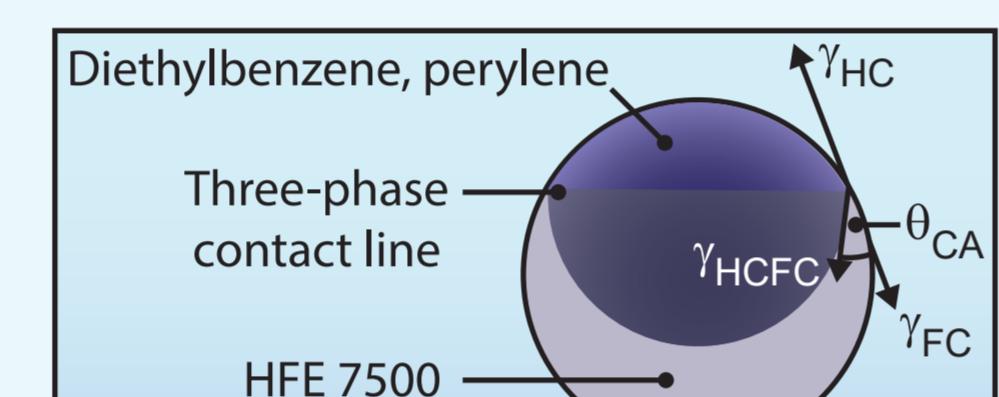


M⁺X⁻

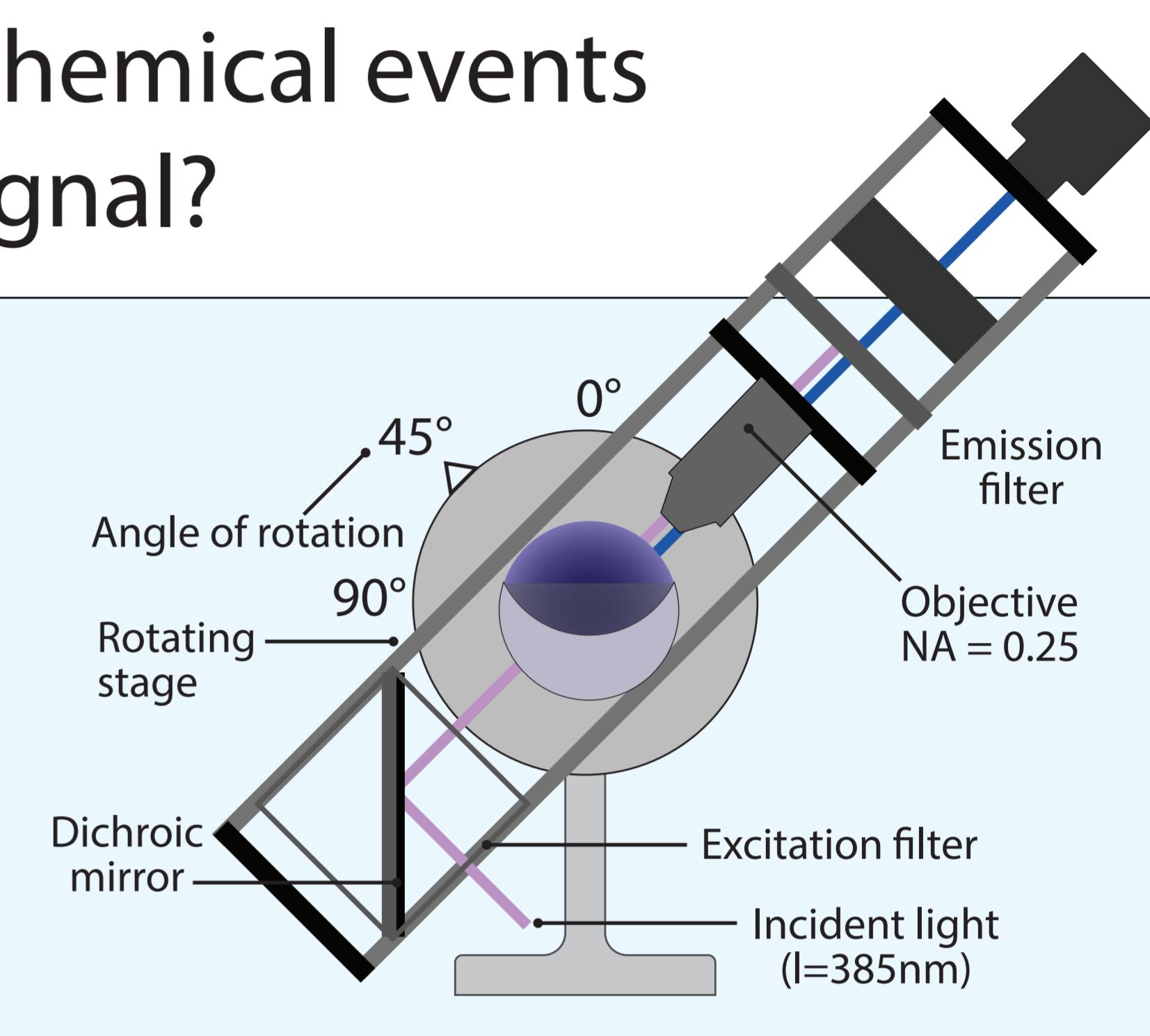


How can we translate nano-scale chemical events into a characteristic macro-scale signal?

Light is directed by the three-phase interface²

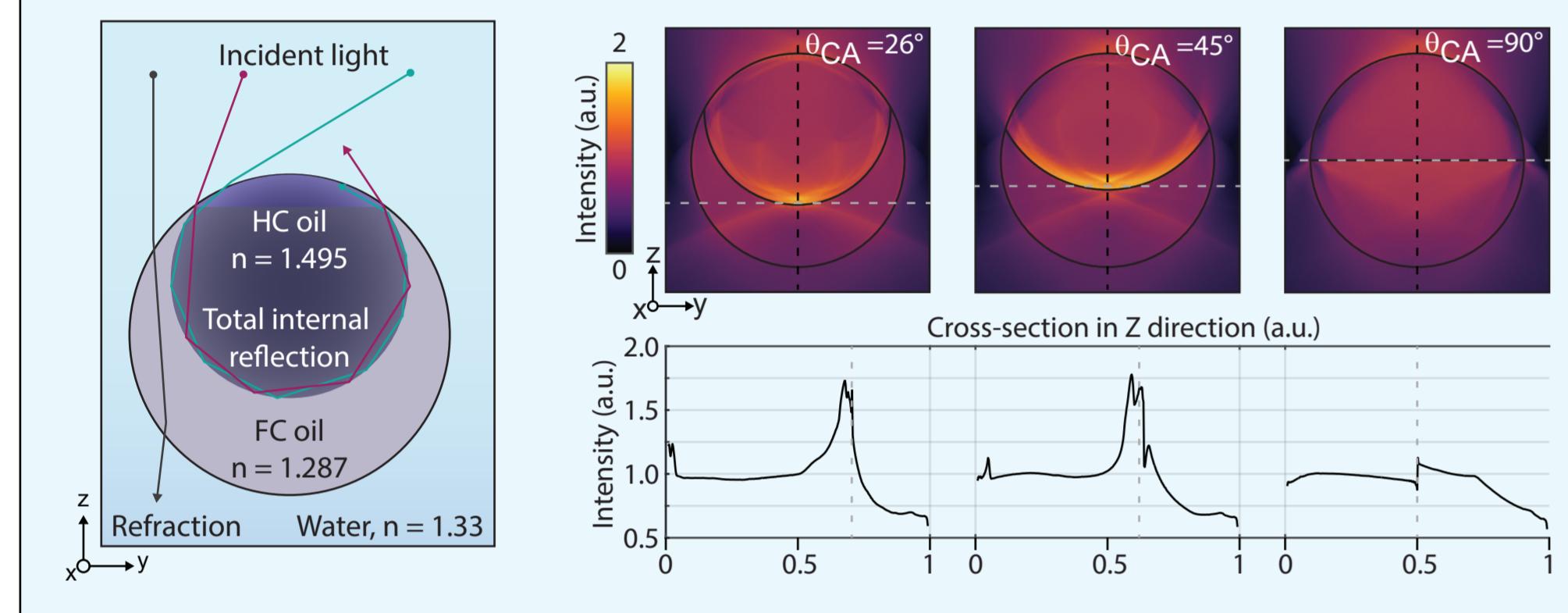


When a fluorescent dye is placed within the hydrocarbon phase, an annular fluorescent ring can be viewed only at particular angles.



Complex droplets align with gravity, a rotating fluorescence microscope is used to image droplets at any angle.

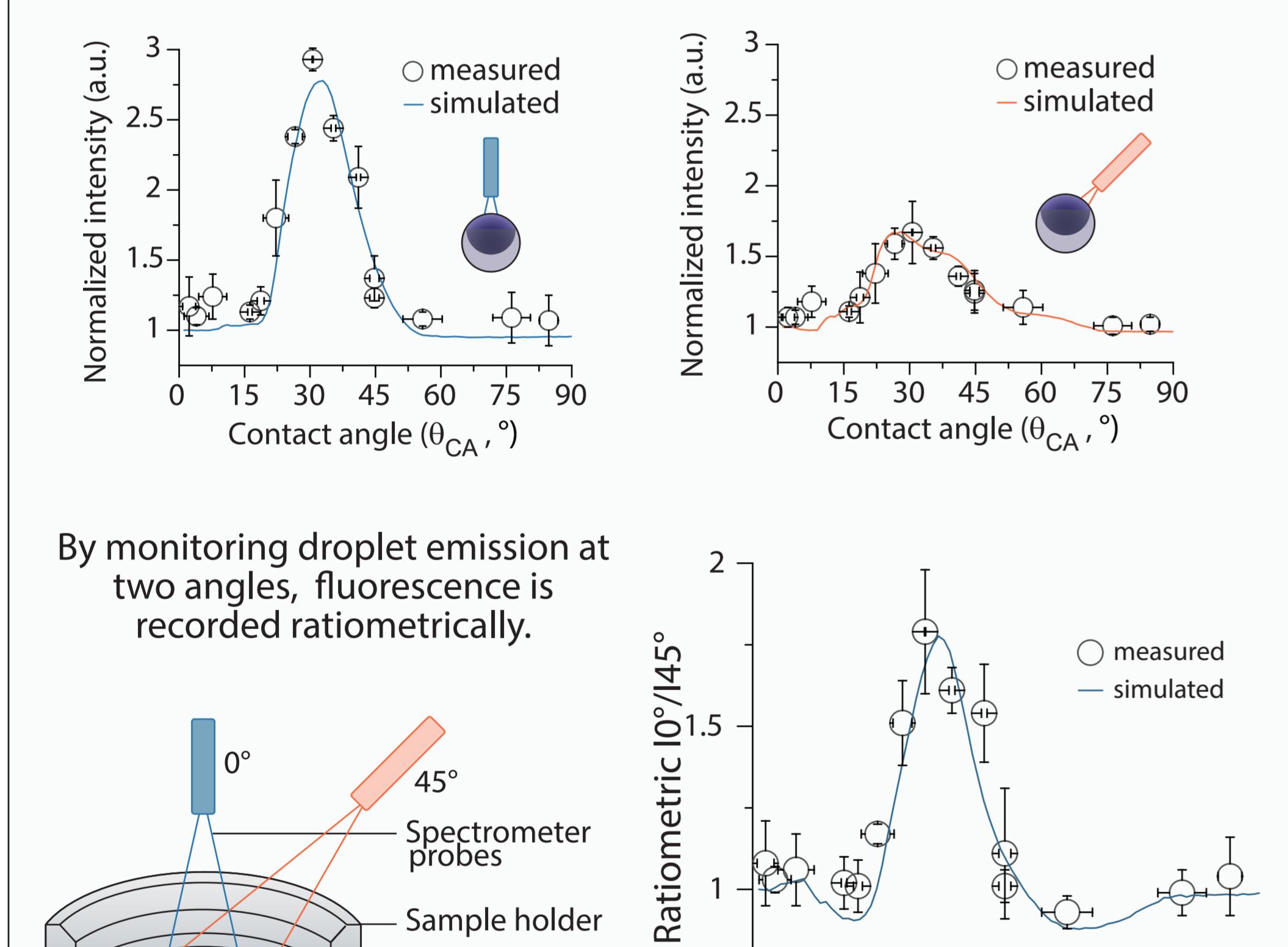
Emulsion droplets collect incident light^{1,2}



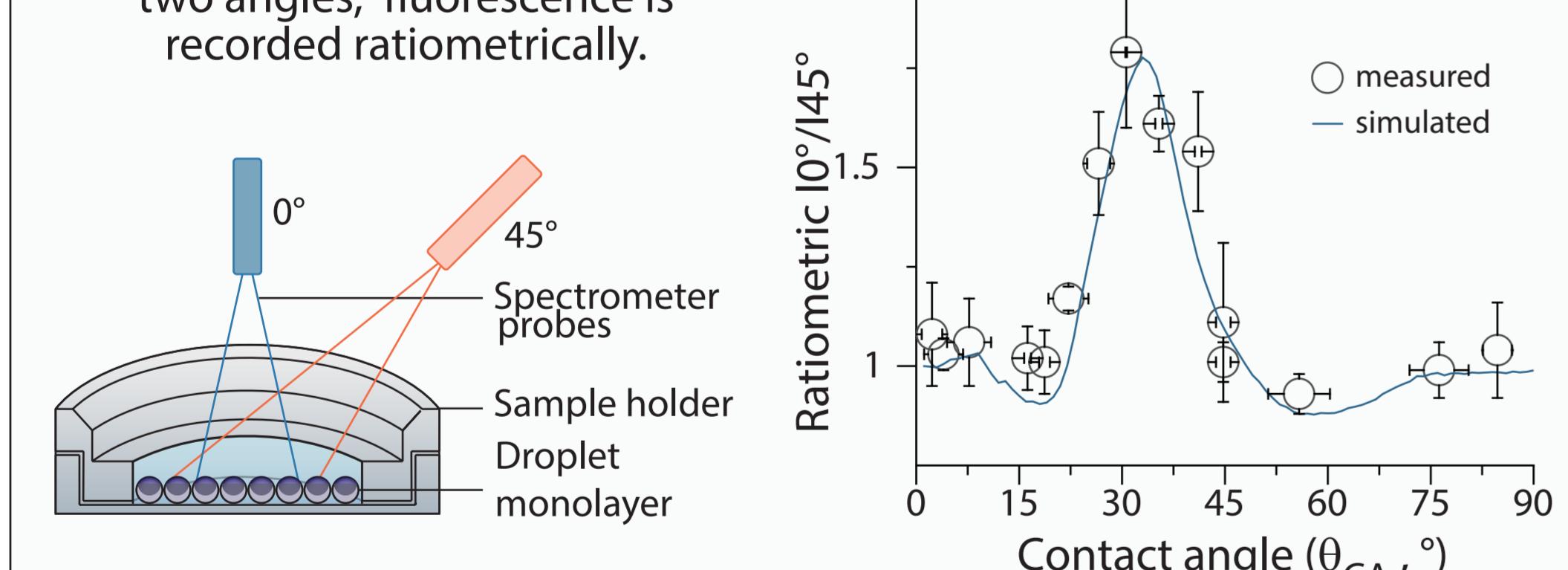
Light totally internally reflects along the internal hydrocarbon-fluorocarbon interface, dependant on refractive indices and droplet morphology.

Droplet monolayers as a referencefree sensor²

We monitor the fluorescence of layers of dyed Janus emulsion droplets.

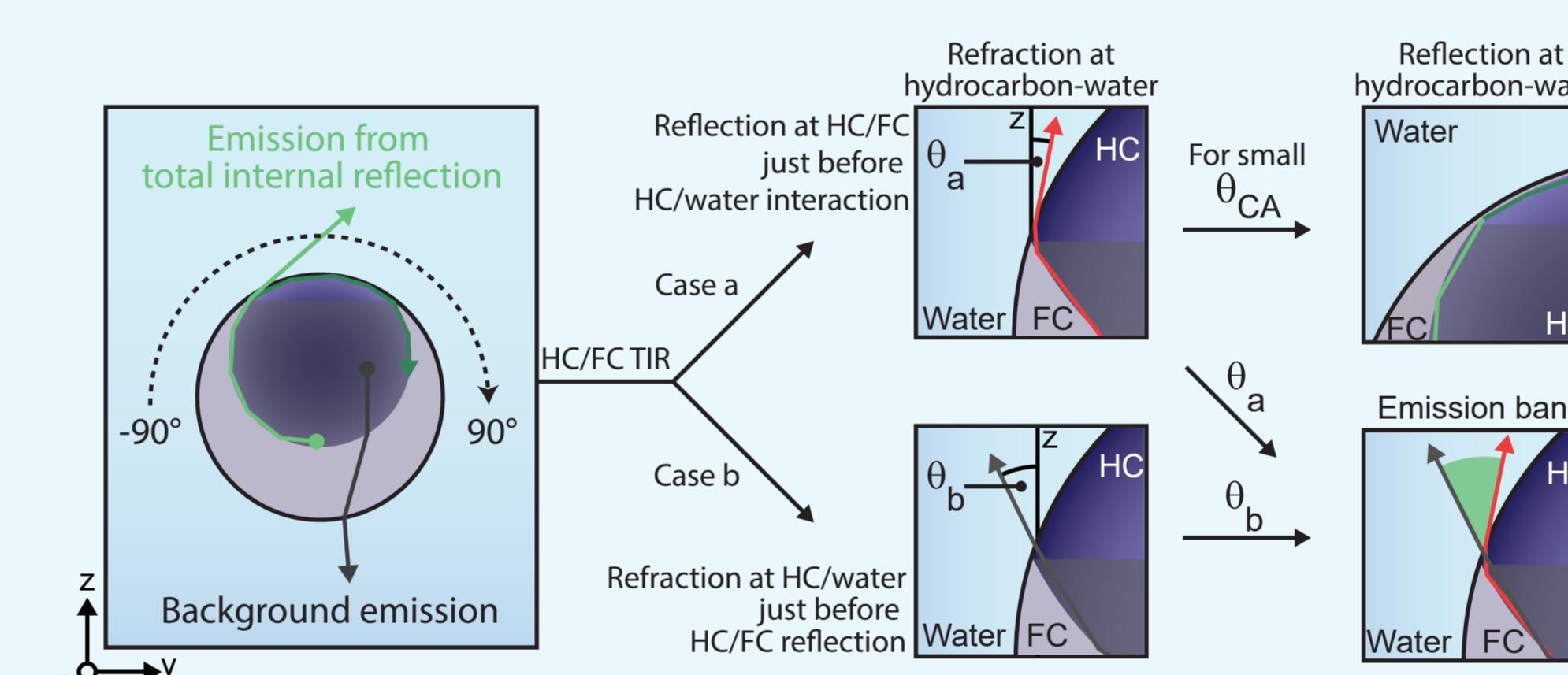


By monitoring droplet emission at two angles, fluorescence is recorded ratiometrically.

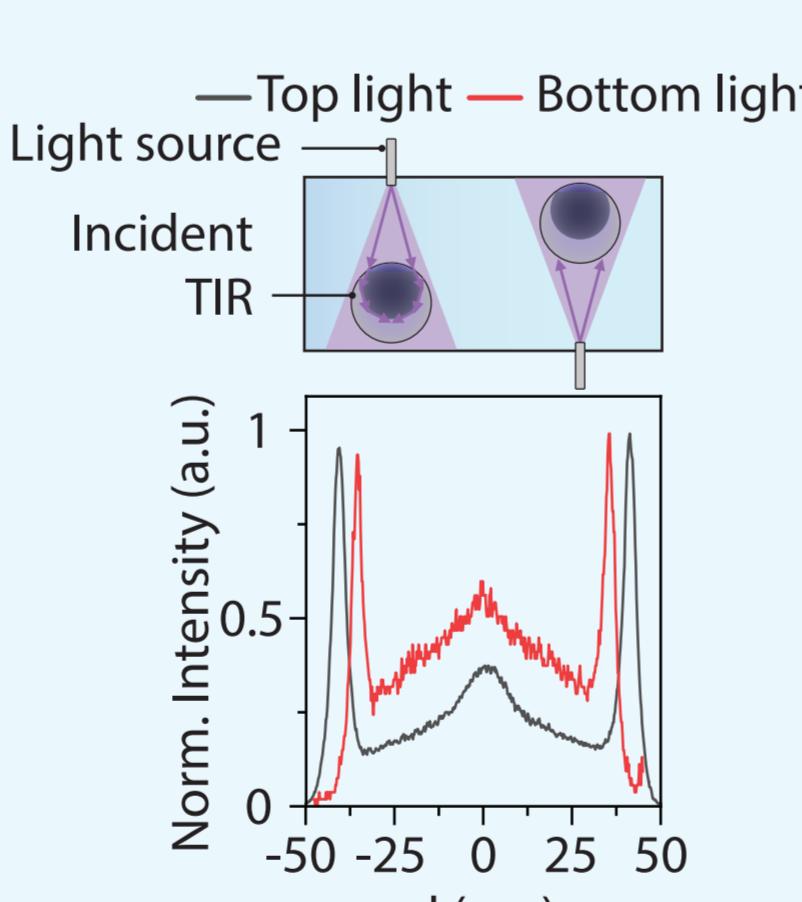


Ratiometric morphology determination is analyte-chemistry independent, and enables polydisperse emulsions for on-site application: translating nano-scale chemical events into macro-scale fluorescence signal.

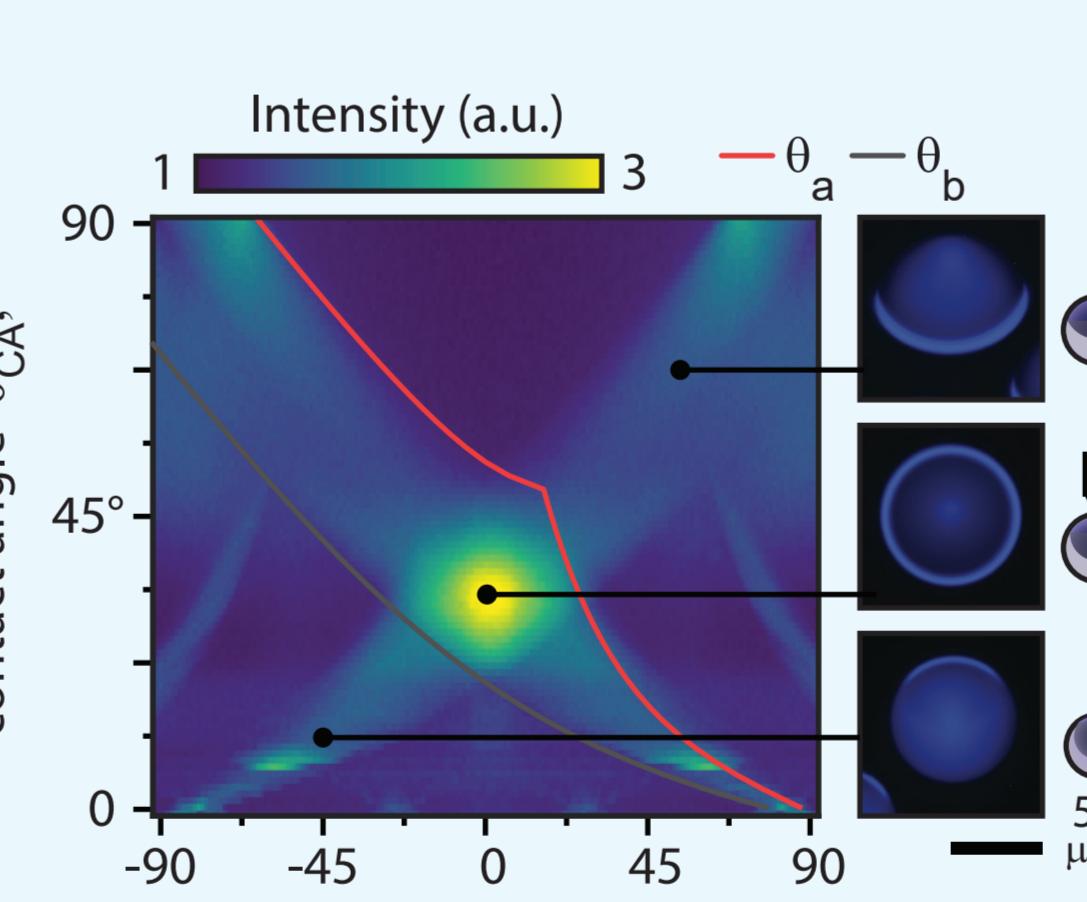
Totally internally reflected rays are interfacially-guided until possible exit²



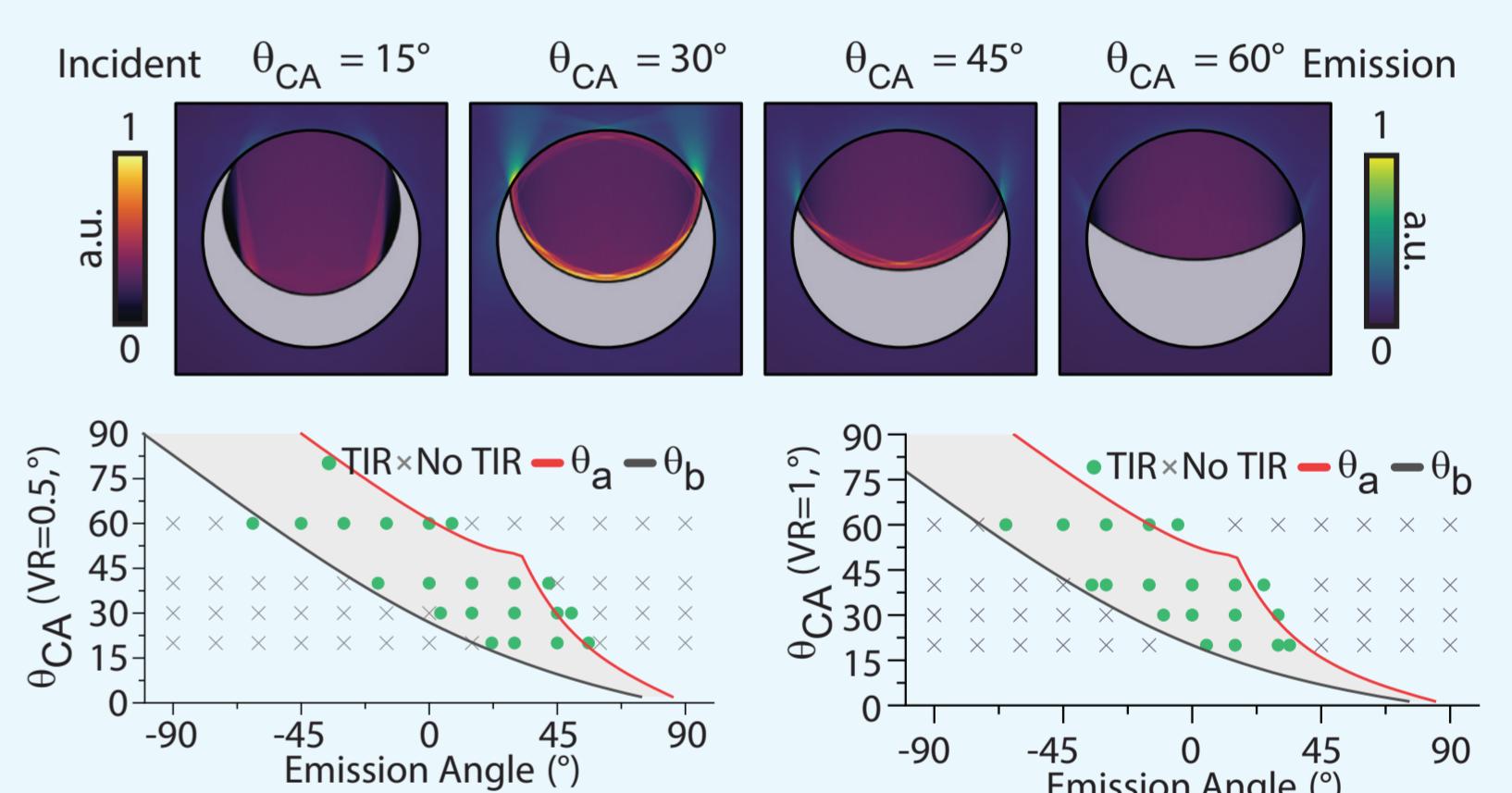
Angular emission can be calculated analytically, and is modelled via ray tracing, displaying a verifiable trend.



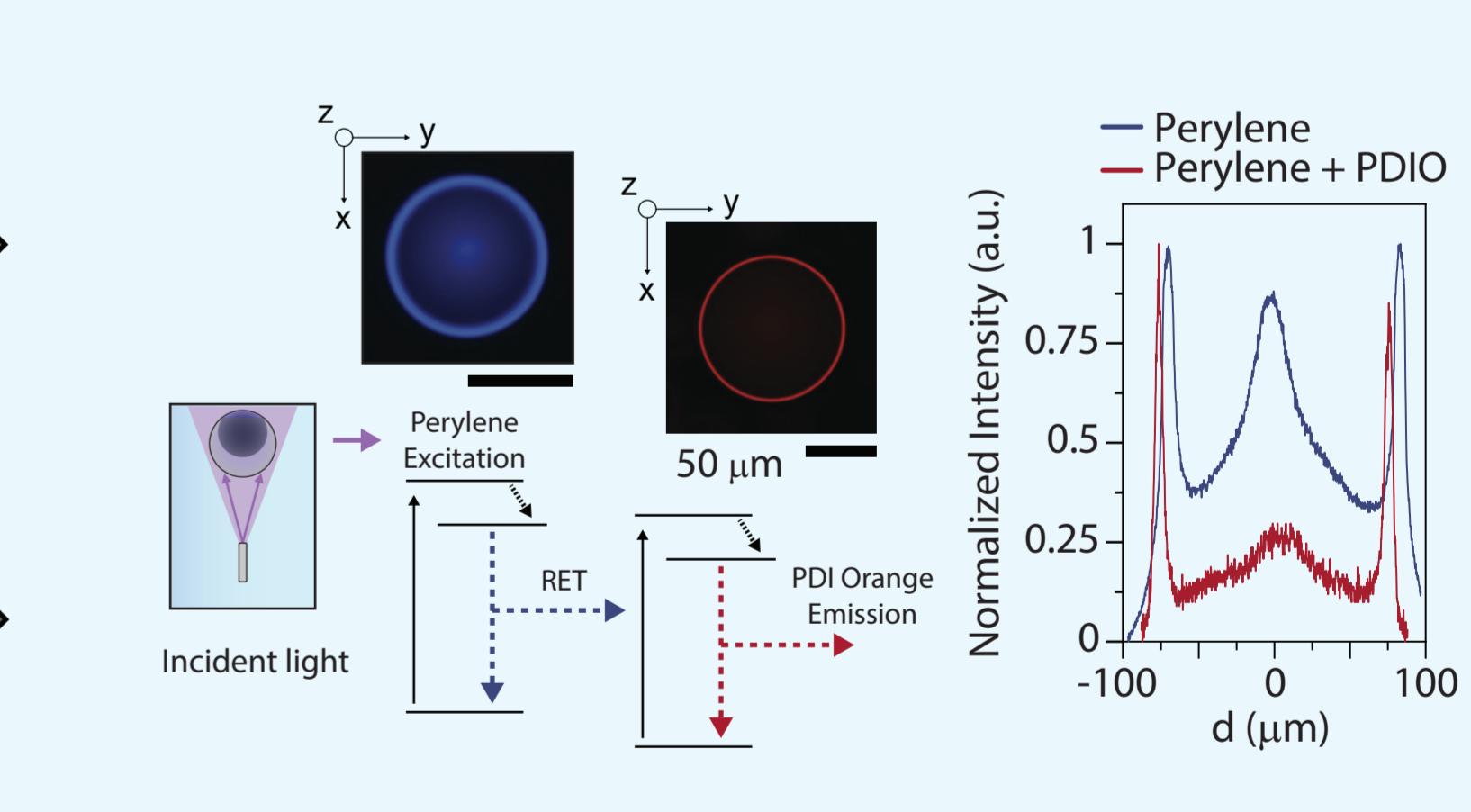
Total internal reflection of incident light enhances fluorescence



Geometrical and ray tracing modelling match experimental results

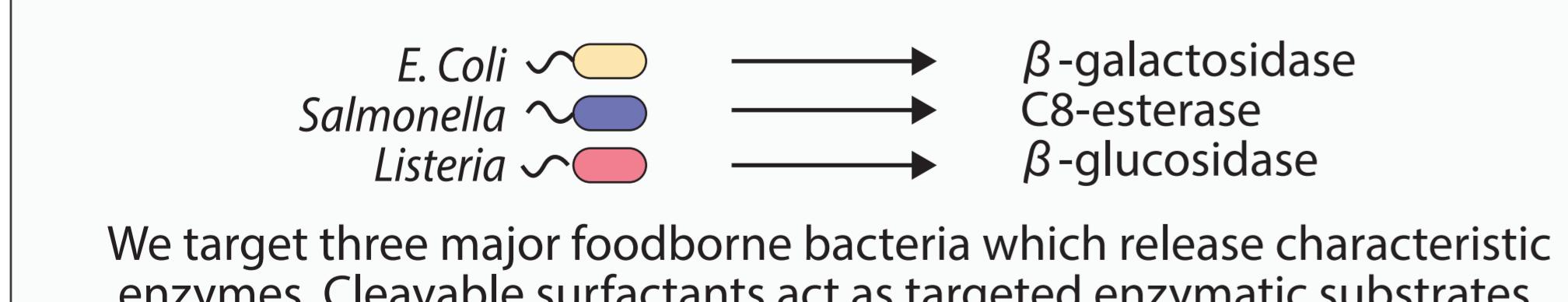


Angular emission can be calculated analytically, and is modelled via ray tracing, displaying a verifiable trend.

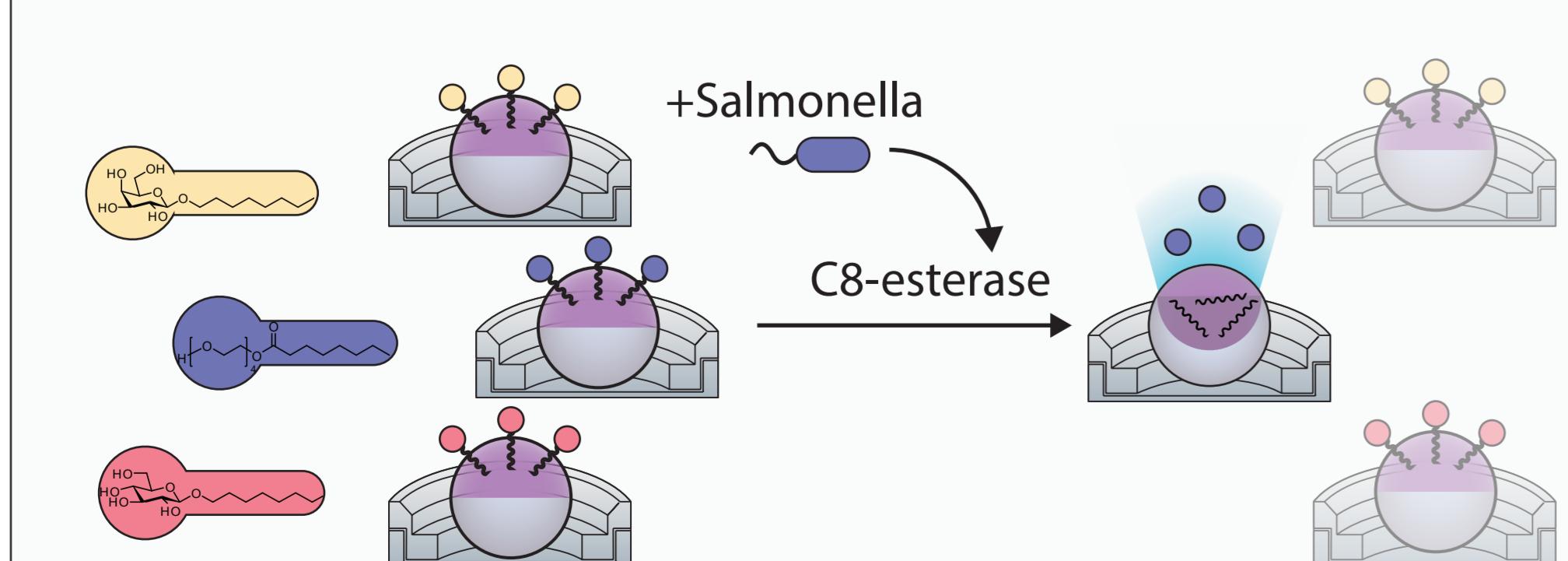


We can include a second dye in the hydrocarbon phase to collect the concentrated perylene emission, enhancing the signal-to-noise ratio of the emission

Droplets as foodborne pathogen sensors³



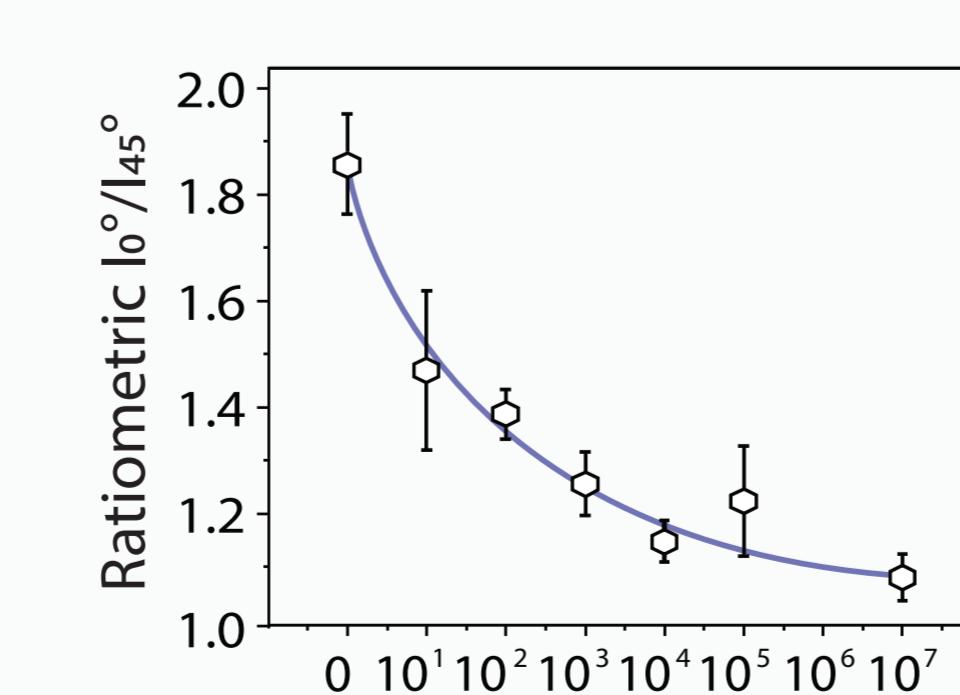
We target three major foodborne bacteria which release characteristic enzymes. Cleavable surfactants act as targeted enzymatic substrates.



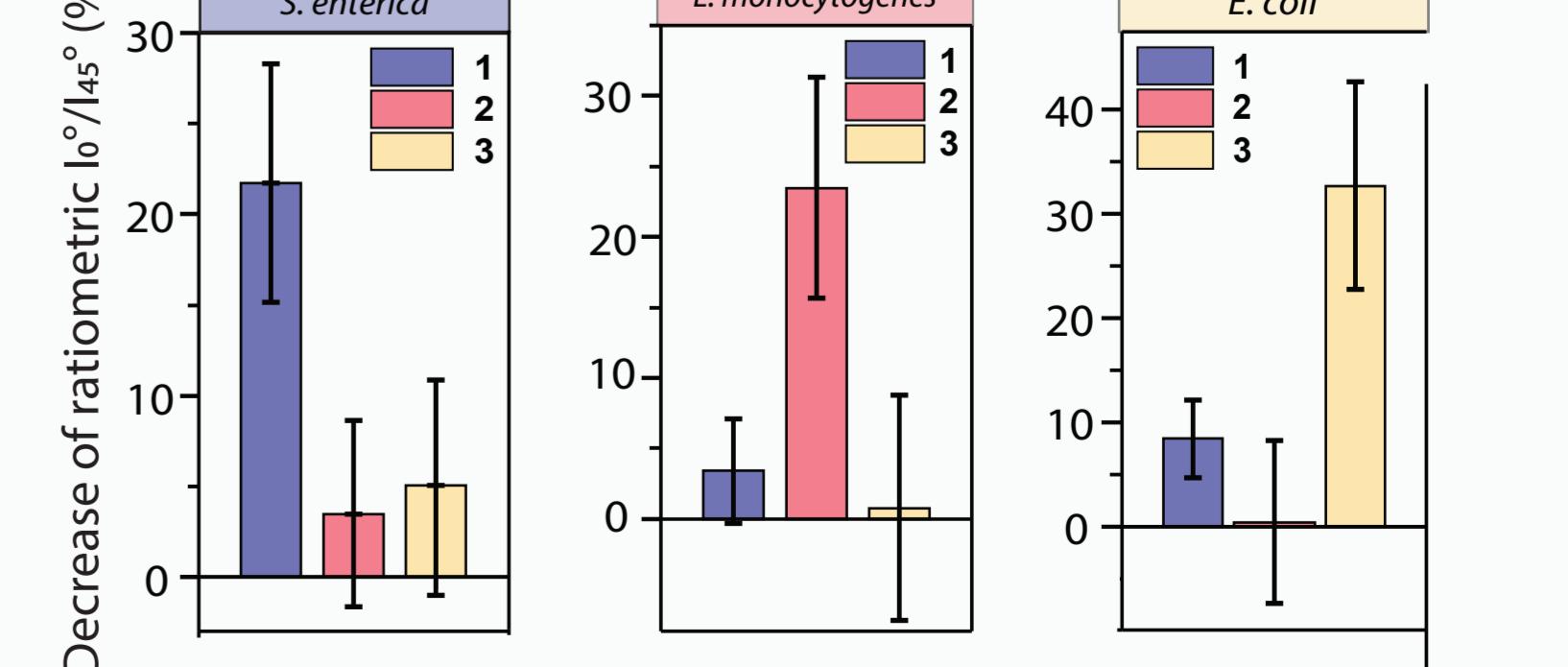
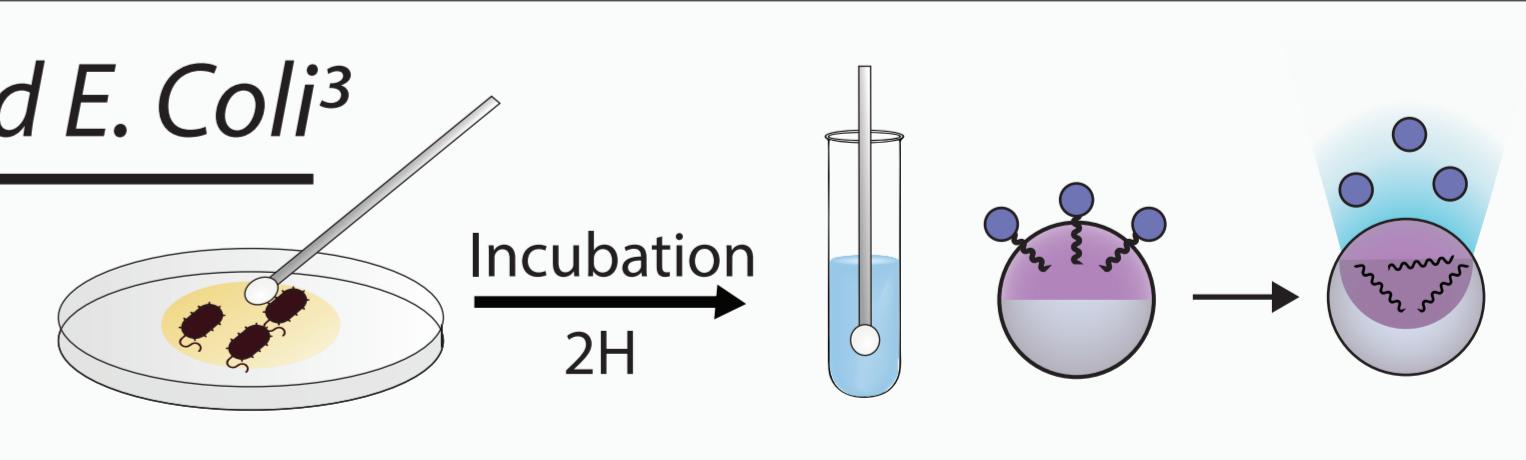
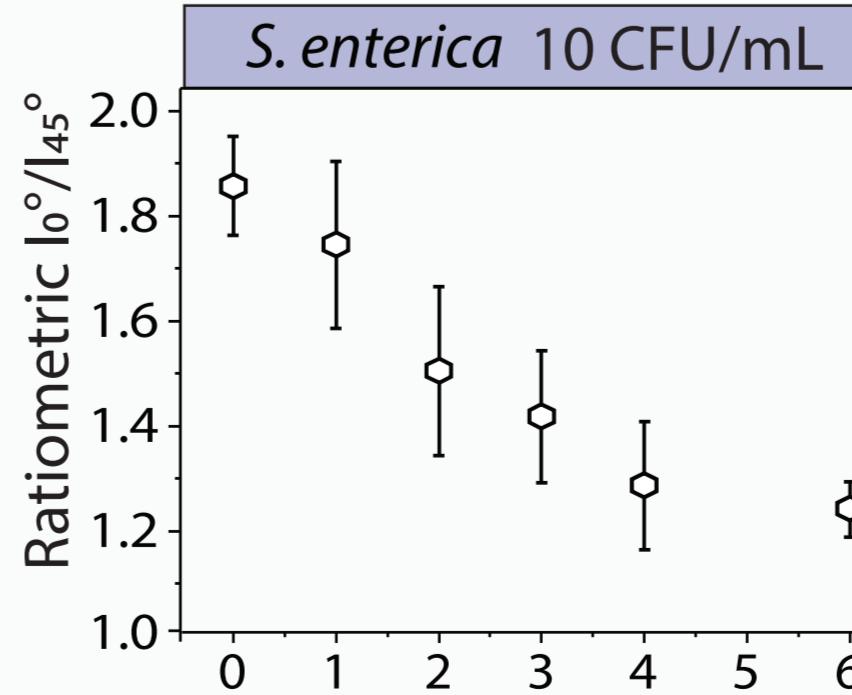
Ratiometric detection of droplet fluorescence serves as a chemistry-independent readout for polydisperse emulsion samples.

Ratiometric detection of *Salmonella*, *Listeria*, and *E. coli*³

1. Bacteria are incubated in substrate solutions
2. After a period of time, droplets are prepared in the solution
3. Ratiometric fluorescence intensity is tested



C8-esterase released by *Salmonella* cleaves the substrate, demonstrating sensitivity to 10 bacterial cells per mL after 2 hours.



Cross tests and swab tests demonstrate high sensitivity and specificity toward targeted pathogens, and with ON-OFF behavior for deployment.