# Nanoengineered Electroactive Polymers:

## *Soft Materials to Solve Hard Challenges in Energy and Health*


**A/Prof Matthew Griffith**

ARC Future Fellow

Director – UniSA Microscopy and Microanalysis

University of South Australia

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# …My Career Explained By Beautiful Babies…

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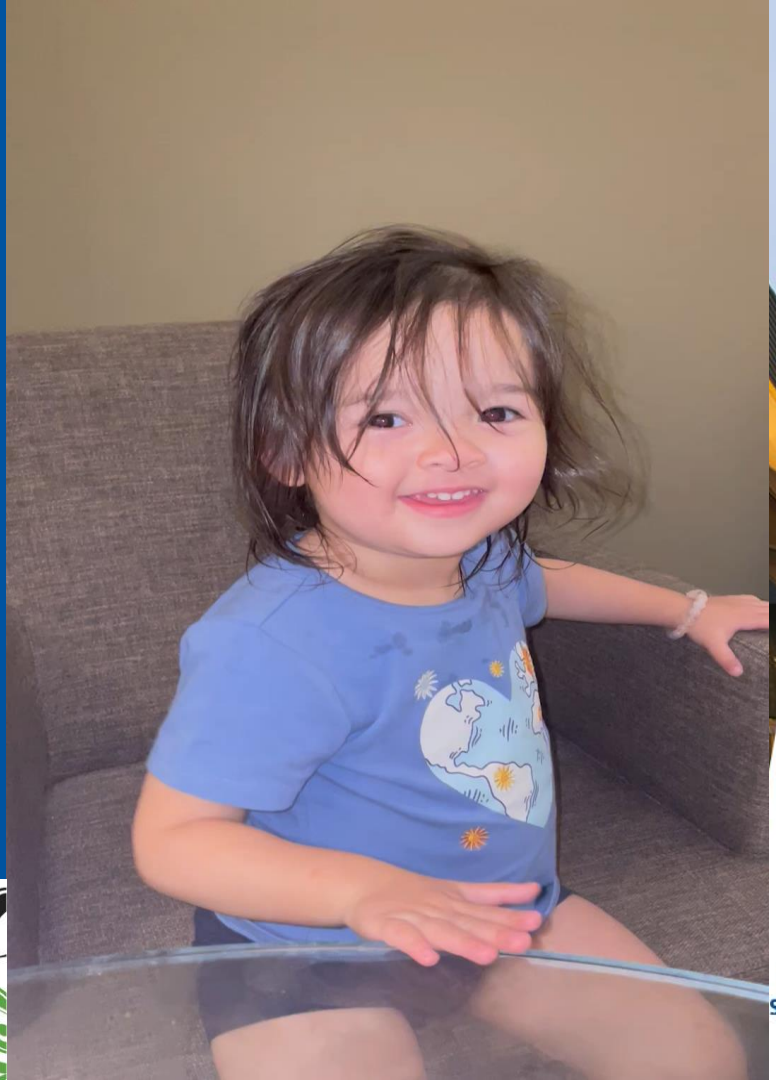

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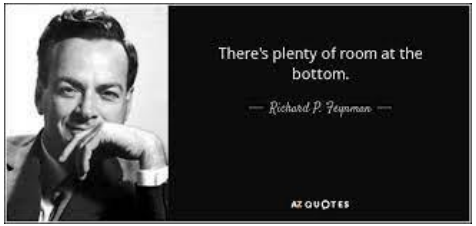
# How do You Have Transformational Impact in Science?

*"What I want to talk about is the problem of manipulating and controlling things on a small scale."*




- Making tiny letters and shapes with atoms
- Building molecular machines ("swallow the doctor")
- Shrinking the computer to the size of your hand
- Building better microscopes to see atoms
- Visualising biological materials like DNA

Ion traps (*Nobel Prize 1989*)
Atom Traps (*Nobel Prize 1997*)

Graphene (*Nobel Prize 2016*)
Molecules that move (*Nobel Prize 2016*)

Integrated Circuit (*Nobel Prize 2000*)
Quantum information (*Nobel Prize 2022*)

S-T Microscope (*Nobel Prize 1986*)
Super-res microscopy (*Nobel Prize 2014*)

Cryo-TE Microscope (*Nobel Prize 2017*)
Sequencing genomes (*Nobel Prize 2022*)

# My Journey

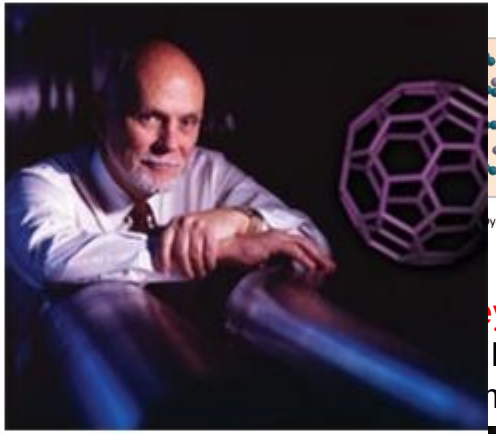
**2008 – 2012 (University of Wollongong)**
PhD

istry

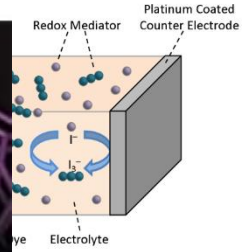
## Humanity's Top Ten Problems for next 50 years

1. ENERGY
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

2004 6.5 Billion People
2050 ~ 10 Billion People



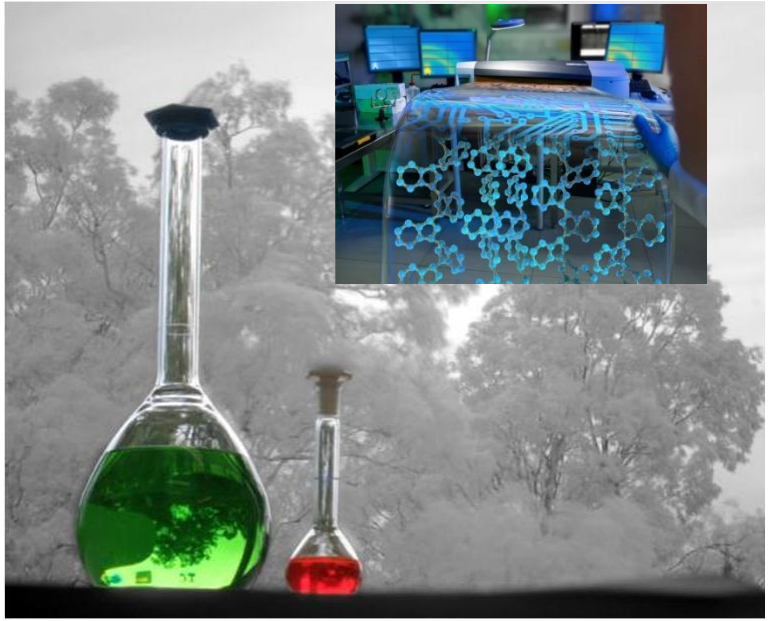
Professor Richard Smalley
1996 Nobel Prize Laureate




y)
Research)
materials)

# Semiconducting Polymers for Energy and Health

- Carbon-based semiconducting materials for electronic devices:



- **Electroactive inks**

(we control the **functionality**)

- **Printable** and **flexible**

(we make it **light** and **cheap**)

- **Soft and carbon-based**

(we can make it **highly biocompatible**)

**Low cost R2R printing manufacture of functional electronic devices**

University of South Australia

**M. J. Griffith** *et. al.*; *Nanotechnology*, **2020**, *9*, 092002

# Centre for Nanoelectronic Materials & Devices


| RESEARCH EXPERTISE | APPLICATIONS IN ENERGY & HEALTH |
|---|---|
| **Material Morphology**<br>• Chemistry, materials engineers | ***Photovoltaics, water splitting***<br>***Photocapacitors, piezoelectrics*** |
| **Device Fabrication**<br>• Chemistry, electronic engineering | *Printed sensors* |
| **Device Characterisation**<br>• Physics | *Radiation detection, radiotherapy*<br>*Drug delivery, nanomedicine* |
| **Cell Culture & Recording**<br>• Biophysics, medicine | *Cell-machine interface studies*<br>*Neuroscience, neural interfacing* |

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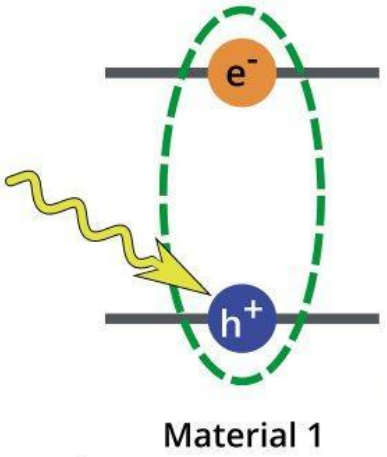
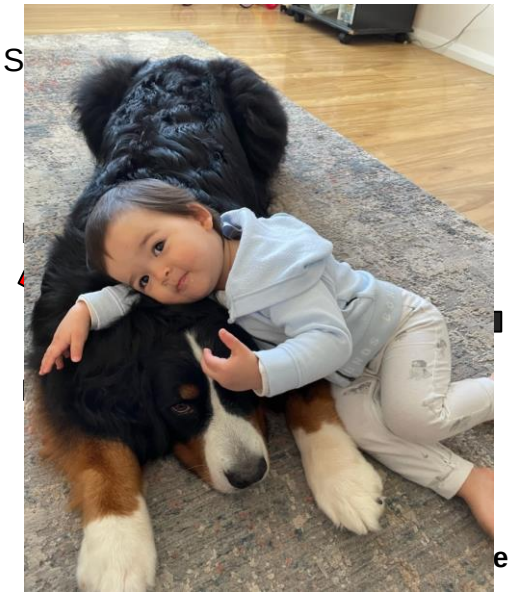
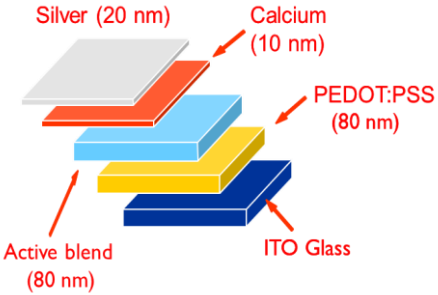
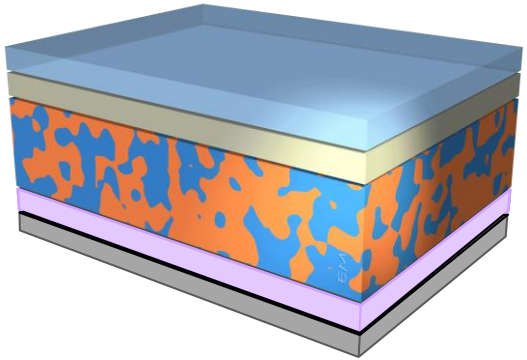
# The Electronic Challenge: Overcoming Sticky Charges

- Charges are “sticky” in OSCs (excitons)
- Need multiple materials to create free charge
- Need complex nanostructures to maximize interfacial area







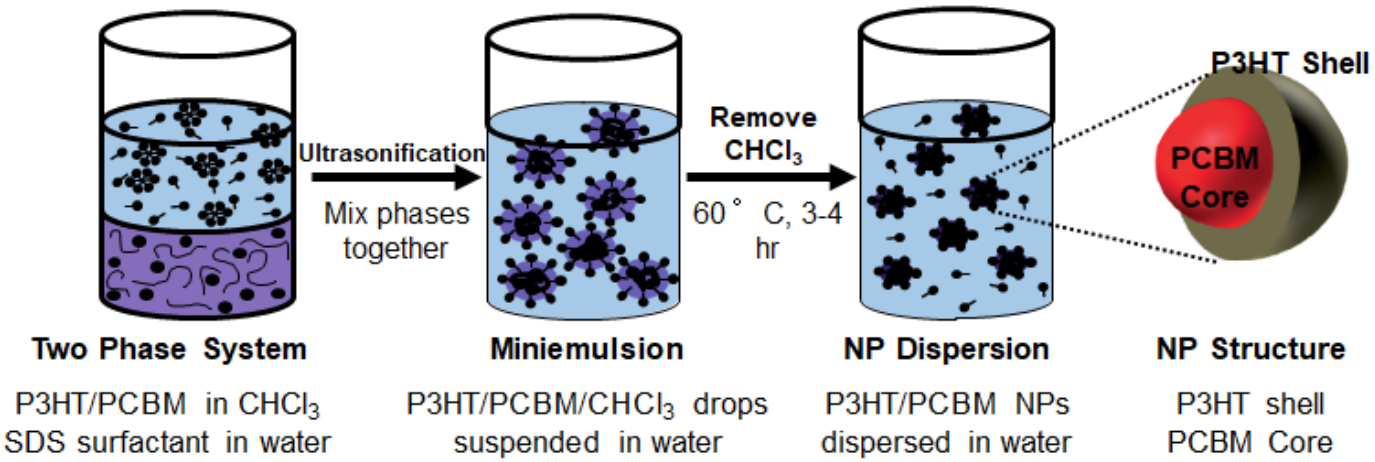
**M. J. Griffith**, J. A. Posar, S. Cottam, J. Stamenkovic, M. Petasecca, *Front. Phys.*, **2020**, *8,* 22.

# The Chemical Challenge: Organic Toxicity

- Organic molecules need organic solvents
- Toxic for humans at scale
- Need materials processed in water

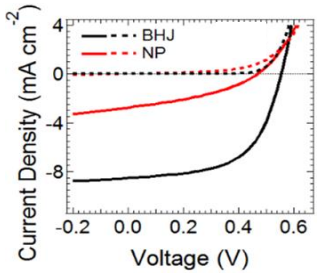
# OSC Nanoparticles: New Synthesis Paradigm

- Create discrete pre-blended D/A nanoparticles
- Water soluble – huge fabrication benefit!
- Control nanostructure in synthesis step (not post-treatment)



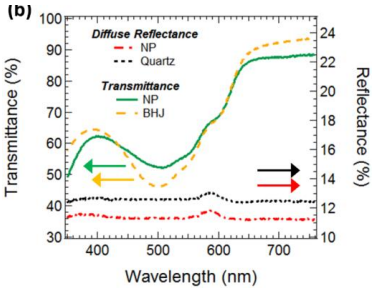

M. F. Al-Mudhaffer, …, **M. J. Griffith**; *MRS Commun.*, **2020**, *10*, 600-608.

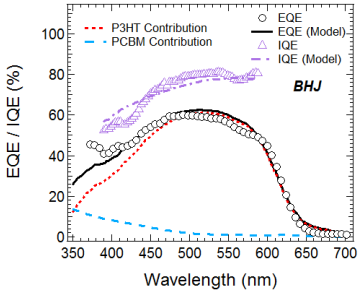
# Understanding OSC-NP Energy Devices

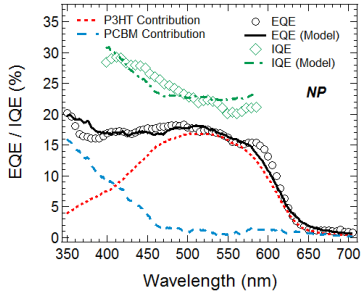


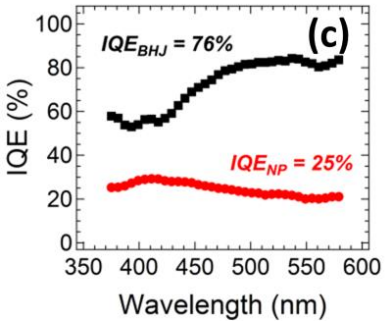

- NP-OPV devices do not work as efficiently
- Optical modelling/measurements show no optical differences (scattering, plasmons etc)

*Mohammed Al-Mudhaffer*



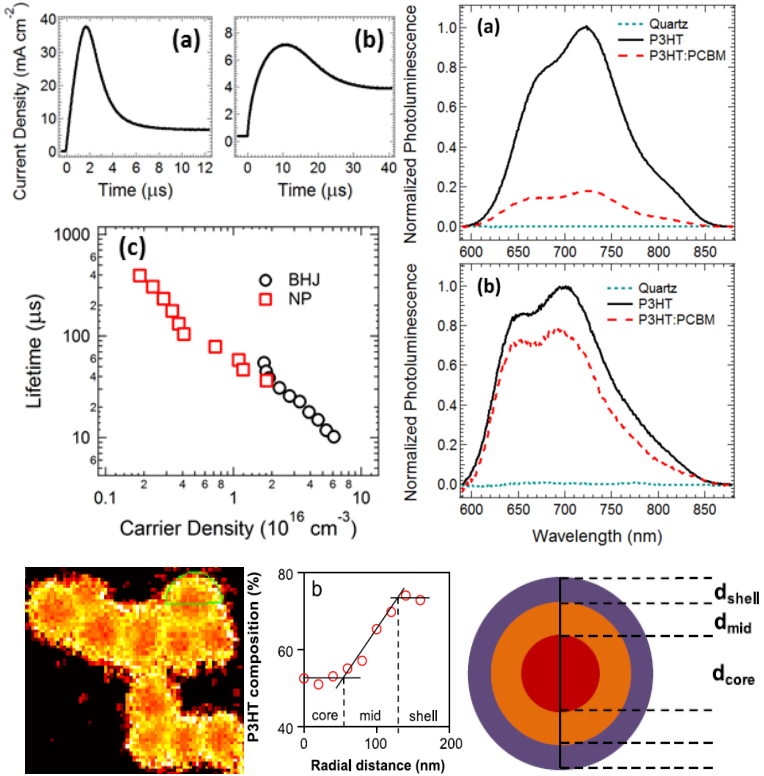




Modelling implies electrical performance (IQE) is poorer in NP systems



M.F. Al-Mudhaffer, …, **M. J. Griffith**; *Sol. Energy Mater. Sol. Cells*, **2017**, *175*, 77-88.

# Understanding OSC-NP Energy Devices



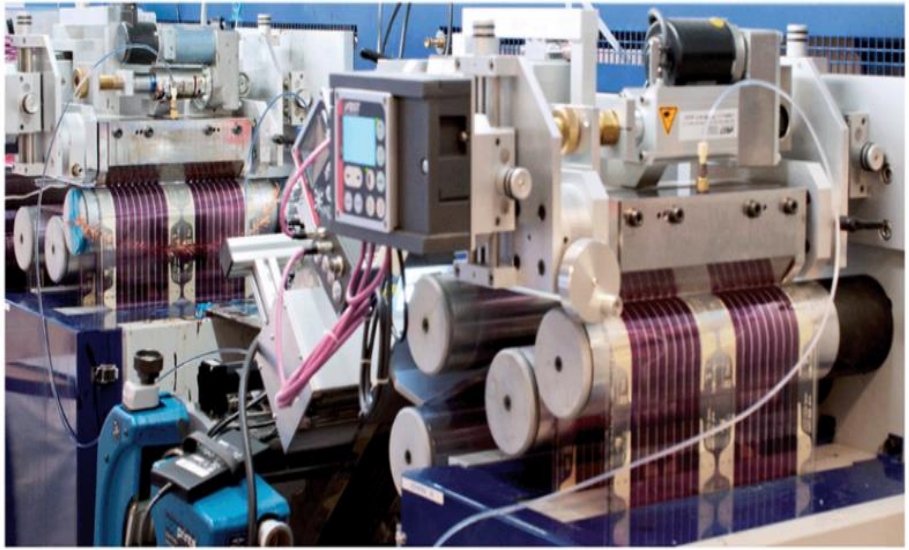

- Measure carrier mobility *photoCELIV* (charge transport) - OK
- Measure carrier lifetime *Transient photovoltage (TPV)* (recombination) - OK
- Measure PL quenching of films (charge generation) – ORIGIN OF PROBLEM
- Suspect core-shell morphology is root of issue

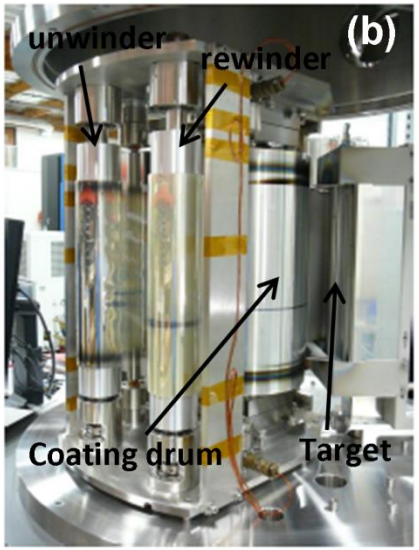
*Dr Mohsen Ameri*

University of South Australia

M. Ameri, …, **M. J. Griffith**, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 10074.

# Scaling Up…






*Prof. Paul Dastoor*

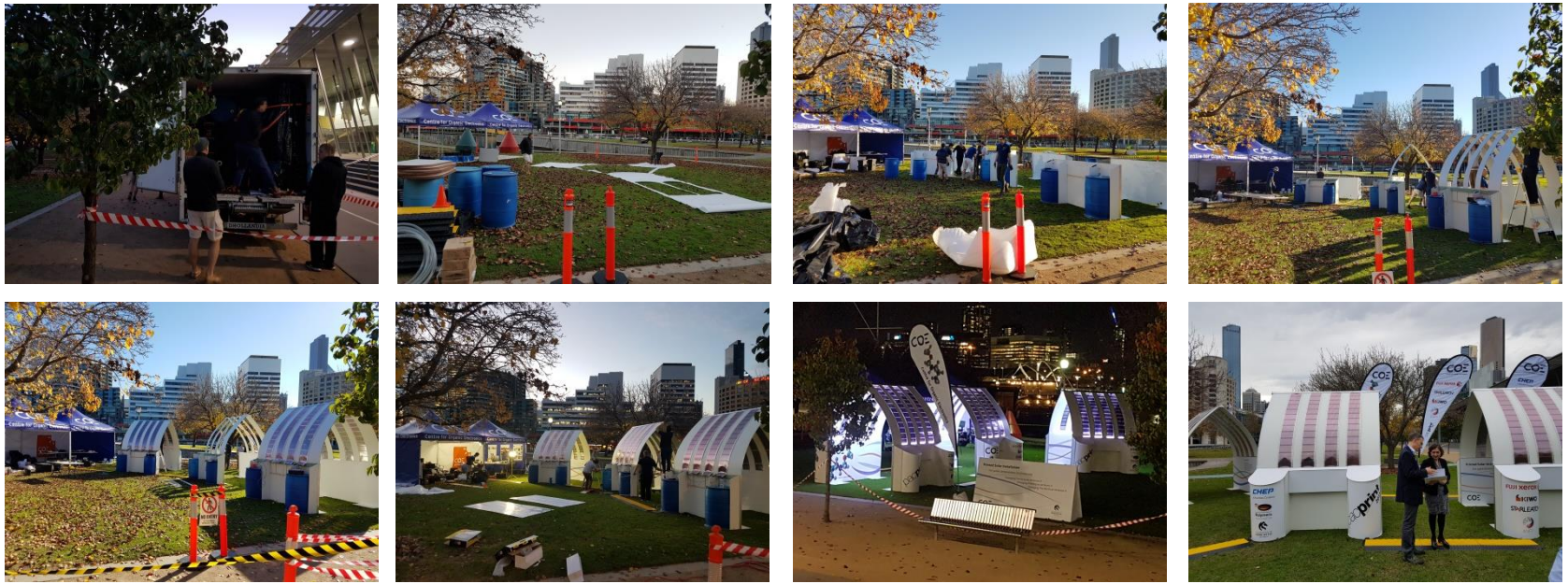
- Acquired R2R coating line and sputter coater
- Print the anode, active layers, required interlayers, then sputter the cathode



**M. J. Griffith**, *et. al.*; *Energy Technol.*, **2015**, *3*, 428-436.

# Research with a Real World Impact

Designed, printed and constructed a public large area solar demo at PacPrint *(Melbourne Exhibition Centre, May 2017)*



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**M. J. Griffith**, N.P. Holmes, D.C. Elkington, S. Cottam, J. Stamenkovic, A.L.D. Kilcoyne, T.R. Andersen; *Nanotechnology*, **2020**, *31*, 092002.

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### Material Morphology
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### Device Characterisation
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*Photovoltaics, water splitting*

*Photocapacitors, piezoelectrics*

*Printed sensors*

*Radiation detection, radiotherapy*

*Drug delivery, nanomedicine*

*Cell-machine interface studies*

*Neuroscience, neural interfacing*

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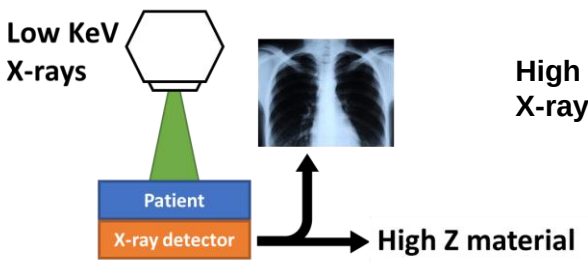
# Printable X-Ray Sensors for Health

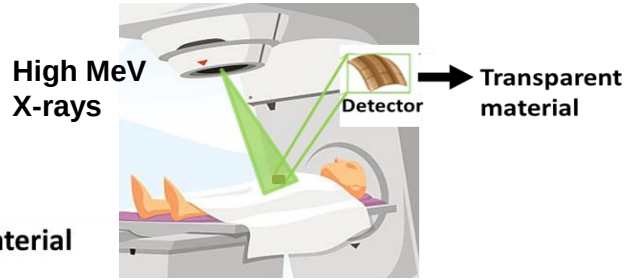
- Ionizing radiation used to image and treat disease.
- 100k radiotherapy treatments in Australia per year.
  - ***Incident reports in 26% of cases!***

**Develop new in-vivo dosimetry for treatment:**

- Tissue equivalent
- Transparent to radiation
- Large and flexible active areas
- Radiation tolerant

**Imaging vs Radiation Therapy:**

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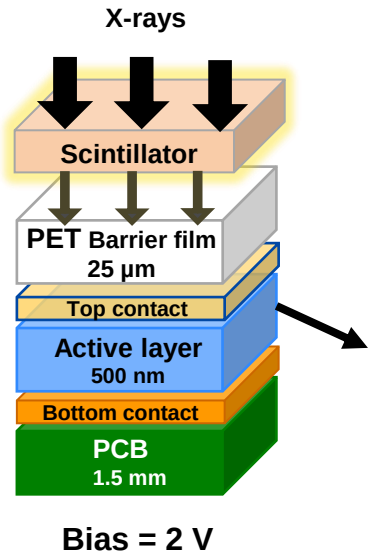
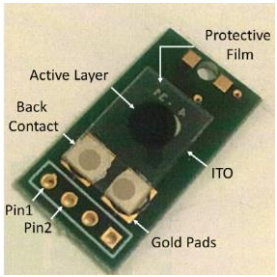
J. A Posar, …, **M. J. Griffith**; *Frontiers Physics*, **2020**, *8,* 22.

# Testing OSC Devices in Clinical Environment

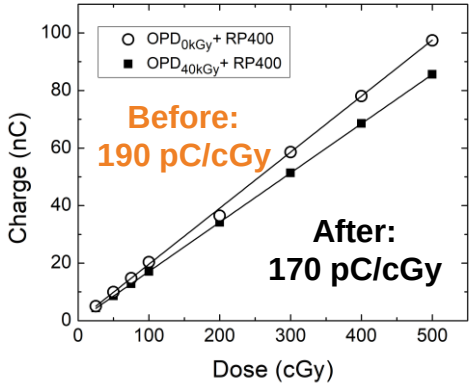
***Tested before and after 40 kGy accelerated irradiation.***



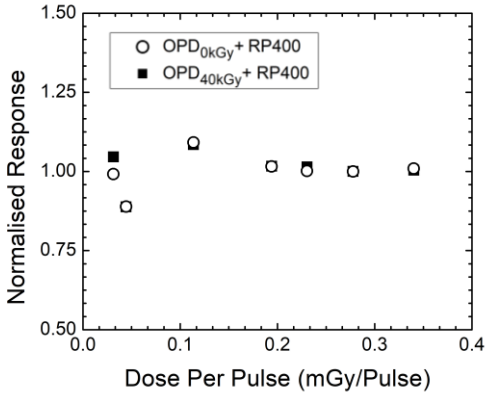

*Dr Jessie Posar*



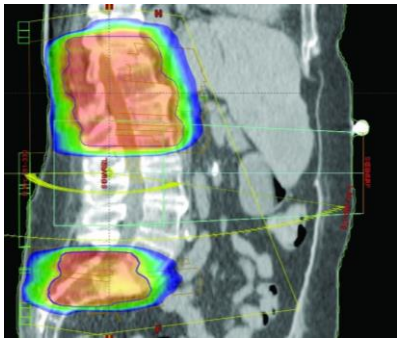

**Linearity**




**Dose-rate dependence**




- Functional dosimeters
- Highly radiation tolerant
- Not so sensitive…



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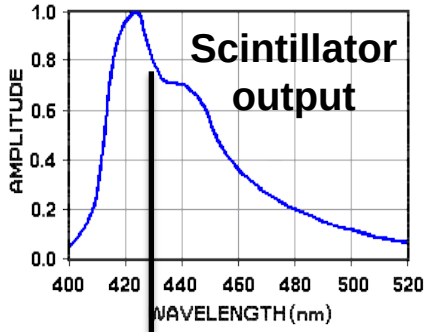
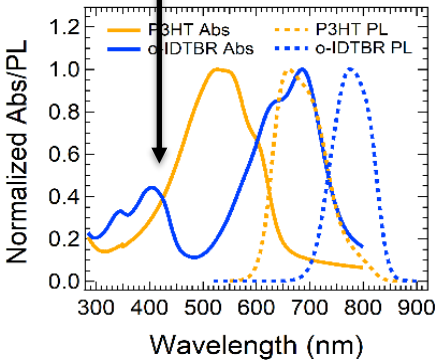
J. A. Posar, …, **M. J. Griffith;** *Med. Phys.* **2020**, *47*, 3658.

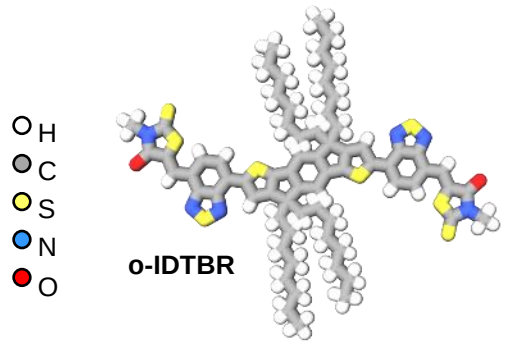
J. A. Posar, …, **M. J. Griffith;** *Phys. Imaging Radiat. Oncol.* **2020**, *14*, 48.

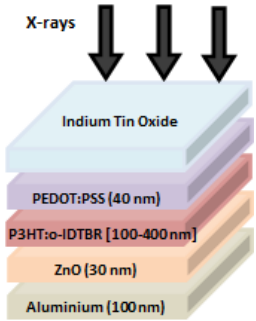
# Tailor Materials to Boost Performance

- New o-IDTBR material enhances coupling with scintillator

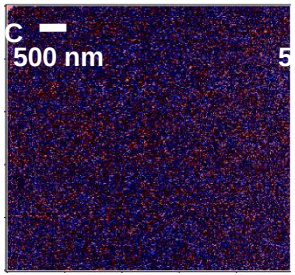


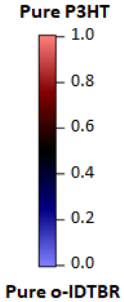



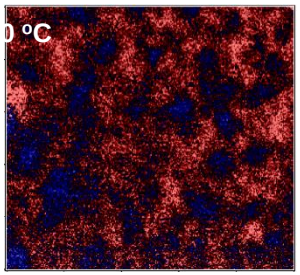



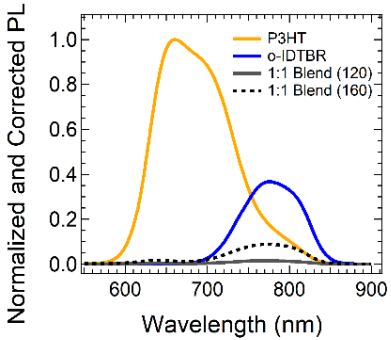




*Sophie Cottam*



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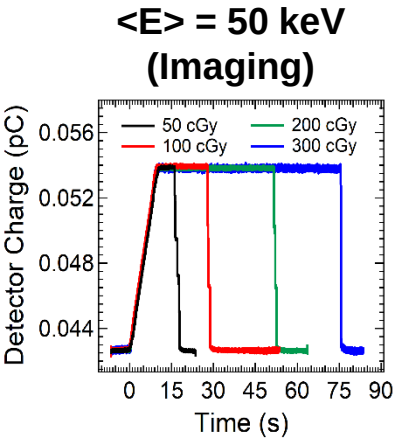
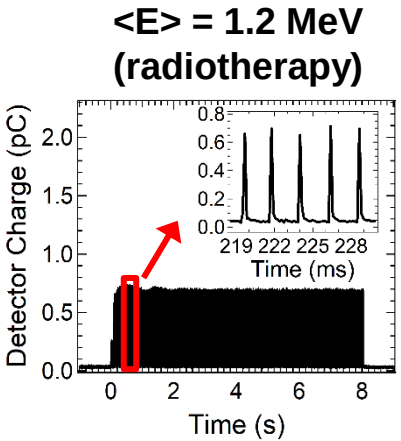
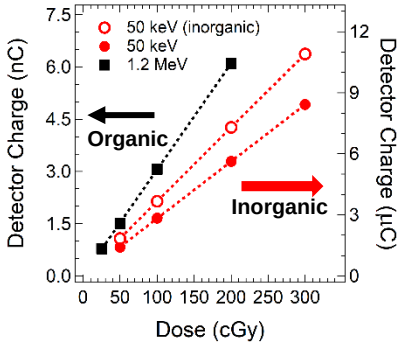
J. A. Posar, …, **M. J. Griffith**; *Adv. Mater. Technol.*, **2021**, *6*, 2001298.

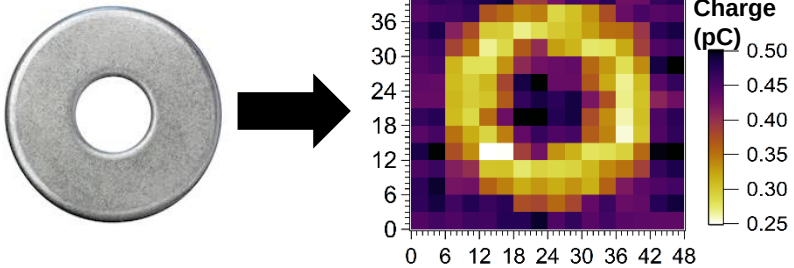
# A New Versatile Radiation Dosimeter

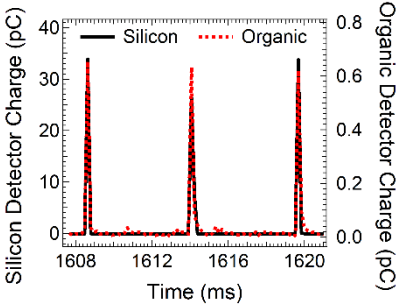
- Detects low & high energies.
- Sensitivity OK, but better with new scintillators.
- Successfully images.
- Fastest ever organic X-ray detector
  - Matches silicon!

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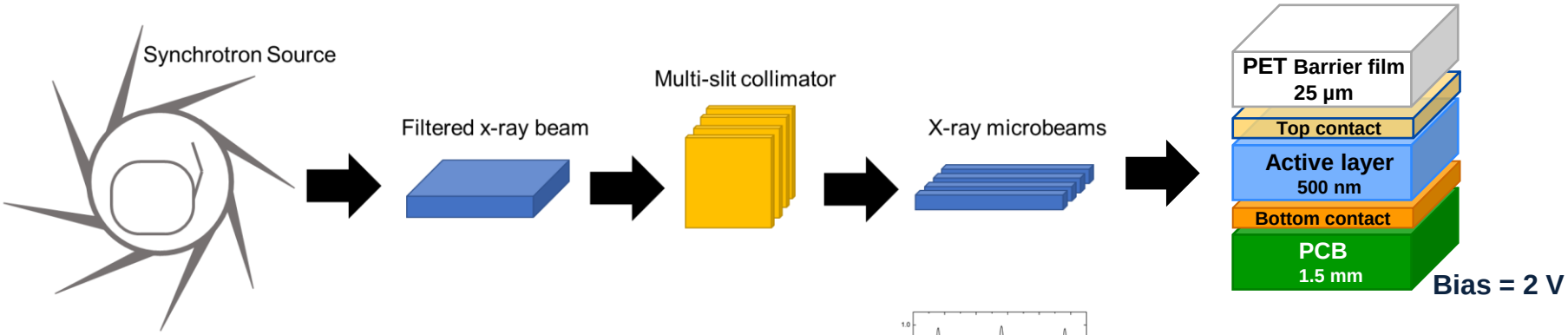
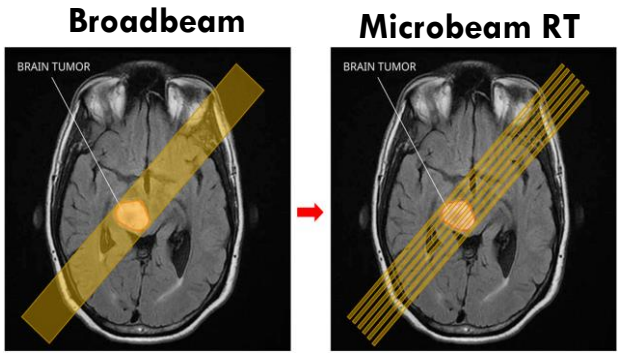
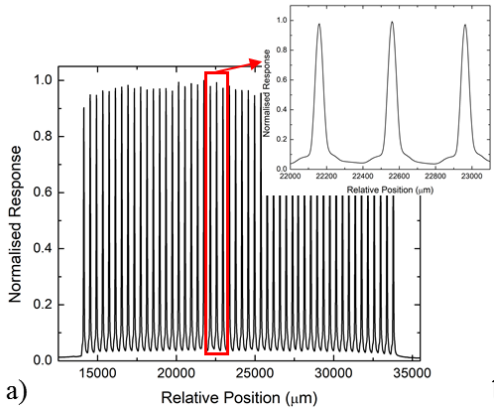
J. A. Posar, …, **M. J. Griffith**; *Adv. Mater. Technol.*, **2021**, *6*, 2001298.

# The Clinical Techniques of the Future




- Can spatially resolve 50 µm beams

University of South Australia

J. A. Posar, …, **M. J. Griffith**; *J. Synchrotron Rad.* **2021**, *28*, 1444.

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*Photovoltaics, water splitting*

*Photocapacitors, piezoelectrics*

*Printed sensors*

*Radiation detection, radiotherapy*

**Drug delivery, nanomedicine**

**Cell-machine interface studies**

**Neuroscience, neural interfacing**

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# Current Research Motivation

- Bioelectronics – discipline at the intersection between physics and living systems.

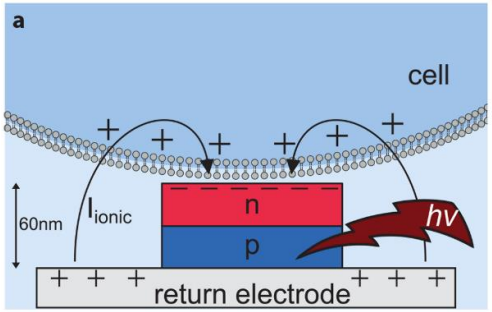
- **Neurons are the primary signal carriers in mammals.**
  - Operate via mechanical, chemical & electrical signals

- We aim to develop materials & devices that talk to neurons **in a language they understand**
  - Treatment of neurological disorders
  - Restoration of sensory function

# New Materials for Biointerfacing

# Solving Cell Adhesion

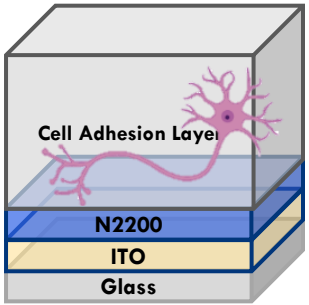
- **Semiconducting polymers are typically hydrophobic and resist adhesion with hydrophilic cells.**




D. Rand, M. Jakešová, G. Lubin, I. Vébraitė, M. David-Pur, V. Đerek, T. Cramer, N. S. Sariciftci, Y. Hanein, E. D. Głowacki; *Adv. Mater.*, **2018**, *30, 1707292.*

- **Solution Approach 1: Chemical structure tuning**
  - Elegant approach, neuron directly contacts designed surface
  - **BUT** Difficult in bioelectronics as changes the electronic properties

- **Solution Approach 1: Create Adhesion Layer**
  - Mimics biology (integrin proteins in extracellular matrix)
  - **BUT** Neuronal cell isolated from electronic material by insulator




**CHALLENGE: Alter nanoscale interface of material for adhesion without influencing electronic properties**

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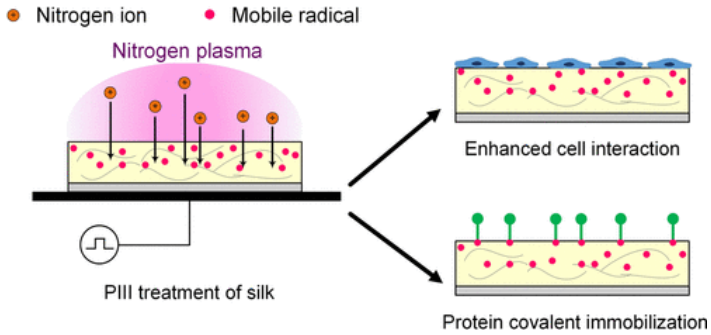
# Solution: Precision Plasma Treatment

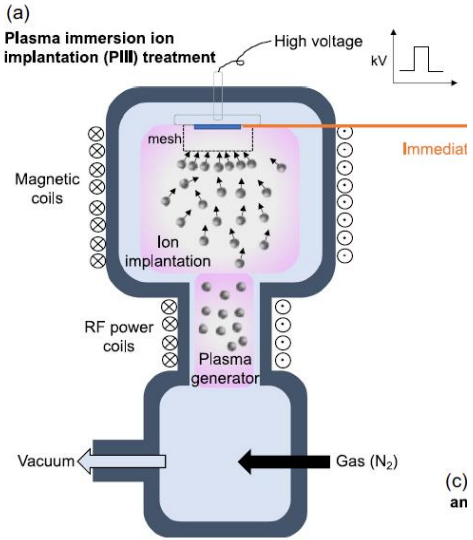
- **Plasma ion implantation (PIII) used to selectively change the surface region of polymer.**

*Dr Clara Tran*

*Prof. Marcela Bilek*

- Previously shown to modulate silk biomaterials to be more adhesive for cells.
  - What about effects on electronic materials?



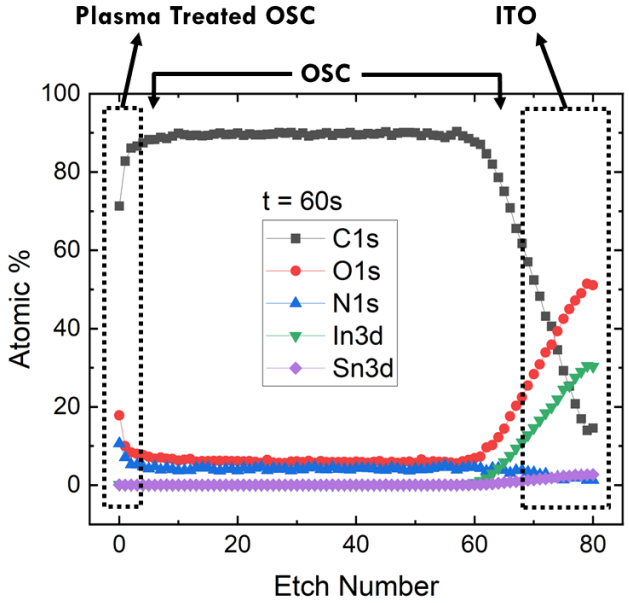



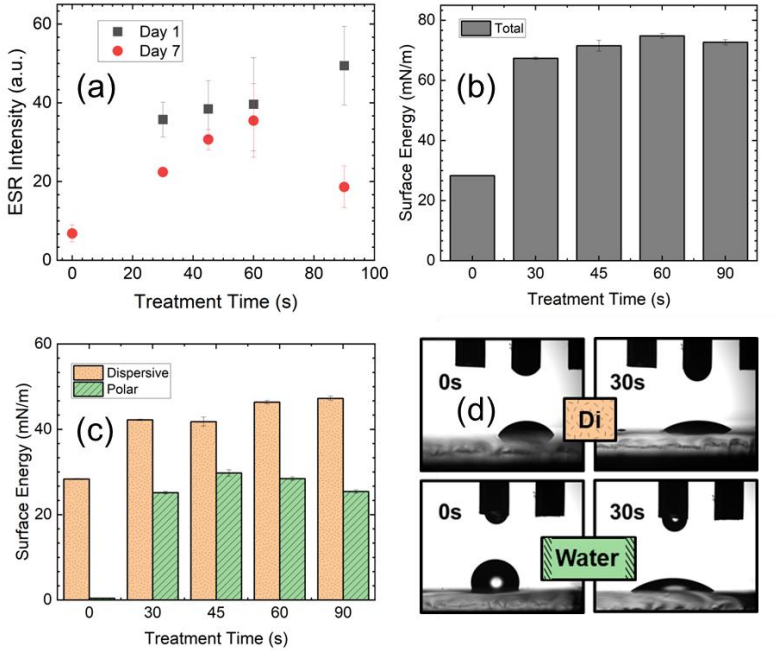



A. Kondyurin, K. Lau, F. Tang, B. Akhavan, W. Chrzanowski, M. S. Lord, J. Rnjak-Kovacina, M. M. Bilek; *ACS Appl. Mater Interfaces*, **2018**, *10*, 17605 .

# Effect of Plasma: Polar Surface with Good Electronics

- Plasma turns surface hydrophilic
- Only treats ~10 nm at surface
- Material electronic properties improved



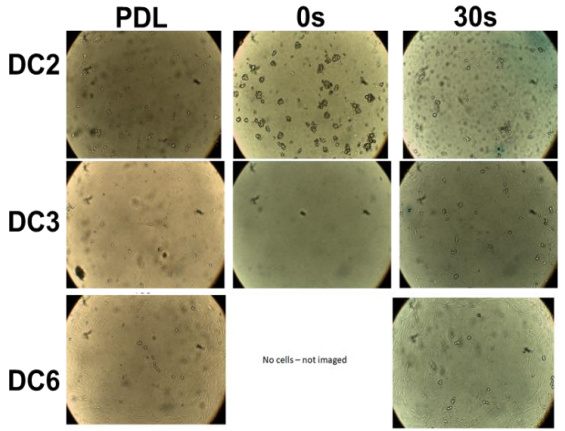



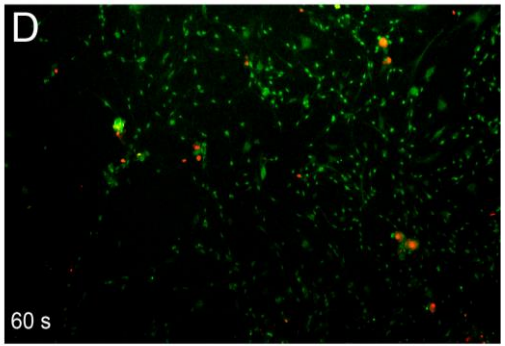

- Significant decrease in contact angle after PIII due to creation of polar contribution to surface energy.

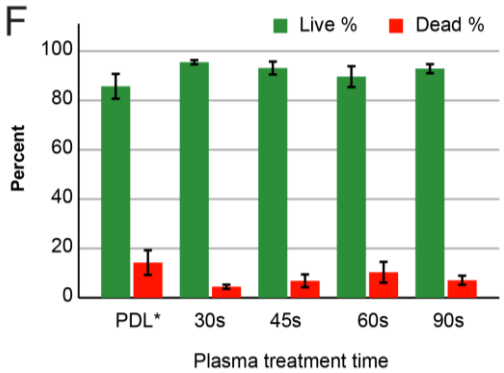
# PIII Treatment Helps Cell Adhesion

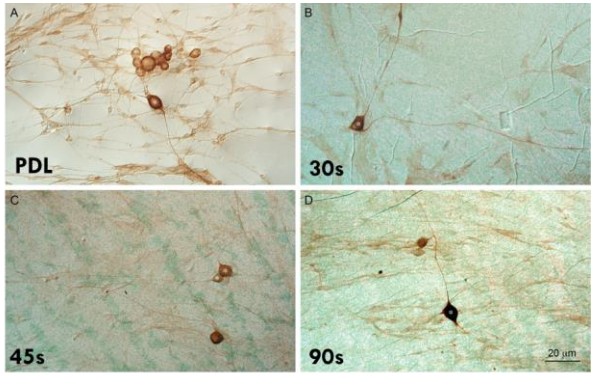
- **Cell Adhesion:**
  - Optical images show cells washed off the 0s film during medium exchange
  - PII treated films similar to PDL control
- **Live/Dead Assay**
  - No change in live/dead for PIII and poly-D-lysine control
- **Neurite Cell-Specific Staining**
  - All show evidence of darkly stained DRG neurons (*) with long projections. In these examples, projections extended from 40µm to 140µm

*A/Prof Rebecca Lim*

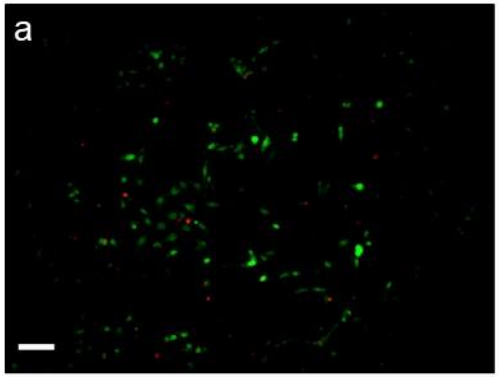


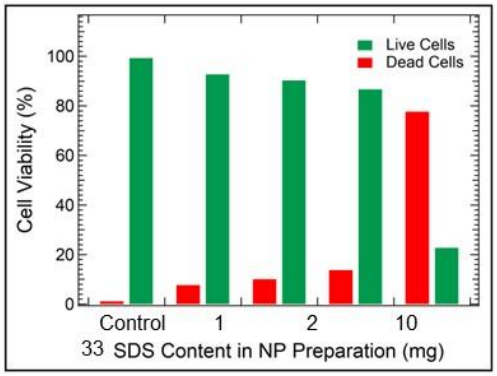



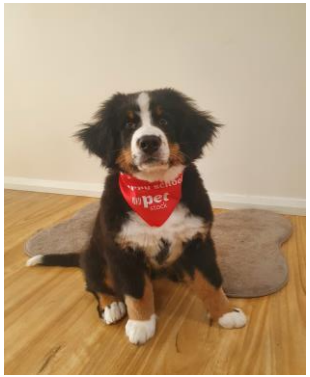



# Establishing Organic Semiconductor Biocomptibility



- Perform cell co-culturing with dissociated mice DRGs
- Live/Dead Assays
  - Establish ratio of living cells to dead cells
- **Require specific mice neuron stain**
- See quite good neurite growth.



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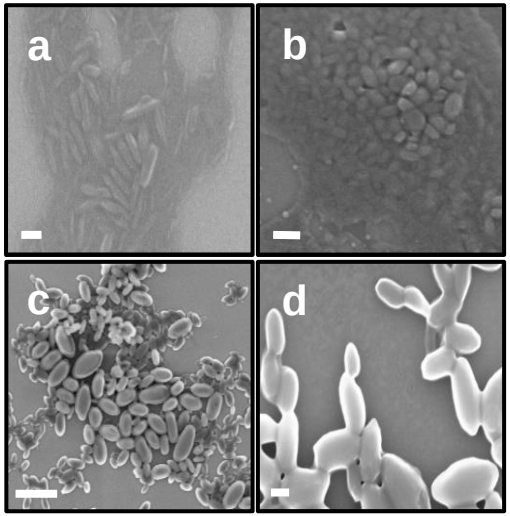
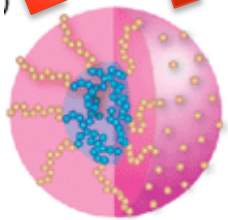
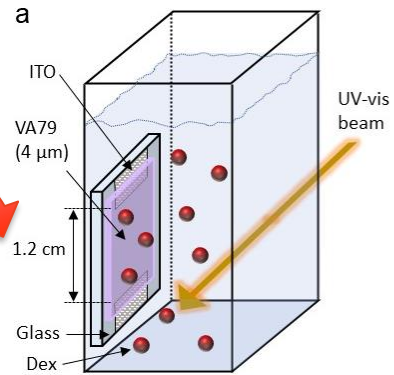
R. Crovador, H. Heim, S. Cottam, K. Feron, V. Bhatia, F. Louie, C. P. Sherwood, P.C. Dastoor, A. M. Brichta, R. Lim, **M. J. Griffith**; *ACS Appl. Biomater.,* **2021**, *4*, 6388-6350.

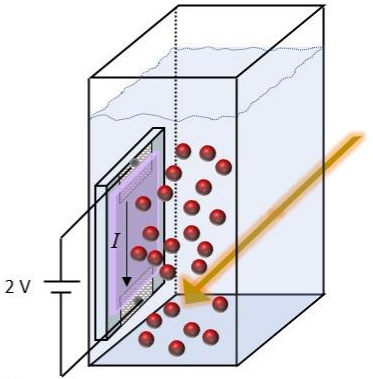
# Embed Anti-inflammatory Drugs into NPs

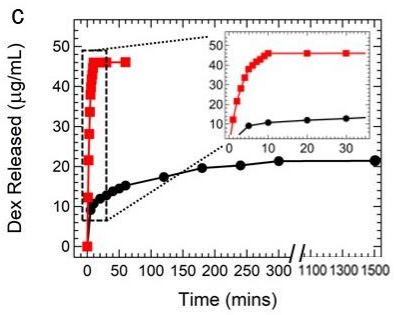


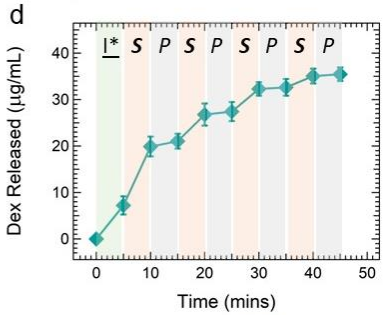

*Rafael Crovador*






I* = Unbound Dex release  Passive  Stimulated

- We can embed dexamethasone into our NP inks
- Control drug loading via NP size
- Control release rate via electrical stimulus

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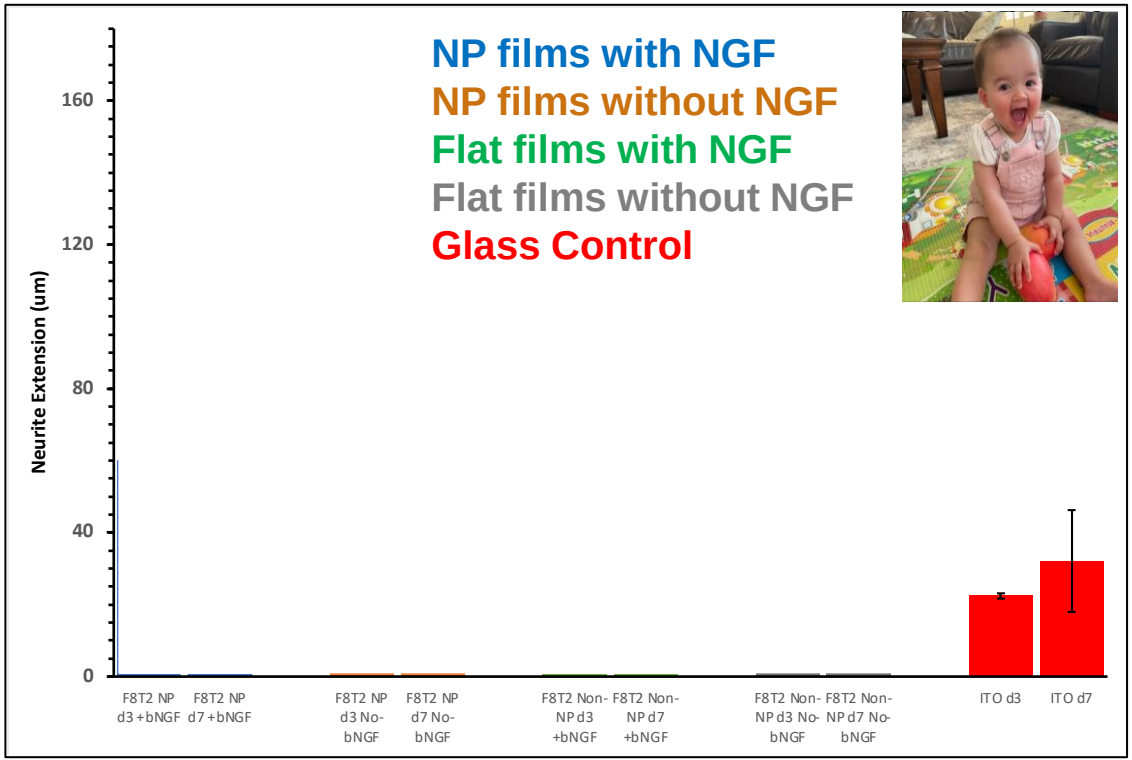
R. Crovador, H. Heim, S. Cottam, K. Feron, V. Bhatia, F. Louie, C. P. Sherwood, P.C. Dastoor, A. M. Brichta, R. Lim, **M. J. Griffith**; *ACS Appl. Biomater.,* **2021**, *4*, 6388-6350.

# NP inks with NGF Promote Neuron Growth






- NP films themselves promote neuron growth (**grey** to **orange**)
- OSCs embedded with NGF promote neuron growth (**grey** to **green**), or (**orange** to **blue**)
- Seeing evidence of mechanical and chemical cues with OSC scaffolds

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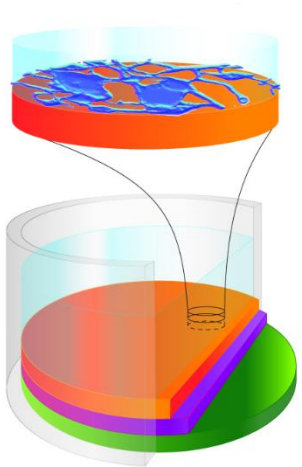
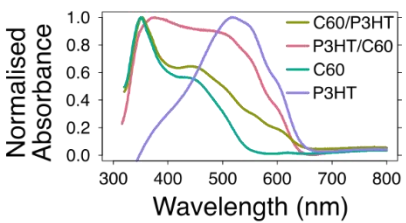
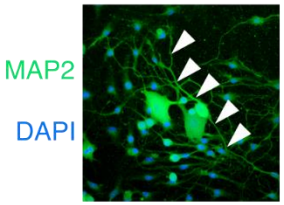
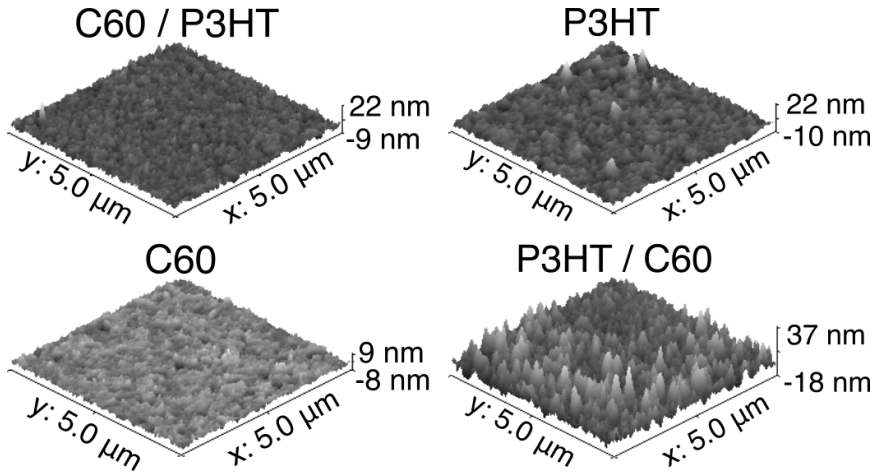
# Neural Interfacing with Organic Semiconductors






## Neural Interfacing

- Neurons cultured onto mono- and bi-layer devices
- Neurons grow and show high cell viability

## Interface Surface Analysis

- Surface roughness comparable for all samples
- Cell viability is due to materials

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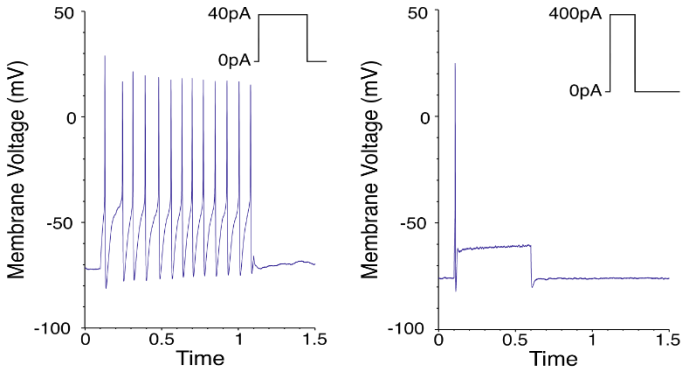
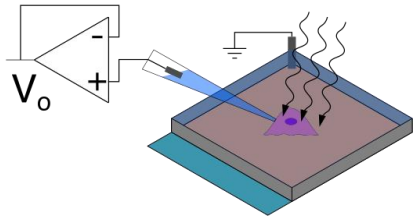
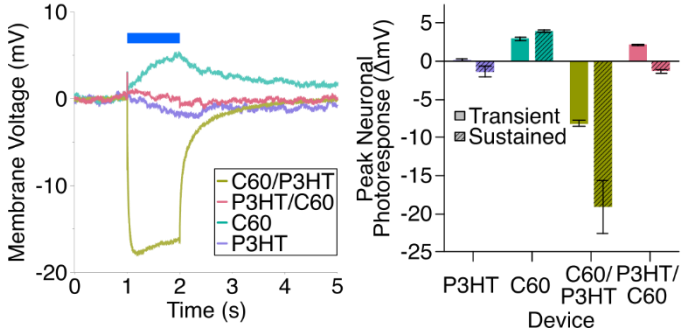
C. Sherwood, D. C. Elkington, M. R. Dickinson, W. J. Belcher, P. C. Dastoor, K. Feron, A. Brichta, R. Lim, **M. J. Griffith**; *J. Selected Topics Quant. Electron.*, **2021**, *27*, 1-12.

# Achieving Optical Neuromodulation

*Dr Connor Sherwood*




- Neurons cultured onto scaffolds are bioactive
- Change in the neuron membrane with purely photoinduced stimuli
- **Polarity of the response is controlled by the device architecture**

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C. Sherwood, …, **M. J. Griffith**; *Adv. Mater. Interfaces*, **2023**, *10*, 2202229.

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# Acknowledgements


## STUDENTS & POSTDOCS

- Dr Connor Sherwood
- Dr Jessie Posar
- Dr Hannah Drury
- Dr Mohsen Ameri
- Rafael Crovador
- Nathan Brichta
- Sophie Cottam
- Mohammed Al-Mudhaffer
- Darcie Anderson

## ACADEMIC COLLABORATORS

- Prof Paul Dastoor (UON; organic materials)
- A/Prof Rebecca Lim, Prof Alan Brichta (UON; neuron culturing)
- Dr Clara Tran, Prof. Marcela Bilek (USyd; plasma treatment)
- Prof Julie Cairney, Dr Vijay Bhatia (USyd; microscopy)
- Prof Anita Ho Baillie, A/Prof Girish Lakhwani (USyd; optoelectronics)
- Prof Attila Mozer, A/Prof Marco Petasecca (UOW; device physics)
- Prof Paul Sellin (Surrey University; optoelectronics)
- Prof Beatrice Fraboni (Bologna University; biomaterials)
- Shogo Mori, Ryuzi Katoh (Shinshu University and NIST, Japan)

## CLINICAL COLLABORATORS

- A/Prof Matthew Simunovic (Sydney Eye Hospital)
- Dr Brendan Tonson (Wollongong Hospital)
- Dr Fiona Louie (Maitland Hospital)

## FUNDING

Australian Government
National Health and Medical Research Council

Australian Government
Australian Research Council

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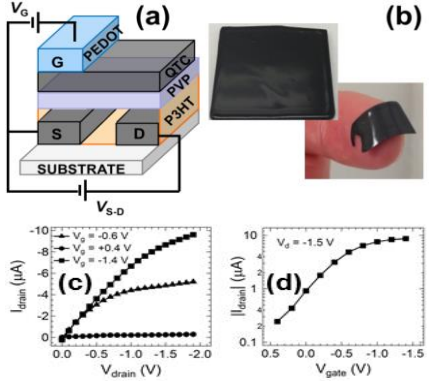
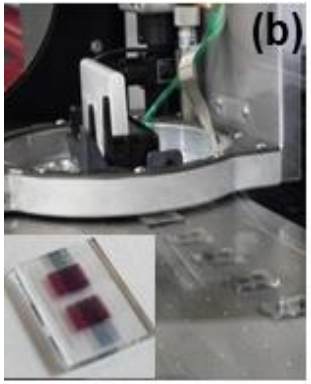
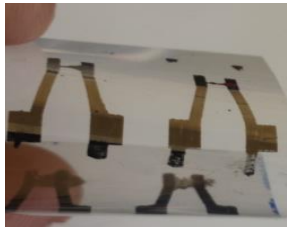
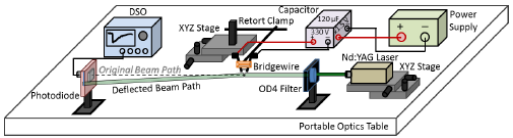
# Working With Industry

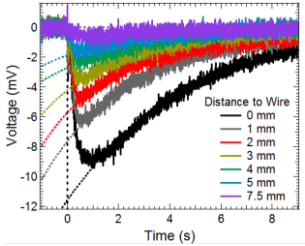



- Industry funded project leader
- Create printed light, pressure and plasma sensors
- Detect underground to detonate explosives
- Safe, secure, remotely programmable
- Cheap and disposable (but not publishable!)
- **Learn to identify and solve real world problems**

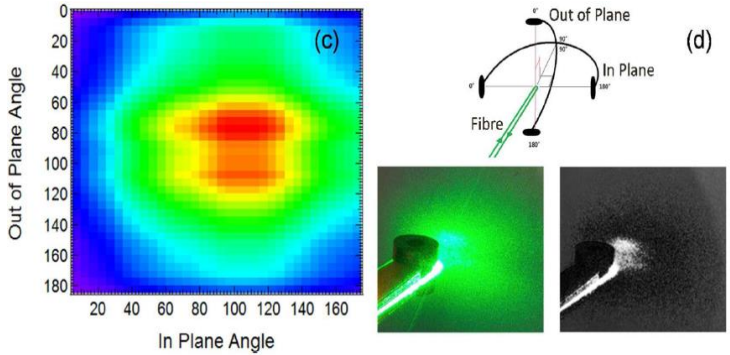


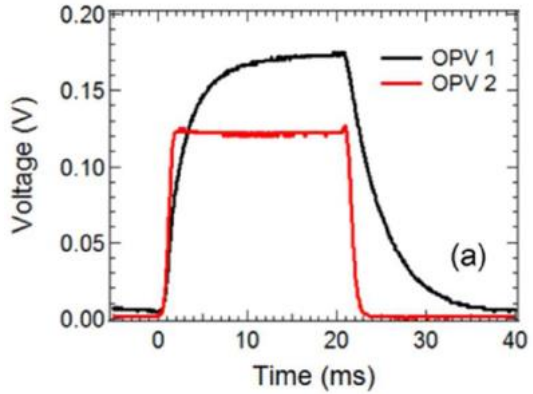


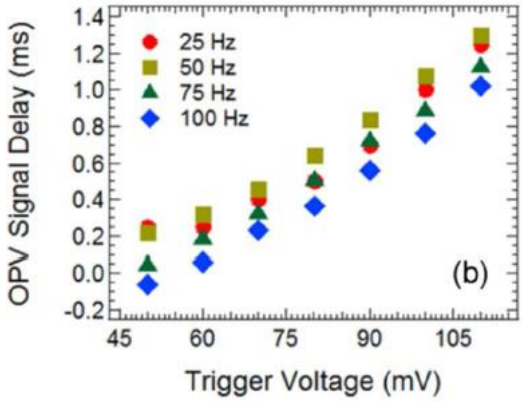





# Printed Photonics Sensors for Mining




- Designed system to detect light from optic fibre with printed OPV
- Leak light from fibre bend
- Use two light sensors and different response for timing

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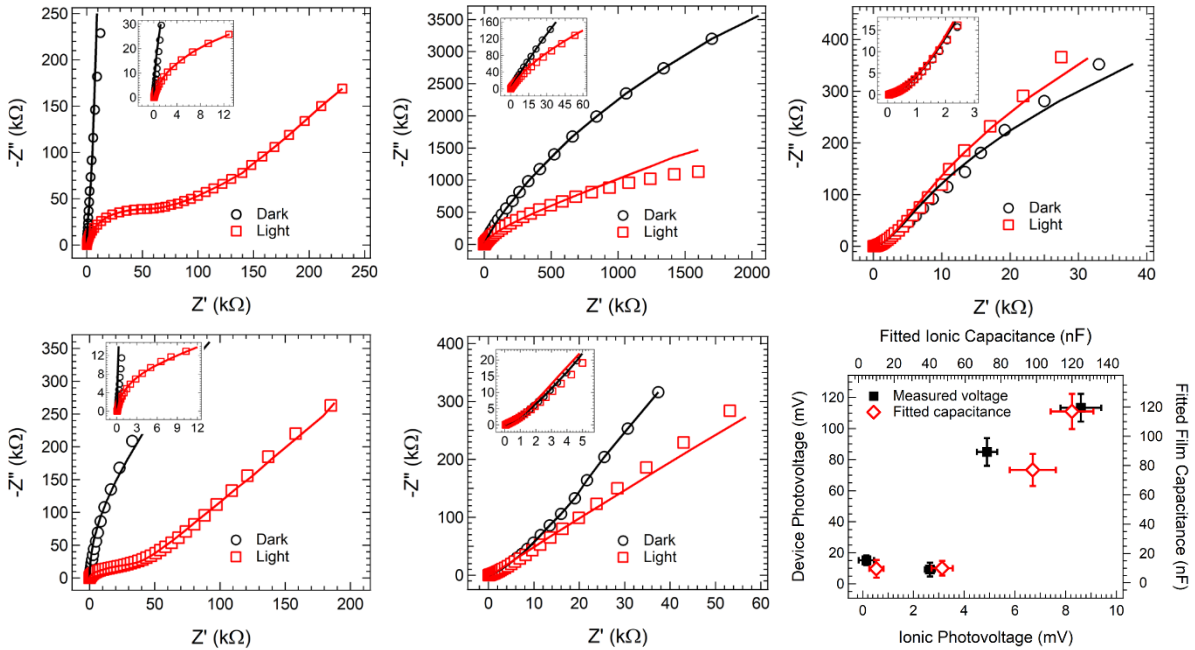
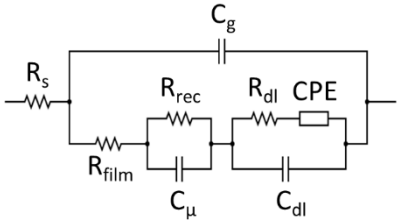
**M.J. Griffith**, *et. al.*; *ACS Appl. Mater. Interfaces*, **2016**, *8*, 7928.

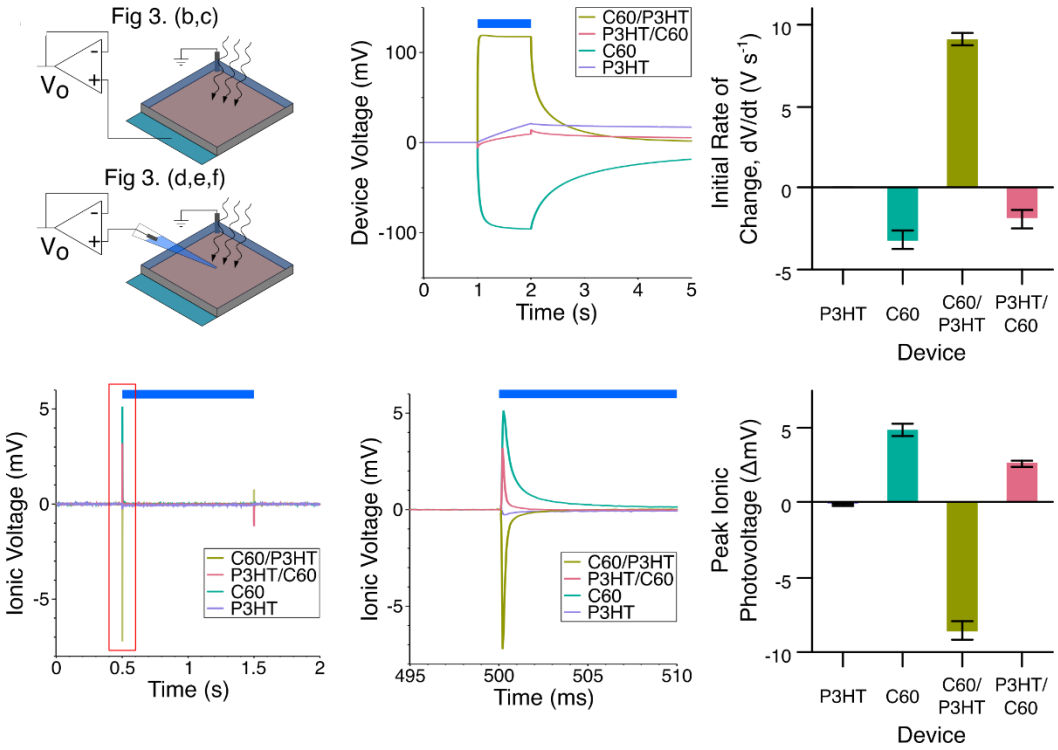
# Impedance Characterisation of Interfaces




- EIS measurements showed surface charge changes correlated to ionic interface capacitance
- Quantitative match to previous measurements

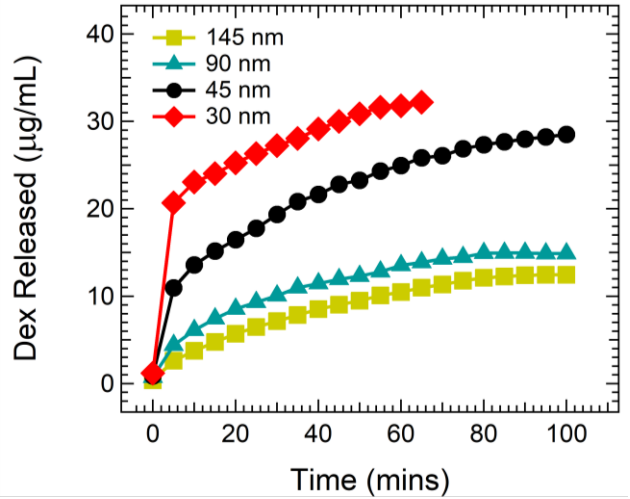
# Generate Photocharge at Biointerface

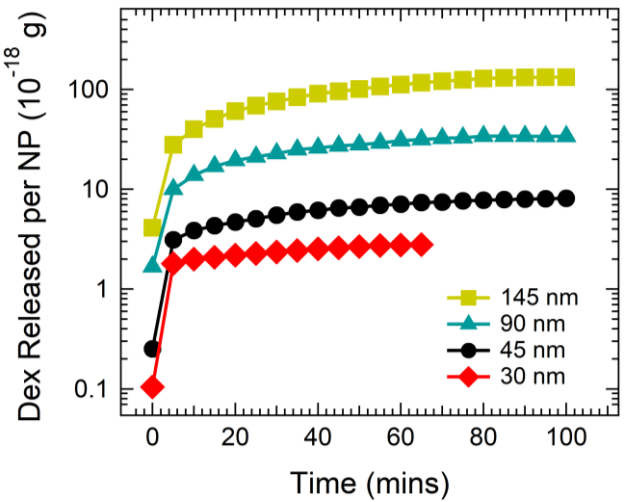


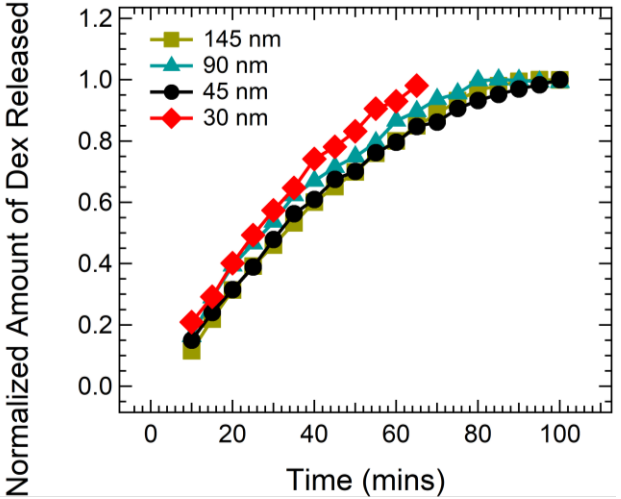

- Surface charge induced by 470 nm light
- Polarity of surface charge inverts when layer structure inverted
- Ionic charge in the electrolyte inversely correlated to surface.
- **Coupling is photocapacitive**


[4]. C. Sherwood, D. C. Elkington, M. R. Dickinson, W. J. Belcher, P. C. Dastoor, K. Feron, A. Brichta, R. Lim, M. J. Griffith; *J. Selected Topics Quant. Electron.*, **2021**, *27*, 1-12.

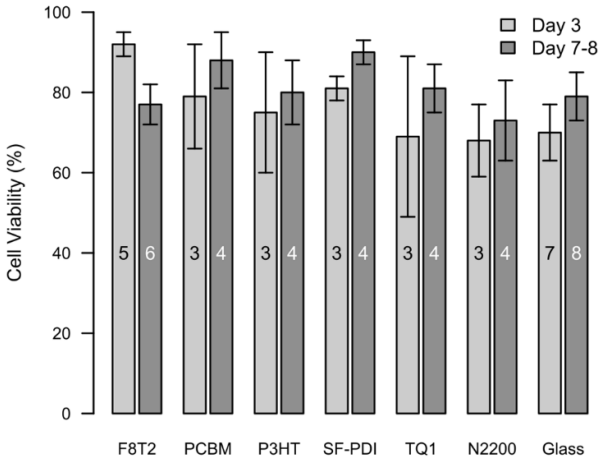
# Drug Release From Polymer NPs: Size vs Kinetics



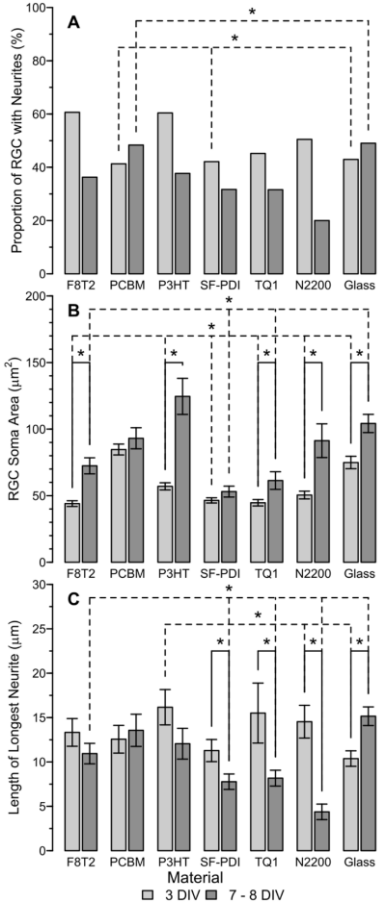



# Human Biocompatibility




Live/Dead Assays show very promising biocompatibility




Functional data shows cell attach, neurite growth limited

Need to be **very** careful to assess with right **cell culture** and right **assessment technique**


[3]. C. Sherwood, R. Crovador, …, **M. J. Griffith**; *Adv. Mater. Inter.* **2023**, 2202229.

# Spatial/Spectral Selectivity via Light

- We have shown that:

1. Neurons grow onto all our printed ink formulations
2. We can stimulate neuron membrane potentials using different coloured illumination of our semiconducting inks.