

**Ultrafast Laser Spectroscopy  
Mini-Symposium –**

**Melbourne 10-11<sup>th</sup> February, 2020**

# Ultrafast Laser Spectroscopy Mini-Symposium 2020

Ultrafast laser spectroscopy has had a proud presence in Australia since the mid 1970s with the group of G. Wilse Robinson at the University of Melbourne – only ~15 years after the first laser was made to operate. This comprised a single shot Nd:glass laser with a picosecond streak camera.

Since that time the definition of “ultrafast” has changed and ultrafast laser systems have developed enormously. The community in Australia (like elsewhere in the world) has also grown significantly with femtosecond laser systems now found in many laboratories around the country, being applied in micromachining, communications, microscopy, THz imaging, and of course various forms of spectroscopy.

We ran an “Ultrafast Laser Users Workshop” in Melbourne in 2010, which covered many of the uses of ultrafast lasers – from multiphoton fluorescence microscopy, attosecond laser science, spectroscopy, or high harmonic generation etc. This was a very successful meeting and we have threatened to run another since then.

The 2020 Mini-Symposium is aimed to concentrate on the ultrafast laser *spectroscopic* applications. This will be a great opportunity for us to all hear about the exciting ultrafast laser spectroscopy that’s being done, both here and in the laboratories of a few of our international colleagues. We hope it will also provide an avenue to publicise what capabilities there are around the country and identify gaps in our infrastructure, establish and strengthen collaborations, and discuss the appetite for hosting one of the international conferences targeting ultrafast phenomena in Australia in the near future.

Thanks for attending this meeting, which we’re sure will be a fruitful meeting and we hope that this can become a more regular occurrence.

Tak Kee (The University of Adelaide)

Jeff Davis (Swinburne University of Technology)

Trevor Smith (University of Melbourne)

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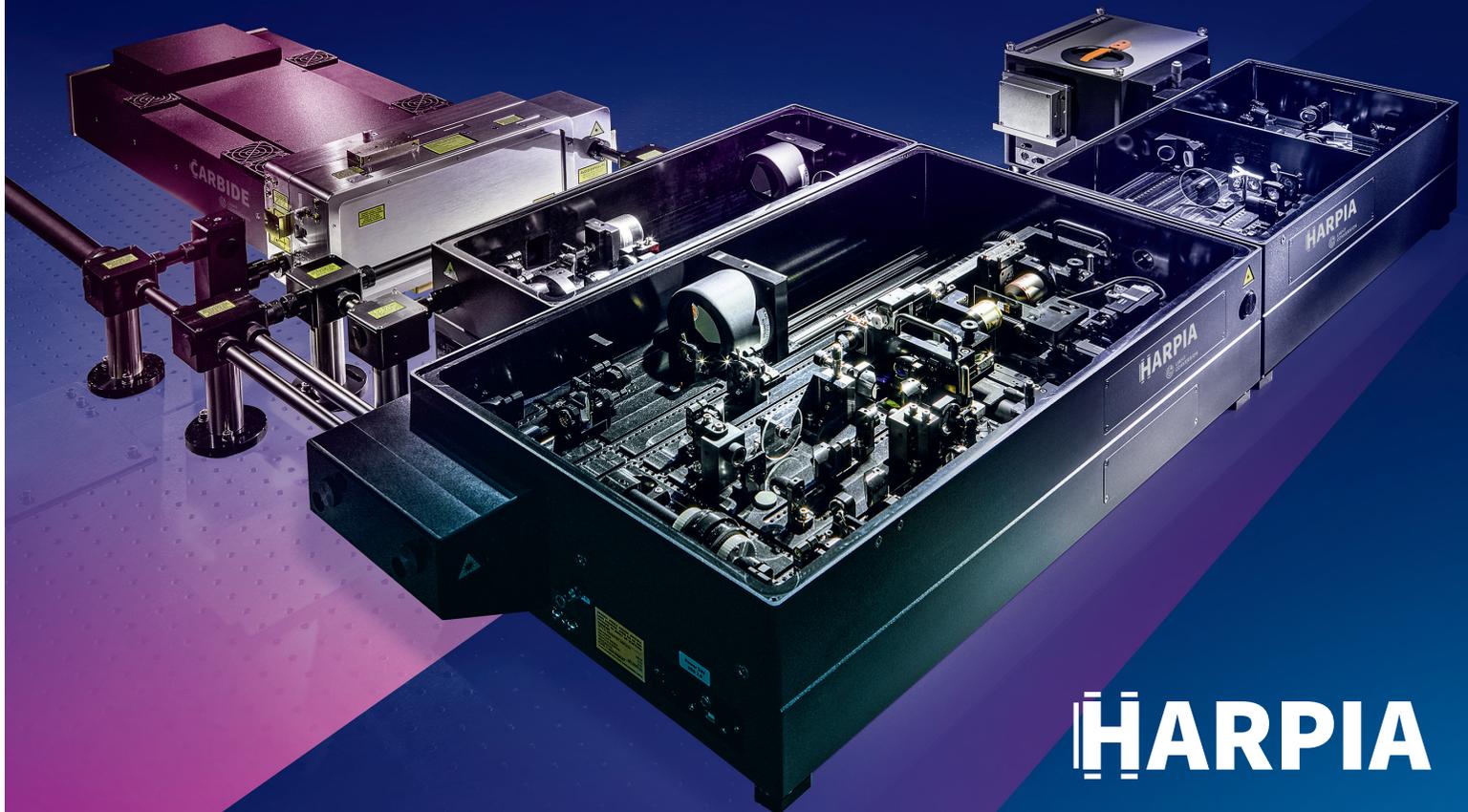
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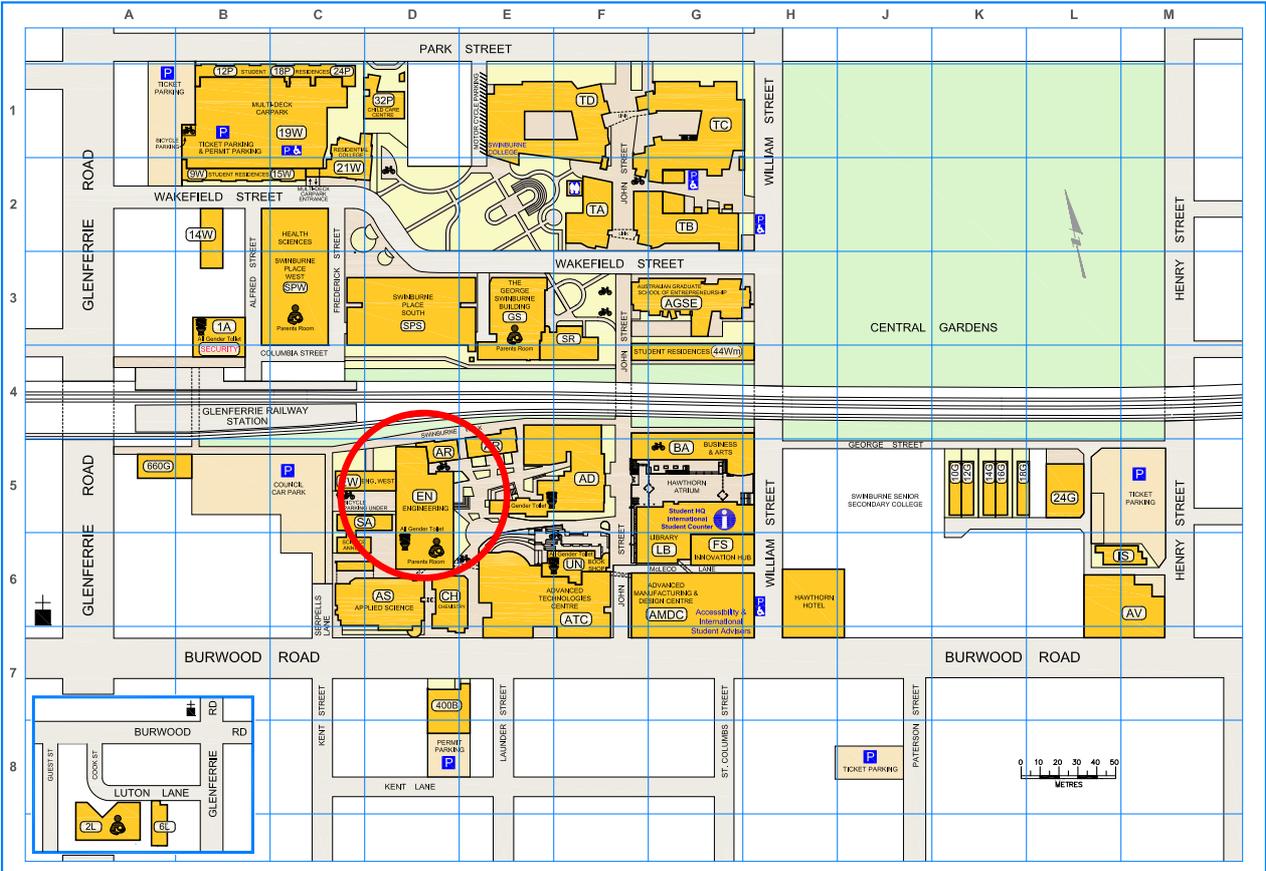
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# Venue

The venue will be theatre EN203



Dinner will be at: Beer DeLuxe, Hawthorn, 329 Burwood Rd., Hawthorn, 3122

# Program

## 10 February MONDAY

10:00 – 10:25 Morning tea

10:25 – 10:30 Opening remarks

Session 1, Chair: Jeff Davis

10:30 – 10:55, Justin Hodgkiss, Ultrafast optical probes of excitonic materials: case studies in organic semiconductors and metal halide perovskites

10:55 – 11:20, Christopher R. Hall, Probing structure and function in photoactive molecular motors and switches with ultrafast transient vibrational spectroscopy

11:20 – 11:45, Saghar Masoomi, Liquid crystallinity as a self-assembly motif for singlet fission materials

11:45 – 12:35, Gregory D. Scholes, Interplay of quantum vibrations during an ultrafast electron transfer reaction

12:35 – 13:35, Lunch

Session 2, Chair: Chris Hall

13:35 – 14:00, Ron Steer, Singlet fission: to see or not to see, that is the question

14:00 – 14:25, Ben Xinzi Zhang, Superposition reaction: excited-state proton transfer on two coupled sites

14:25 – 14:50, Jeff Davis, Multi-dimensional coherent spectroscopy

14:50 – 15:15, Paul Shaw, Understanding the photo-physical properties of fluorescent chemical sensors

15:15 – 15:45, Afternoon tea

Session 3, Chair: Kyra Schwarz

15:45 – 16:10, Isabella Wagner, Gating ultrafast emission spectra and dynamics by transient grating photoluminescence spectroscopy

16:10 – 16:35, Evan G. Moore, Using a sledgehammer to crack a nut: ultrafast studies of sensitised lanthanide luminescence

16:35 – 17:00, James A. Hutchison, Ultra-fast studies of light-matter strong coupling

17:00 – 17:25, Stuart Earl, Pulse duration effects on Floquet-Bloch states in monolayer transition metal dichalcogenides

17:25 – 17:50, Yasuhiro Tachibana, Transient absorption and emission spectroscopies to develop solar energy conversion devices

17:50 – 23:59, drinks and dinner at Beer Deluxe (329 Burwood Road, Hawthorn)

### **11 February TUESDAY**

Session 4, Chair: Tak Kee

09:00 – 09:25, Xiaoming Wen, Slowed cooling of hot carriers in hybrid perovskites

09:25 – 09:50, Patrick Tapping, Two-dimensional electronic spectroscopy using rotating optical flats

09:50 – 10:15, Eliezer Estrecho, Spectroscopy of high-density exciton-polariton condensates

10:15 – 10:40, Jessica de la Perrelle, 2D electronic spectroscopy of TIPS-pentacene and development of a flexible data analysis framework

10:40 – 11:10 Morning tea

Session 5, Chair: Patrick Tapping

11:10 – 11:35, Paul J. Low, Shining a light on conjugated compounds and complexes

11:35 – 12:00, Agustin Schiffrin, Ultrafast control of electrons in materials with the electric field of light

12:00 – 12:25, Shyamal Prasad, The ultrafast (and a bit slower) characterisation of singlet fission and triplets using absorption and photoluminescence

12:25 – 12:50, Jonathan Tollerud, Femtosecond covariance spectroscopy

12:50 – 13:50 Lunch

Session 6, Chair: Trevor Smith

13:50 – 14:15, Kyra Schwarz, Nanoscale capacitor-like charge build-up in an organic bulk heterojunction

14:15 – 14:40, Egle Bukarte, Tracking energy and electron transfer in biological systems using two-dimensional electronic spectroscopy

14:40 – 15:05, Laszlo Frazer, Using visible transient absorption and excitons to measure phonon kinetics

15:05 – 15:30, Trevor Smith, Ultrafast transient absorption microscopy

15:30 - 15:35 Closing remarks

# Ultrafast optical probes of excitonic materials: case studies in organic semiconductors and metal halide perovskites

Prof. Justin Hodgkiss



**Justin Hodgkiss** is co-director of the MacDiarmid Institute and a Professor in Physical Chemistry at Victoria University of Wellington. His research group has pioneered ways of manipulating laser pulses to understand ultrafast processes including light-to-current conversion in solar photovoltaic cells. Justin completed his undergraduate studies at the University of Otago, before undertaking his PhD at MIT, postdoctoral research in Cambridge, and returning to New Zealand in 2009.

Excitonic materials, including organic and low dimensional semiconductors, offer tremendous potential for optoelectronic devices including photovoltaics, lighting, and photonic devices. We have developed a series of time-resolved and non-linear optical spectroscopy experiments that resolve different properties of photoexcitations in these materials. In this talk, I will highlight their application to studying exciton diffusion in the new class of fused-ring electron acceptors, which now outperform fullerenes in record efficiency OPVs. We showed that their exciton diffusion coefficients exceed most other organic semiconductors by over two orders of magnitude, mostly due to their strong self-overlap for energy transfer and their low energetic disorder – raising the prospect that the bulk heterojunction architecture may be circumvented.<sup>1</sup> A second case study concerns photoinduced refractive effects in metal halide perovskites, where our novel interferometric method directly reveals intrinsic transient spectra and reconciles previous inconsistencies in their interpretation.<sup>2</sup>

## References:

- [1] Chandrabose, S. *et al*, *J. Am. Chem. Soc.* **2019**, *141*, 6922.
- [2] Tamming, R. R., *et al*, *ACS Photonics*, **2019**, *6*, 345.

# Talk Title: Probing Structure And Function In Photoactive Molecular Motors and Switches With Ultrafast Transient Vibrational Spectroscopy

**Speaker name:** Christopher R. Hall



**Chris** specialises in ultrafast electronic and vibrational spectroscopy of semiconductor nanostructures, proteins and molecular systems. He is a research fellow within the ARC Centre of Excellence in Exciton Science in the School of Chemistry at the University of Melbourne. Before this he was a postdoctoral researcher at the University of East Anglia, Norwich (UK). In 2019 he was awarded the Asian Photochemical Association Young Researcher Prize.

**Abstract:** Photoactive molecular motors and switches, based on light-driven changes in molecular structure, are utilised in a wide range of applications. Major achievements in the area include the development of light-powered molecular machines (Feringa, Nobel Prize Chemistry 2016), light-activated protein switches to control biological function (optogenetics), and switchable fluorescent proteins for super-resolution imaging. Further development of these systems requires a complete understanding of the excited-state processes following excitation. Transient Absorption (TA), Femtosecond Stimulated Raman Spectroscopy (FSRS) and Transient Infrared Spectroscopy (TIR) are powerful techniques that have proven effective for studying ultrafast electronic and structural dynamics over the course of a photochemical reaction. Utilising these techniques, we explore the electronic and structure changes driving the Feringa molecular motors and develop new methods to probe protein photoswitches and signalling pathways.

Molecular rotary motors are the building blocks of complex molecular machines. A key requirement for many applications is the ability to control the direction of rotation of the rotor. In the Feringa motors, unidirectional motion relies on light-driven conversion from a stable to a metastable conformation, which then relaxes through a thermally driven helix inversion in the ground state. With TA and FSRS spectroscopy, we characterise the electronic dynamics and structural changes that take place over the course of this reaction.[1] Photoexcitation of the intermediate state, before the forward reaction is complete, can drive rotation of the rotor in reverse direction. FSRS and TA measurements suggest the reverse reaction involves a different reaction coordinate to the forward direction, not predicted by existing computational models.[2] Combined, these measurements provide unique insight into the excited-state surface that describes this reaction.

The real-time observation of structure change at the heart of protein function remains a major challenge.[3] Ultrafast pump-probe methods record dynamics in light activated proteins, but the assignment of spectroscopic observables to specific structure changes is difficult. We incorporate the unnatural amino acid (UAA) azidophenylalanine (AzPhe) at key positions in the H-bonding environment of two BLUF (blue light using flavin) domain proteins to test this approach. Steady state and ultrafast time resolved infrared difference measurements of the azido mode reveal site-specific information on the nature and dynamics of light driven structure change.[4] This shows AzPhe can be an effective probe of structure change in proteins.

With a TIR spectroscopy facility being developed at the University of Melbourne, I will also briefly discuss the new capabilities and directions of research this will enable.

### References:

1. Hall, C.R., J. Conyard, I.A. Heisler, G. Jones, J. Frost, et al., *Ultrafast Dynamics in Light-Driven Molecular Rotary Motors Probed by Femtosecond Stimulated Raman Spectroscopy*. Journal of the American Chemical Society, 2017. **139**(21): p. 7408-7414.
2. Hall, C.R., W.R. Browne, B.L. Feringa, and S.R. Meech, *Mapping the Excited-State Potential Energy Surface of a Photomolecular Motor*. Angewandte Chemie International Edition, 2018. **57**(21): p. 6203-6207.
3. Laptенок, S.P., A.A. Gil, C.R. Hall, A. Lukacs, J.N. Iuliano, et al., *Infrared spectroscopy reveals multi-step multi-timescale photoactivation in the photoconvertible protein archetype dronpa*. Nature Chemistry, 2018. **10**(8): p. 845-852.
4. Hall, C.R., J. Tolentino Collado, J.N. Iuliano, A.A. Gil, K. Adamczyk, et al., *Site-Specific Protein Dynamics Probed by Ultrafast Infrared Spectroscopy of a Noncanonical Amino Acid*. The Journal of Physical Chemistry B, 2019. **123**(45): p. 9592-9597.

## **Talk Title:** Liquid crystallinity as a self-assembly motif for singlet fission materials

**Speaker name :** Saghar Masoomi



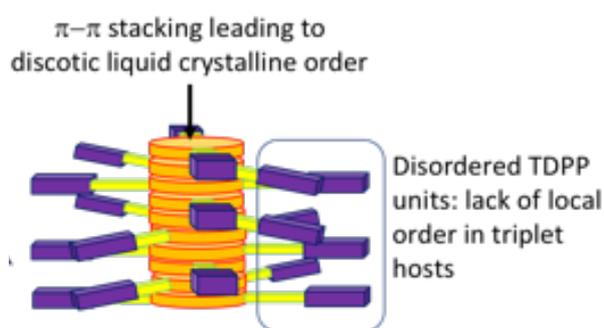
**Saghar Masoomi** is currently a PhD candidate in the University of Melbourne. She is interested in conducting research on singlet fission, 3<sup>rd</sup> generation photovoltaic and up conversion material.

### **Abstract:**

The major loss mechanism in single-junction PVs is due to the higher energy photons which lose the excess energy above the bandgap as heat (thermalisation losses), leading to a maximum theoretical efficiency of 32% for a single-junction PV, the Shockley-Queisser limit.<sup>1</sup> A process that has the potential to increase this limit to 45% is to use high energy photons to produce two electron-hole pairs. In organic materials, such a photophysical process is called as singlet fission (SF), the spin allowed conversion of a singlet excited state into two triplets by an assembly of two or more chromophores. SF has been reported and extensively studied in crystalline acenes, and more recently acene dimers to better understand the fundamental photophysics and materials requirements for this process. Incorporation of these SF materials into functional solar cells, although demonstrating modest efficiency enhancements, have had limited success. In our efforts to produce higher efficiency printed organic solar cells we had the desire to incorporate solution processible SF materials in printed organic solar cells, however most of the reported SF materials are highly crystalline and either do not promote SF in the amorphous solid state or controlling crystallisation is difficult.

We aimed to develop a new class of SF materials that are more amenable to inclusion into solar cell devices, and remove the “local-order constraint”. In this study, we investigate the use of hexa-peri-hexabenzocoronene (HBC) as a self-organizing core to promote singlet fission in amorphous films. Using design criteria outlined by Busby et al.<sup>2</sup>, suggesting an Acceptor-Donor-Acceptor (A-D-A) structure may support SF, we have used strong  $\pi$ - $\pi$  interactions of a fluorenyl-substituted hexabenzocoronene (FHBC) donor to promote strong self-assembly, coupled with thienyl-substituted diketopyrrolopyrrole (TDPP) as the triplet host. To design this

system, we consider different SF requirement including i) energy level requirement for SF that is  $E(S_1) \geq 2E(T_1)$ , ii) strong self-association through the core, and iii) solution processability. Thin films of the discotic liquid crystalline FHBC(TDPP)<sub>2</sub> material forms hexagonally packed columns<sup>3</sup> (Figure 1). SF studies on FHBC(TDPP)<sub>2</sub> demonstrate a triplet yield of 150% in amorphous thin films, increasing to 170% in thermally annealed films. This constitutes a new class of singlet fission materials.



**Figure 1.** A schematic representation of self-association in FHBC(TDPP)<sub>2</sub>. hexabenzocoronene (HBC, core D) provides strong promoting discotic liquid crystalline order. The TDPP units act as triplet hosts which remain disordered removing any local order for the dithienyldiketopyrrolopyrrole (TDPP, A) acceptor units.

## References

- [1] Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells *J. Appl. Phys.* 1961, 32, 510-519.
- [2] Busby, E.; Xia, J.; Wu, Q.; Low, J. Z.; Song, R.; Miller, J. R.; Zhu, X. Y.; Campos, L. M.; Sfeir, M. Y. A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor-acceptor organic materials *Nat. Mater.* 2015, 14, 426-33.
- [3] Wong, W. W. H.; Subbiah, J.; Puniredd, S. R.; Purushothaman, B.; Pisula, W.; Kirby, N.; Muellen, K.; Jones, D. J.; Holmes, A. B. Liquid Crystalline hexa-peri-hexabenzocoronene-diketopyrrolopyrrole organic dyes for photovoltaic applications *J. Mater. Chem.* 2012 22, 39, 21131-21137.

# Talk Title: Interplay of Quantum Vibrations During an Ultrafast Electron Transfer Reaction

**Speaker name:** Prof. Gregory D. Scholes



**Greg Scholes** is the William S. Tod Professor of Chemistry at Princeton University and Director of the Energy Frontier Research Center *BioLEC*. Originally from Melbourne, Australia, he started his independent career at the University of Toronto where he was the D.J. LeRoy Distinguished Professor. Greg is the Editor-in-Chief of the *Journal of Physical Chemistry Letters*, Co-Director of the Canadian Institute for Advanced Research program *Bioinspired Solar Energy*, and a Professorial Fellow at the University of Melbourne. He was elected a Fellow of the Royal Society (London) in 2019 and a Fellow of the Royal Society of Canada in 2009.

## Abstract:

Electron transfer (ET) reactions are common throughout chemistry and biology, for example they are central to energy transduction and photoredox chemistry, amongst other processes. Building on the original theoretical foundation for understanding the ET mechanism, decades of theoretical and experimental progress has led to the hypothesis that quantum vibrational modes can play a governing role in ET reactions. Vibrations enable a dramatic speed up for some ET reactions, or control of ET by suppressing and enhancing reaction paths. Despite these, and other, compelling examples of the function of vibrations in ET reactions, experimental resolution of the mechanism of interplay of ET with vibrations has eluded researchers. Here we report ultrafast coherence experiments that resolve how quantum vibrations participate during an ET reaction. We observe ballistic ET (ca. 30 fs) along a reaction coordinate comprising high-frequency promoting vibrations. Along another vibrational coordinate, the system becomes impulsively out of equilibrium as a result of the ET reaction. That leads to generation—by the ET reaction, not the laser pulse—of a new coherence along this second reaction coordinate in a mode associated with the reaction product. This surprising spontaneous launch of a vibrational wavepacket shows that coherence can be generated by a separation of timescales in chemical dynamics, and not solely by pulsed laser photoexcitation. Moreover, because this coherence is generated by the ET, it provides a marker on the reaction coordinate that allows us to determine the hierarchy of geometrical relaxation pathways that coincide with ET, and that suppress coherent recurrence of the reactant state in the quantum dynamics.

## Singlet fission: to see or not to see, that is the question.



Ron Steer is Distinguished Professor Emeritus in the Department of Chemistry, University of Saskatchewan, Canada, and a frequent visitor to the School of Chemistry, University of Melbourne. His main research interests are centred on the spectroscopy and photophysics of polyatomic molecules that exhibit measurable fluorescence and/or transient absorption from excited electronic states higher in energy than the lowest excited singlet.

### Abstract:

Arguments will be presented that the process of singlet fission (SF) from an electronic excited state higher in energy than the lowest excited singlet (e.g.  $S_2$ ) can occur in any molecular dimer or aggregate that produces  $S_2$  by triplet-triplet annihilation (TTA), and might be observable provided chromophore substitution and/or vibrational activation allows the system to meet the SF energy conservation requirements. Whether the products of the  $S_2 + S_0$  SF process are observable depends on the rates of the steps *en route* to  $2 T_1$  compared with the rates of competing processes such as  $S_2$  to  $S_1$  internal conversion,  $S_2$  excimer quenching and TTA to  $T_2 + S_0$ . Azulene and some of its derivatives [1] may meet the requirements needed for observation of the  $S_2$  SF process. A recent example in which SF from  $S_2$  to  $2 T_1$  is observed even though TTA via  $2 T_1$  to  $S_2 + S_0$  is energetically impossible has been provided by Ni, *et al.* [2] using a covalently linked cofacial perylene dimer.

### References:

[1] R.P. Steer, *J. Photochem. Photobiol. C*, **2019**, *40*, 68-80.

[2] W. Ni, G.G. Gurzadyan, J. Zhao, Y. Che, X. Li, L. Sun, *J. Phys. Chem. Lett.* **2019**, *10*, 2428-2433.

# Superposition reaction: excited-state proton transfer on two coupled sites

**Speaker name:** Ben Xinzi Zhang



**Ben Zhang** is a Ph.D. candidate working with Prof. Gregory Scholes at Princeton University. He was introduced to optical spectroscopy as an undergraduate researcher in Prof. Elizabeth Harbron's lab at the College of William & Mary, characterizing the kinetics of energy transfer from conjugated polymer nanoparticles to photochromic dopants. After learning about broadband pump-probe spectroscopy in graduate school, he developed an interest in experimental descriptions of quantum phenomena in chemical systems. He is also an avid chemistry teacher, science journalist, and photographer.

## **Abstract:**

Despite the pre-eminence of quantum mechanics in modern descriptions of the molecular world, practising chemists typically think of chemical reactions in a classical fashion—occurring in distinct spatial and temporal steps. However, we suggest that an ultrafast laser pulse may induce quantum mechanical interference effects in reactions that involve particles as heavy as a proton, as long as the reactant molecule fulfils certain symmetry and coupling requirements. Specifically, we present here pump-probe results on Pigment Yellow 101 (2,2'-dihydroxy-1,1'-naphthalazine) in solution at room temperature, whose two symmetrical O—H...N sites are simultaneously primed for intramolecular proton transfer when photoexcited. Yet evidence shows that only one of the two sites undergoes transfer within the first 100 fs. This led us to believe that the initial superposition excitation of the two identical sites must collapse to allow for the eventual asymmetrical transfer, hinting at the possibility of observing an interference effect through the proton transfer reaction itself. To measure the rate of the femtosecond reaction, we frequency-doubled a near-infrared NOPA output and compressed it with a pair of chirped mirrors into a 400–450 nm broadband pulse with a Gaussian FWHM duration of ~18 fs fitted from its FROG trace. Preliminary analyses have shown that, when both sites are identical, the measured transfer rate is slightly faster than the control molecule in which one of the sites has its proton exchanged for a deuteron. This minute yet discernible acceleration of the symmetrical reaction could serve to exemplify quantum superposition as an observable principle in the nuclear dynamics of chemical reactions.

## Talk Title: Multi-Dimensional Coherent Spectroscopy

Speaker name: A/Prof. Jeff Davis



**Jeff Davis** leads the ultrafast spectroscopy group at Swinburne, within the newly formed Centre for Optical Sciences. He did his PhD at the University of Cambridge doing time resolved spectroscopy and has been in the field in various forms ever since. He is currently a CI in the ARC Centre of Excellence for Future Low-Energy Electronics Technologies, where he applies various ultrafast techniques to probe and control various 2D materials.

### Abstract:

Multidimensional Coherent Spectroscopy is based on transient four-wave mixing but with the phase information detected as well as the amplitude[1]. These techniques have been optimised to reveal interaction between different states within complex systems. It has been applied successfully to molecular and bio-molecular systems as well as semiconductors, where new understanding has been realised[2].

In this talk I will describe some of our recent work applying this technique to more complicated materials, where the underlying interactions are crucial to the macroscopic properties, but are not completely understood. Specifically, I will describe our initial measurements of exciton polaritons in a GaAs quantum well embedded in a microcavity. I will also describe our even more ambitious measurements of the coherent dynamics in a high-temperature cuprate superconductor, where we see novel signatures not seen in simpler systems [3].

### References:

- [1] J.O. Tollerud, J.A. Davis, *Coherent multi-dimensional spectroscopy: Experimental considerations, direct comparisons and new capabilities*, Progress in Quantum Electronics, **55**, 1-34 (2017)
- [2] J.O. Tollerud, ST Cundiff, J.A. Davis, *Revealing and Characterizing Dark Excitons Through Coherent Multidimensional Spectroscopy*, Phys. Rev. Lett. 117, 097401 (2016)
- [3] F Novelli, J.O. Tollerud, D. Prabhakaran, J.A. Davis, *Persistent coherence of quantum superpositions in an optimally doped cuprate revealed by 2D spectroscopy*, Science Advances (accepted), arXiv:1712.03598v2 (2019)

## Talk Title : Understanding the photo-physical properties of fluorescent chemical sensors

Speaker name: Dr Paul Shaw



**Paul Shaw** is a member of the leadership team of the Centre for Organic Photonics & Photonics at UQ. His research focuses on the use of spectroscopy to understand the fundamental properties of organic optoelectronic materials and how these relate to their performance in applications such as solar cells, light-emitting diodes and sensing.

### Abstract :

Fluorescence-based detection of chemical vapours has attracted much interest because of the potential for detectors that have high-sensitivity, compact form factor, simple operation and low-cost. The detection of nitro-containing explosives has been a particular success story with fluorescence-based sensors commercially available since 2005. Such sensors respond to the presence of explosives with a reversible decrease in the fluorescence intensity. There are many processes that control the real-time fluorescence quenching of thin films by analyte vapours, such as, the non-radiative quenching process by which the sensor exciton decays, the analyte-sensor intermolecular binding interaction, and the diffusion process for the analyte vapours into and within the film.[1]

In this talk I will describe how we have applied ultrafast spectroscopy towards understanding the photo-physical processes that govern the response of fluorescent sensors to nitro-containing explosives.[2] In particular, I will focus on work we have done to establish the role of exciton diffusion in fluorescence-based sensing. While exciton diffusion has been historically judged to be one of, if not the primary, causes for the high sensitivity of many conjugated polymers to nitro-containing vapours, this mechanism required very long exciton diffusion lengths and could not explain the high sensitivity of non-polymeric sensing materials. We used transient absorption spectroscopy to measure the exciton diffusion length in a pentaptycene-containing poly(phenyleneethynylene)-based polymer, which is an established material for the detection of explosive vapours.[3] The results showed that the exciton diffusion length was  $\sim 7.5$  nm, which is comparable to that of many organic semiconductors but shorter than had been previously thought. Measurements of the analyte vapour uptake using a quartz crystal microbalance showed that the concentration of analyte vapour

in the film was greater than had been previously assumed, negating the need for long exciton diffusion lengths. I will conclude by briefly discussing the implications of these results on the development of sensor materials for real-time detection.

### **References:**

[1] Shaw, P. E. & Burn, P. L. Real-time fluorescence quenching-based detection of nitro-containing explosive vapours: what are the key processes? *Phys. Chem. Chem. Phys.* **19**, 29714–29730 (2017).

[2] Geng, Y. *et al.* Unambiguous detection of nitrated explosive vapours by fluorescence quenching of dendrimer films. *Nat. Commun.* **6**, 8240 (2015).

[3] Ali, M. A. *et al.* Detection of Explosive Vapors: The Roles of Exciton and Molecular Diffusion in Real-Time Sensing. *ChemPhysChem* **17**, 3350–3353 (2016).

# Talk Title: Gating Ultrafast Emission Spectra and Dynamics by Transient Grating Photoluminescence Spectroscopy

Speaker name: Isabella Wagner



**Isabella Wagner** is currently a PhD student in the research group of Prof. Dr. Justin Hodgkiss. Isabella received her Master of Science degree in Chemistry in 2018 from the Julius-Maximilians University of Wuerzburg, Germany.

## Abstract:

The evolutions of photoluminescence (PL) spectra are insightful probes for photoexcitation dynamics in various material systems. However, the PL spectral dynamics have rarely been experimentally accessed in sub-picosecond region, which is the crucial timescale for photophysics and photochemical processes. The technical challenges for conventional TRPL methods are fundamentally compromised by spectral bandwidth (fluorescence upconversion), time resolution (streak camera), or high background noise (optical Kerr gate). Recently, a new technique grating was developed in our research group using laser induced transient to capture the dynamics of transient PL spectra.<sup>[1]</sup>

The transient grating photoluminescence spectroscopy (TGPLS) has been applied to address several ultrafast phenomena, including ultrafast resonant energy transfer,<sup>[2]</sup> structural relaxation,<sup>[3]</sup> and exciton dynamics.<sup>[4]</sup> Here, we will show several examples of ultrafast photoexcitation dynamics in advanced materials using this novel technique and some new technical developments using a high repetition fiber laser as light source.

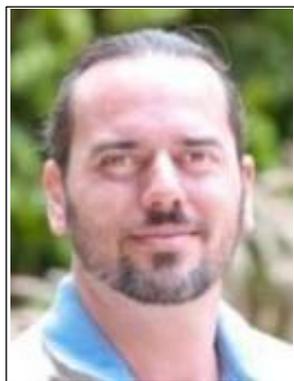
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## Talk Title: Using a Sledgehammer to Crack a Nut: Ultrafast Studies of Sensitised Lanthanide Luminescence.

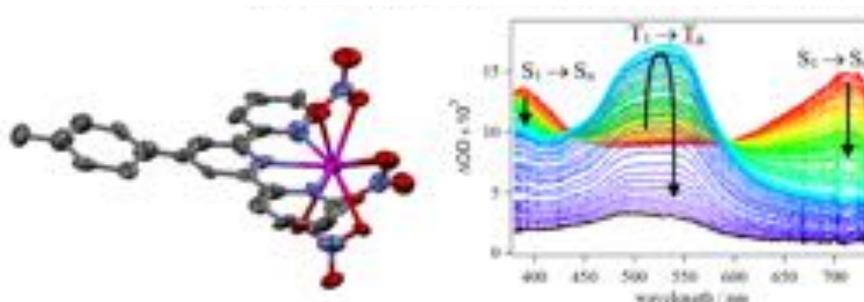
Speaker name: Dr. Evan G. Moore



**Evan Moore** is a Senior Lecturer in Inorganic Chemistry at the University of Queensland, where he also manages the Photochemistry and Ultrafast Laser Spectroscopy facility (UQ-PULSE). He completed his PhD studies at UQ in 2004, and undertook postdoctoral research fellowships in Berkeley, Melbourne, and Bologna, before returning to Brisbane in 2012.

### Abstract:

Trivalent lanthanide complexes have attracted considerable interest, particularly with  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$ , due to their applications as long-lived ( $\mu\text{sec}$  to  $\text{msec}$ ) luminescent probes in biotechnology.<sup>1</sup> However, since direct  $f-f$  absorption is Laporte forbidden, and therefore weak, organic groups are typically required as ‘antenna’ to absorb light and then transfer this excitation to the metal center. Although metal based emission is long-lived, the intersystem crossing and energy transfer processes involved with the antenna effect have not been investigated, but occur on the ultrafast timescale.



**Figure 1.** X-ray crystal structure of  $[\text{Tb}(\text{TolTpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$  and observed transient absorption (TA) spectrum in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{ex}} = 266 \text{ nm}$ ,  $\Delta t = 200\text{fs} - 1.6\text{ns}$ ).

We have utilised the unique  $S_1 \rightarrow S_n$  and  $T_1 \rightarrow T_n$  transient signatures of an organic 4'-*p*-tolyl-[2,2':6',2'']-terpyridine (TolTpy) ligand to monitor the excited singlet and triplet state population dynamics for a series of isostructural  $[\text{Ln}(\text{TolTpy})(\text{NO}_3)_3]$  complexes. Femtosecond transient absorption (TA) and femtosecond optical-gated (FOG) fluorescence upconversion techniques have revealed an extremely rapid decay of the

initially populated  $S_1$  excited state, largely independent of the internal heavy atom effect, while the  $T_1$  decay kinetics in this system instead correlate with the density of accepting states on the metal cation, yielding observed lifetimes spanning from the picosecond to microsecond time domains. A brief summary of the ultrafast facilities available at UQ-PULSE in Brisbane will also be provided.

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# Talk Title: Ultra-Fast Studies of Light-Matter Strong Coupling

Speaker name: Dr James A. Hutchison



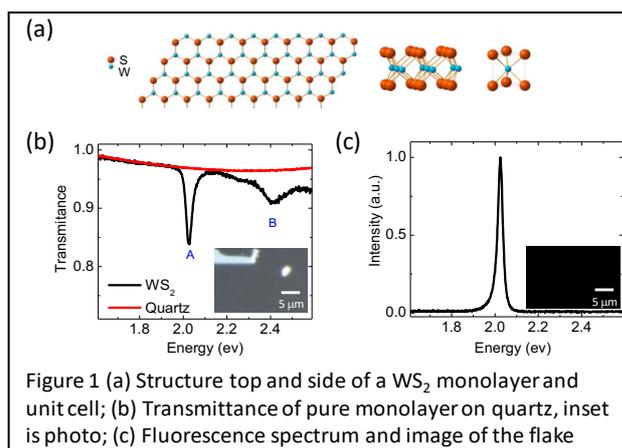
**James Hutchison** is currently an Australian Research Council (ARC) Future Fellow at the School of Chemistry, the University of Melbourne, working in optical materials. Previously he held an ARC DECRA fellowship at the same institution and a tenured researcher position with the CNRS in Strasbourg, France, working on plasmonics and strong light-molecule coupling. He also worked on single molecule/particle imaging during a post-doc in the Hofkens labs, KU Leuven, Belgium.

## Abstract:

This talk will discuss the interfacing of organic molecular systems and transition metal dichalcogenides (TMD) monolayers to metallic photonic nanostructures, and potential ultra-fast measurements that might illuminate their study.

Recently several examples have emerged of organic thermochemistry being influenced by the strong coupling of reactant vibrational modes to the vacuum field of optical cavities [1]. To date however, no consensus exists as to mechanisms at play. Mid-IR transient absorption spectroscopy may be able to shed light on this important problem.

TMD monolayers exhibit an effective 2D honeycomb lattice lacking inversion symmetry (Fig. 1a). These materials have *Valleys* in momentum space that can be separately addressed by left or right circularly polarized light. Our recent work on coupling Valley excitons to chiral plasmonic structures will also be discussed [2].



## References:

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## **Talk Title:** Pulse duration effects on Floquet-Bloch states in monolayer transition metal dichalcogenides

**Speaker name:** Dr Stuart Earl



**Stuart** did his PhD in semiconductor-plasmon interactions at the University of Melbourne, looking at methods to harness the phase change of vanadium dioxide to produce dynamically tunable plasmonic arrays. His current research is focussed on optically detecting the phase transition from trivial to topological insulator in transition metal dichalcogenide monolayers as part of the Davis ultrafast microspectroscopy group at Swinburne university of Technology

### **Abstract:**

Monolayer transition metal dichalcogenides are direct bandgap semiconductors with a novel combination of properties that permit dynamic manipulation of their band structure. Application of a below-bandgap ultrashort laser pulse has already been shown to be equivalent to the optical Stark effect [1], while use of an above bandgap pulse has been predicted to drive a phase transition to a topological insulating state [2]. This predicted topological phase change arises through the perspective of Floquet theory, in which a Hamiltonian with a time-dependent perturbation is transformed into a linear, time-independent one with an infinite, periodic set of eigenstates spaced by the energy of the driving field. Floquet analysis assumes an infinite, monochromatic driving field, and so it is necessary to understand how the use of ultrashort laser pulses to observe this phase transition affects it.

We have used two-colour pump-probe spectroscopy to drive the optical Stark effect in MoS<sub>2</sub> and WS<sub>2</sub> to observe the impact of varying the duration of the driving field from 33 to 67 fs. Figure 1 shows the resulting peak Stark shift of the A exciton of the monolayer as a function of peak intensity for the two pulse fluences used in the experiment, in agreement with the predictions of Floquet theory. These findings suggest that pulses as short as 33 fs do not alter the response of the system, and therefore may be used to characterise the predicted topological phase change in future experiments.

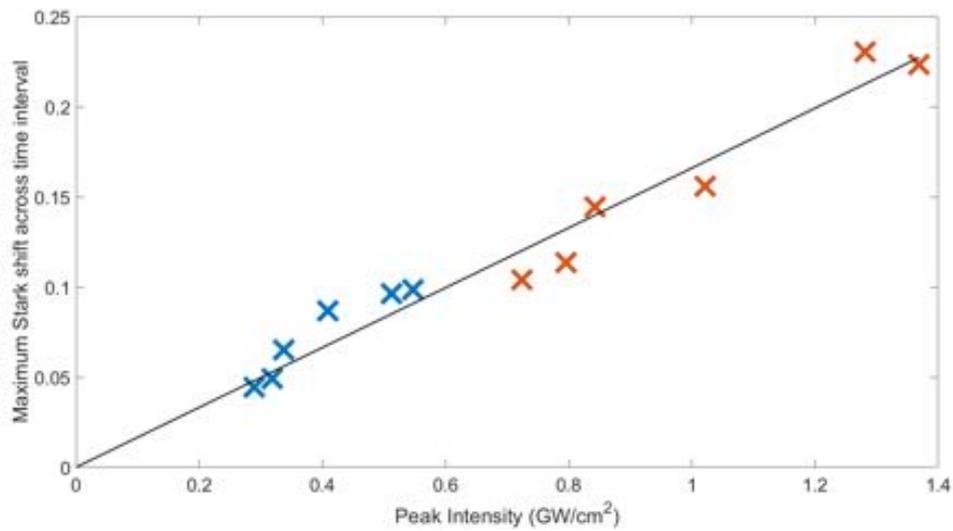


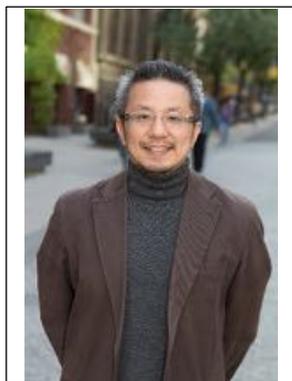
Figure 1: Peak Stark shift of the A exciton in an exfoliated WS<sub>2</sub> monolayer, calculated from the spectral weight transfer, as a function of peak intensity for pulses fluences of 20 μJ/cm<sup>2</sup> (blue crosses) and 50 μJ/cm<sup>2</sup> (red crosses). Six different pulses durations ranging from 33fs to 67fs were used.

## References:

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## **Talk Title:** Transient Absorption and Emission Spectroscopies to Develop Solar Energy Conversion Devices

**Speaker name:** Prof. Yasuhiro Tachibana



**Yasuhiro Tachibana** is currently a professor and a program manager of M. Eng. Sustainable Energy at School of Engineering, RMIT University and a guest associate professor at Faculty of Science, Osaka University, Japan. Prof. Tachibana received his B. Eng. (1992) and M. Eng. (1995) in applied chemistry at Osaka University. From 1995 to 1998, he conducted a PhD course at Imperial College London, U K. He continued his study as an EPSRC research fellow, and received his Ph.D. degree in 2000.

### **Abstract:**

Solar energy conversion devices such as photovoltaics or solar water splitting devices can generate abundant energy from the sun light as the most attractive clean energy generation sources. Their function is controlled by photo-induced charge separation and recombination reactions. That is, the device functions efficiently if the charge separation occurs swiftly and efficiently while their charge recombination is retarded. Material design is subsequently crucial to maximise photo-induced charge separation efficiency and to minimise charge recombination process. Transient absorption and emission spectroscopies are the most useful techniques to monitor photo-generated charge carriers and their interfacial transfer dynamics.

In this presentation, we will show how transient absorption and emission spectroscopies can be employed to develop photo-active materials to be applied for photovoltaic devices and solar water splitting devices.[1, 2]

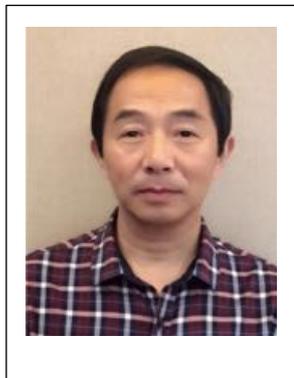
This work was supported by Japan Science and Technology agency, PRESTO program (Photoenergy Conversion Systems and Materials for the Next Generation Solar Cells), JSPS KAKENHI (Grant Number 16K05885 and 19H02813), Japan and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant number 2017-75, 2018-87, 2019-50), Japan. We also acknowledge supports from ARC DP fund (DP180103815) and ARC LIEF fund (LE170100235), Australia.

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## Talk Title: Slowed cooling of hot carriers in hybrid perovskites

Speaker name: Dr Xiaoming Wen



Xiaoming Wen is a research leader focusing on photophysics of advanced materials at Swinburne University of Technology in Australia. He was awarded PhD in 2007 from Swinburne. He performed research at University of Melbourne, University of New south Wales in Australia. His expertise includes ultrafast and time resolved micro-spectroscopy, and electron/exciton/phonon dynamics in nanomaterials. He published >150 refereed journal papers, such as Nature Communications, Advanced Energy Materials, Nano Letters; including 7 ESI highly cited papers (top 1%).

### Abstract:

Organic-inorganic hybrid perovskites are very promising for next generation high efficiency low cost solution fabricated solar cells with quickly increased conversion efficiency over 25%. In addition, perovskites are promising candidate for photonic application, such as LED, light source, detector and sensors due to the high efficient luminescence. Understanding the photogenerated carrier dynamics in the materials and devices is critically important for designing and improving solar related materials and devices.

Using ultrafast transient absorption, the carrier temperatures is extracted as a function of the time delay after the fs laser excitation. It is very interesting to found that the ultrafast cooling processes usually occurring in conventional semiconductors exhibit significantly slowed down, up to hundreds of picoseconds in halide perovskites. By performing comprehensive theoretical and experimental investigations, we proposed the mechanism of acoustic-optical phonon up-conversion is responsible for observed phonon bottleneck and thus slowed cooling. This unique property suggests that the hybrid perovskites are promising for the high efficiency hot carrier solar cells, with efficiency over the *Shockley-Queisser* limit of 33% for single junction solar cells. Moreover, high efficient photocatalysis can be potentially achieved because it is found the extra dynamic energy in hot carriers can result in significantly increased activity of catalysts.

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3. T Pu, J Li et al Universal passivation strategy to slot-die printed SnO<sub>2</sub> for hysteresis-free efficient flexible perovskite solar module, **Nature communications** 9 (2018), 4609
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# Talk Title : Two-dimensional Electronic Spectroscopy Using Rotating Optical Flats

Speaker name : Dr Patrick Tapping



**Patrick Tapping** is a post-doctoral researcher in the Department of Chemistry at the University of Adelaide, working in Tak Kee's laser spectroscopy group. His PhD work used theoretical and spectroscopic techniques to study energy and charge transport in organic semiconductors, such as conjugated polymers and singlet fission/triplet upconversion materials. He has recently completed construction of a 2D electronic spectrometer which will enhance the capabilities of the Adelaide laboratory.

## Abstract :

Two-dimensional electronic spectroscopy (2DES) is a Fourier transform technique which uses a sequence of broadband visible laser pulses to add an excitation energy axis to the directly detected energy axis of a pump-probe experiment.<sup>1</sup> With a superior ability to correlate electronic interactions and follow energetic pathways,<sup>2</sup> it has been used to study a variety of photoactive materials such as semiconductors and light-harvesting compounds, as well as photosynthetic systems.<sup>3,4</sup>

The technique relies on precise timing of the laser pulse sequence, typically to sub-fs accuracy. Pulse delays are often achieved using translating glass wedges or electronically controlled pulse shapers. We have recently demonstrated 2DES using rotating optical flats (ROFs) to produce the required pulse sequence, which offer reduced spectral dispersion artefacts (chirp) relative to translating wedge designs, and a cost an order of magnitude lower than that of pulse shapers.<sup>5</sup>

This presentation will outline the capabilities and limitations of the ROF-based 2D spectrometer, as well as the technical and engineering issues which must be considered when implementing the design. The techniques used to achieve the required precision may be broadly applicable to many optical spectroscopy techniques, potentially increasing the quality of acquired data or allowing the use of lower-cost hardware.

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# Talk Title : Spectroscopy of high-density exciton-polariton condensates

**Speaker name:** Dr. Eliezer Estrecho



**Eliezer Estrecho** is a postdoctoral fellow at the Australian National University (ANU) node of the ARC Centre of Excellence in Future Low-Energy Electronics Technologies (FLEET). He completed his PhD at ANU in 2018 and he is currently studying the properties of high-density condensates of exciton-polaritons in GaAs-based microcavities and working towards condensation of exciton-polaritons in atomically thin transition metal dichalcogenides.

## Abstract:

Bose-Einstein condensates of exciton polaritons, quasiparticles arising from the strong coupling of excitons in a semiconductor and photons confined in an optical cavity, are dissipative macroscopic quantum systems that exist on a solid-state platform up to room temperature [1]. Due to their dissipative nature, these condensates are inherently non-equilibrium, which makes their dynamics and phases richer than those of the atomic counterparts. Furthermore, this platform can be used to create practical devices that exploit non-classical properties of macroscopic quantum systems.

Our group at ANU studies the properties of exciton-polariton condensates stemming from the interplay between their dissipative nature, energy relaxation, and nonlinearity. We employ spatial structuring of the excitation laser to create and confine the condensate, and image the condensate emission to measure the polariton distribution in position and momentum space with both time and energy resolution.

In this talk, I will discuss how the thermal reservoir of uncondensed exciton polaritons, dissipation, and energy relaxation compete at low densities, and how the condensate interactions dominate in the high-density regime—the Thomas-Fermi limit. In this limit, we directly measure the polariton interaction strength, a key parameter of the system with the reported uncertainty in its values reaching 4 orders of magnitude [2]. In addition, we observe collective oscillations of the condensate [3] which can be used to understand its intriguing superfluid and thermodynamic properties. I will conclude with our ongoing work towards understanding the behaviour of the condensates at even higher densities, where the fermionic nature of the excitons in the polariton cannot be neglected, and a crossover towards a type of Bardeen–Cooper–Schrieffer condensate is predicted to occur [4]. This regime is achievable under pulsed excitation

[cite the single-shot paper], but is short-lived. Therefore, time-resolved spectroscopy beyond the streak camera resolution would be useful in probing its unknown properties.

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[4] Byrnes et al, BCS Wave-Function Approach to the BEC-BCS Crossover of Exciton-Polariton Condensates, *Phys. Rev. Lett.* **105**, 186402 (2010)

# Talk Title: 2D Electronic Spectroscopy of TIPS-pentacene and Development of a Flexible Data Analysis Framework

**Speaker name:** Jessica de la Perrelle



**Jessica de la Perrelle** is currently studying a Master of Philosophy under A/Prof. Tak Kee at the University of Adelaide. Her research centres around the study of organic semiconductors using 2D electronic spectroscopy.

## Abstract:

2-dimensional electronic spectroscopy (2DES) is an ultrafast pump-probe spectroscopy with a number of advantages over similar techniques, such as transient absorption. 2DES uses short pulses (13 fs duration) to achieve high resolution in the waiting time between the arrival of the pump and probe pulses. In addition, both the pump and probe include a continuum of energies, in contrast to transient absorption where typically only the probe may be a continuum. As a result, 2DES experiments have high resolution in waiting time, probe energy and pump energy, making this spectroscopic technique ideal for studying complex systems that undergo ultrafast processes. An example of such a system is polycrystalline pentacene, which undergoes the exciton downconversion process singlet fission within 100 fs of excitation.<sup>1</sup>

The data obtained from 2D spectrometers is typically a large 3-dimensional data set that contains detailed information about the system: the position of 2D peaks gives the energies of the electronic or vibronic transitions of the system in both the ground and excited states; cross peaks indicate correlation between two transitions or chromophores; peak line shapes are influenced by spectral diffusion; and oscillations during waiting time can arise from vibrational or electronic coherence. Interpreting such complex behaviour is made easier by a variety of signal processing techniques as well as quantum mechanical models. Because of the rarity of these instruments and the diversity of the systems that they have been used to study, there is no universal analysis method for interpreting 2DES data, however there have been a number of new methods developed within the last 5 years.<sup>2-4</sup>

We suggest a flexible analysis framework that can be broadly applied to 2DES data. The framework begins with model-independent techniques: centre line slope analysis<sup>2</sup> for peak line shapes; Fourier transforms along the waiting time axis to extract frequencies associated with coherences; and time-frequency transforms<sup>3</sup> in the case of

oscillatory features with significant changes in amplitude over waiting time. The data may then be fit to a model of suitable complexity, ranging from simple multi-exponentials to a detailed kinetic scheme. Additionally, oscillatory features identified from Fourier transforms may be added into the model as complex exponentials, allowing simultaneous global fitting of coherence frequencies, dephasing rates and kinetic rate constants.<sup>4</sup>

As an example, we performed 2DES experiments on a dilute solution of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-Pn). The analysis framework has been used to identify the decay associated spectrum that corresponds to the S<sub>1</sub> state of TIPS-Pn. Two coherence frequencies and their coherence associated spectra were also identified (800 and 1037 cm<sup>-1</sup>). This solution-phase experiment enables an understanding of how TIPS-Pn behaves in isolation, and lays the groundwork for investigating the dependence of singlet fission on disorder in crystalline and amorphous TIPS-Pn nanoparticles. This system is also one of the first to be investigated using our newly-built instrument, which features a novel method of controlling delay times between pulses.<sup>5</sup>

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# Shining a Light on Conjugated Compounds and Complexes

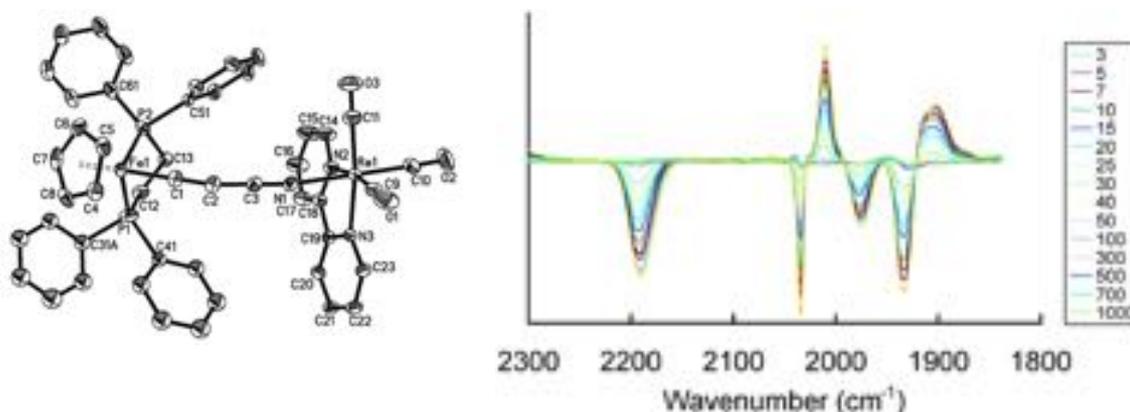
**Speaker name:** Prof. Paul J. Low



**Paul Low** was appointed Professor of Chemistry at the University of Western Australia in 2013, relocating from the Department of Chemistry, Durham University. Paul's work concerns a broad spectrum of activity from synthetic organometallic chemistry, mixed-valence chemistry and electron transfer processes, and molecular electronics. He has held major research fellowships from the UK EPSRC and Australia's ARC, and was awarded a Wilhelm Bessel Research Award (2015) from the Alexander von Humboldt Foundation in recognition of his work in these areas.

## Abstract:

Molecular compounds with  $\pi$ -conjugated electronic structures offer a fascinating array of optoelectronic properties that can be exploited to develop a wide range of molecular and polymeric materials, whilst also offering insight into fundamental aspects of intramolecular charge transfer processes and the electronic structures and dynamics of excited states. This presentation will discuss the use of time-resolved Raman and IR spectroscopies, transient absorption spectroscopy and allied methods including cavity ring down and fluorescence spectroscopies to probe molecular dynamics and electronic structures of a series of organic compounds and organometallic complexes.



*Figure 1* The crystallographically determined structure of the heterometallic cation  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^+$  (as the  $\text{PF}_6^-$  salt) difference ps-TRIR (490 nm excitation); the legend shows the time delay (ps) for each acquisition.

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## **Talk Title:** Ultrafast control of electrons in materials with the electric field of light

**Speaker name:** Dr. Agustin Schiffrin



**Agustin Schiffrin** is currently a Senior Lecturer at Monash University, ARC Future Fellow and Chief Investigator of the ARC Centre of Excellence in Future Low-Energy Electronics Technologies. He obtained his M.Sc. in Physics in 2003 from the Ecole Polytechnique Fédérale de Lausanne. In 2008 he obtained his PhD in Physical Chemistry from the University of British Columbia. After Postdoctoral Research Fellowships at the Max Planck Institute of Quantum Optics, Garching, and the Quantum Matter Institute of the University of British Columbia, he joined Monash in 2015 as a Lecturer. His research interests are in the fields of low-dimensional nanomaterials, surface nanophysics and ultrafast electron dynamics in the solid-state.

### **Abstract:**

Electronics technologies rely on the control of electric current in solid-state devices. The faster currents can be turned on and off, and the lower the energy dissipated in the process, the higher the performance and efficiency of the system. Here, I review the feasibility of generating and controlling electric current in semiconductors and insulators with few-cycle optical waveforms, within a single cycle of light, and on a timescale of  $\sim 1$  femtosecond.

In the case of an insulator, an intense few-cycle optical pulse can transform the material into a state of highly increased polarizability (and hence conductivity) – reversibly and free from breakdown – allowing directly measurable electric currents to be driven, directed and switched by the instantaneous light electric field. This phenomenon is attributed to optical-field-induced Wannier-Stark shifts of electronic levels, resulting in adiabatic, highly nonlinear Zener-like interband tunneling.

In the case of a semiconductor, similar ultrafast all-optical generation and control of electric current can be realised, but at lower optical field strengths, and with a lower degree of nonlinearity (due to the smaller bandgap-to-photon energy ratio). This effect can be explained within a non-tunneling scenario, as the result of interference between multiphoton excitation pathways in the presence of field-induced intraband carrier motion.

This approach demonstrates the capability of controlling the electrical conductivity of materials with the electric field of light, reversibly, and on ultrafast optical timescales,

giving rise to out-of-equilibrium electronic properties that can fundamentally differ from those in the ground state.

## **Talk Title:** The Ultrafast (and a bit slower) characterisation of singlet fission and triplets using absorption and photoluminescence

**Speaker name:** Shyamal Prasad



**Shyamal Prasad** has an interest in applying spectroscopic techniques to understand the photophysics of material systems and has experience in ultrafast spectroscopy and organic photovoltaics. Currently working at the ARC Centre of Excellence in Exciton Science at the UNSW node on a project that involves using excitonic materials to improve the performance of silicon solar cells. Previously studied at Victoria University of Wellington understanding the photophysics of organic solar cells.

### **Abstract :**

The high external quantum efficiency (EQE), low cost, and widespread adoption of silicon solar cells provide a convenient platform from which to apply excitonic light management to improve performance. By harnessing singlet fission, to split photons that have more than twice the energy of the silicon bandgap, and triplet fusion (also known as triplet-triplet upconversion), to combine two photons from below the silicon bandgap the theoretical efficiency limits are increased from 25% to above 46%.<sup>1</sup>

The process of exciton generation to eventual injection into silicon will involve multiple competing pathways, therefore following the photo-generated states through the materials systems will provide valuable insight. Because to process involves both singlet and longer-lived triplet states lifetimes will cover the timescales from picoseconds out to milliseconds. Towards this goal, a summary of the characterisation technique available in the Schmidt laboratory at UNSW and a few recent measurements will be presented.

In particular; temperature-dependent singlet fission in TIPS-Tc characterised by microsecond photoluminescence and time-resolved transient absorption. Calculations of intersystem crossing yield in novel Bodily containing complexes. And, finally, with the possibility of becoming ultrafast, steady-state magnetic field measurement on triplet fission materials.

**References:** [1]Tayebjee, M. J. Y.; Gray-Weale, A. A.; Schmidt, T. W. *J. Phys. Chem. Lett.*, **2012**, *3*, 2749-2754.

## Talk Title: Femtosecond covariance spectroscopy

Speaker name: Dr. Jonathan Tollerud



**Jonathan Tollerud** is currently a beam line scientist working at Swinburne University in the Ultrafast Micro-Spectroscopy Lab. During his PhD at Swinburne, he developed novel selective multidimensional spectroscopy techniques, implemented the first coherent multidimensional spectroscopy apparatus in Australia, and used it to for studies of coherent interactions in a diverse range of systems including semiconductor quantum wells, high-T<sub>c</sub> cuprate superconductors, and molecular systems.

Before returning to Swinburne, he did a post doc at the T-REX beamline housed at the FERMI FEL in Trieste Italy, where he helped to develop covariance-based spectroscopic tools for nonlinear femtosecond measurements.

### Abstract:

The broad success of ultrafast nonlinear spectroscopy in both investigations of fundamental physics and application driven measurements of material properties have relied heavily on pulse-to-pulse consistency and minimization of noise, which has led to massive efforts towards engineering robust and stable lasers and also heavily informed the design of optical layouts. In contrast, covariance-based techniques used in other fields (e.g. photoionization electron spectroscopy and mass spectrometry) have shown that higher order statistical tools provide access to a wealth of information that would be considered noise in a mean-value based measurement. Nonlinear femtosecond spectroscopy is a good candidate for covariance-based measurements because the nonlinear nature of the interaction leads to comparatively large changes in the measured signal from small changes in the input. In this context, noise in a femtosecond laser is not necessarily a liability to be mitigated but can act as a unique and powerful asset.

In this talk I will describe how we have recently applied such a scheme to measure a stimulated Raman scattering spectrum in  $\alpha$ -quartz<sup>1</sup>. The nonlinear Raman process launched by a noisy ultrafast pulse in the sample encodes correlations between different spectral components, which can then be extracted by measuring spectrally resolved covariance. I will show how this signal can be enhanced with uncorrelated stochastic fluctuations in the pulse spectrum.

Finally, I will describe how this scheme could in turn provide richer information compared with the standard nonlinear femtosecond techniques that are based on averages over many repetitions with well-behaved laser pulses, while requiring a much

simpler experimental setup and less stringent requirements on the source laser. These proof-of-principle results also suggest that covariance-based schemes will improve the applicability of femtosecond nonlinear spectroscopy in wavelength ranges where stable, transform-limited pulses are not available, such as X-ray free-electron lasers which naturally have spectrally noisy pulses ideally suited for this approach.

### **References:**

[1] Jonathan Owen Tollerud, Giorgia Sparapassi, Angela Montanaro, Shahaf Asban, Filippo Glerean, Francesca Giusti, Alexandre Marciniak, George Kourousias, Fulvio Billè, Federico Cilento, Shaul Mukamel, and Daniele Fausti. Femtosecond covariance spectroscopy. *PNAS*, 116 (12), 5383-5386, 2019.

## Talk Title: Nanoscale Capacitor-like Charge Build-up in an Organic Bulk Heterojunction



**Speaker name:** Dr. Kyra Schwarz

**Kyra Schwarz** is a postdoctoral researcher at Princeton University. Originally from Adelaide, South Australia, she undertook her undergraduate studies at the University of Adelaide. She completed a PhD at the University of Melbourne investigating light–matter interactions, focussing on the impact of nanoscale morphological control on light-harvesting in emerging solar cell materials. Kyra joined the Scholes group at Princeton University in 2017, where she works on understanding and utilizing design principles—including those inspired by nature—for directing and regulating light-initiated energy flows in a variety of systems.

**Abstract:** Organic photovoltaic (OPV) efficiencies continue to rise, raising their prospects for solar energy conversion. However, researchers have long considered how to suppress the loss of free carriers by recombination—poor diffusion and significant Coulombic attraction can cause electrons and holes to encounter each other at interfaces close to where they were photogenerated. Our recent investigations have uncovered that donor–acceptor bulk heterojunction morphology can go beyond its established role in generating excitons and charges, and can act as a network of tiny capacitors, where adjacent free charges are held away from the interfaces of nanoscale domains. Using femtosecond transient spectroscopies, we report the nanosecond grow-in of a large transient Stark effect, caused by nanoscale electric fields of  $\sim 487$  kV/cm between photogenerated free carriers in the device active layer.[1] We find that particular morphologies of the active layer lead to an energetic cascade for charge carriers, suppressing pathways to recombination, which is  $\sim 2000$  times less than predicted by Langevin theory. This in turn leads to the build-up of electric charge in donor and acceptor domains—away from the interface—resistant to bimolecular recombination. Interestingly, this signal is only experimentally obvious in thick films, due to the different scaling of electro-absorption and photo-induced absorption signals in transient absorption spectroscopy. Rather than inhibiting device performance, we show that devices up to 600 nm thick maintain efficiencies of  $>8\%$  because domains can afford much higher carrier densities. The particular nanoscale morphologies that cause the capacitive charging of domains will be discussed, as will their potential in keeping attracted carriers at ‘arm’s length’, protecting them from bimolecular recombination.

### References:

[1] Kyra N. Schwarz, Gregory D. Scholes, David J Jones, and Kenneth P. Ghiggino et al., Reduced Recombination and Capacitor-like Charge Buildup in an Organic Heterojunction. *JACS*, **Just Accepted Manuscript**. DOI: 10.1021/jacs.9b12526

## **Talk Title:** Tracking energy and electron transfer in biological systems using two-dimensional electronic spectroscopy

**Speaker name:** Egle Bukarte



**Egle Bukarte** is currently a PhD student in Lund University, Sweden, prof. Donatas Zigmantas two-dimensional electronic spectroscopy group. In 2019 she was granted an Optics and Photonics Education Scholarship by SPIE, for potential contributions to the field of optics, photonics or related field. She is also a member of The International Society of Photosynthesis Research; The Chemical Society in Lund; The Lund Laser Center and Lund Laser Center – Female Research Network.

### **Abstract:**

Two-dimensional electronic spectroscopy is a unique and very powerful tool for probing ultrafast processes in light-sensitive systems [1,2]. During the experiment, three laser pulses interact with the system - the first two collectively acting as a pump and the third one probing the sample absorption [3]. Varying the times between three pulses, an entire evolution of molecular excitation can be recorded, therefore, a vast amount of information is obtained from only a single experiment. This information includes couplings between optical transitions, relaxation lifetimes, excitation energy transfer rates and evidences about charge transfer.

In this contribution, a broadband two-dimensional electronic spectroscopy experiments on bacterial Reaction centres will be presented. Responsible for initial charge separation steps of photosynthesis, Reaction centres are systems where both processes of excitation energy transfer and electron transfer are present. Following this example, ways to distinguish between two transfer processes (energy vs. electron) will be discussed.

### **References:**

- [1] J. Dostál, J. Pšenčík, D. Zigmantas, In situ mapping of the energy flow through the entire photosynthetic apparatus. *Nat. Chem.* 8, 705–710 (2016).
- [2] D. Paleček, P. Edlund, S. Westenhoff, D. Zigmantas, Quantum coherence as a witness of vibronically hot energy transfer in bacterial reaction center. *Sci. Adv.* 3, 9 (2017).
- [3] M. Cho, Two-dimensional optical spectroscopy (2009).

## **Talk Title:** Using visible transient absorption and excitons to measure phonon kinetics

**Speaker name:** Dr Laszlo Frazer



**Laszlo Frazer** is currently a Research Fellow at the Centre of Excellence in Exciton Science at Monash University. He was previously at UNSW and before that at the Energy Frontier Research Centre for Computational Design of Functional Layered Materials at Temple University. His PhD is from Northwestern University, where he was a Ryan Nanoscience fellow. Dr. Frazer won the Exciton Science Publication Prize in 2017.

### **Abstract:**

Electron-phonon scattering is the most important energy loss mechanism in all electronic devices which are not superconducting. The emission of phonons from electron-hole plasma is the primary limit on the efficiency of photovoltaic devices operating above the bandgap. In cuprous oxide ( $\text{Cu}_2\text{O}$ ) there is no luminescence from electron-hole plasma. Therefore, we searched for optical phonons emitted by energetic charge carriers using phonon-to-exciton upconversion transitions. We found 14 meV phonons with a lifetime of  $0.916 \pm 0.008$  ps and 79 meV phonons that are longer lived and overrepresented. It is surprising that the higher energy phonon has a longer lifetime.

### **References:**

[1] Frazer, L., Schaller, R. D., Chang, K. B., Chernatynskiy, A., & Poepelmeier, K. R. (2017). Seeing the invisible plasma with transient phonons in cuprous oxide. *Physical Chemistry Chemical Physics*, 19(2), 1151-1157.

## Talk Title: Ultrafast Transient Absorption Microscopy

Speaker name: Prof. Trevor Smith



**Trevor Smith** leads the Ultrafast and Microspectroscopy Laboratories in the School of Chemistry at the University of Melbourne. He has worked with Profs. David Phillips and Garry Rumbles at Imperial College, London and Hiroshi Masuhara in Osaka University. He is currently a CI in the ARC Centre of Excellence in Exciton Science, where the research activities of his group focus on coupling time-resolved laser spectroscopy and optical microscopy techniques for studying advanced materials including semiconductor nanoparticles and polymers.

### Abstract:

To comprehensively study thin films of advanced materials requires sophisticated optical imaging methods capable of providing both high (<100 nm) spatial and temporal (<ns) resolution.<sup>1</sup> We are developing time-resolved structured illumination microscopy (SIM)<sup>2</sup> and stimulated emission depletion (STED) microscopy methods to provide high spatial resolution with picosecond temporal information. However, the temporal resolution achievable with these methods is insufficient to fully probe the dynamics within materials of interest in areas such as photovoltaic devices.

In this talk I will summarise some of the time-resolved optical microscopy techniques we have developed, and are currently developing, to investigate thin films of organic photovoltaic materials, perovskites and semiconductor nanomaterials probing their spatio-temporal information. I will outline our femtosecond transient absorption microscopy instrument and discuss future developments.

### References:

- [1] X. Hao, L.J. McKimmie and T.A. Smith, “Spatial Fluorescence Inhomogeneities in Light Emitting Conjugated Polymer Films”, *J. Phys. Chem. Lett.* 2, 1520–1525 (2011)
- [2] X. Hao, L.M. Hirvonen and T.A. Smith, “Nanomorphology of polythiophene-fullerene bulk-heterojunction films investigated by structured illumination optical imaging and time-resolved confocal microscopy”, *Meth. Appl. Fluor.* 1, 015004/1-8 (2013)