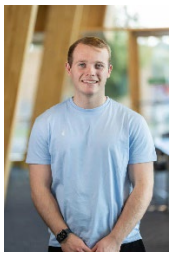
UCD School of Chemistry – BOC Gases Graduate Research Awards – Joint Winners 2024/25



Ruairi Crawford

Research Title: Flow Photochemistry for the Sustainable Synthesis of Bioactive Entities

Supervisor: Professor Marcus Baumann

In Ruairi's PhD research, azides were identified the ideal precursors to access structurally diverse N-containing heterocycles. Azides can easily extrude N2 by either photochemical or thermal conditions, to produce reactive nitrene species. Despite their synthetic utility, numerous safety concerns, such as their explosive nature and associated toxicity limit their use, especially on scale both in academia and industry. However, flow chemistry has demonstrated how "forbidden chemistries" can be performed effectively and safely due to superior control offered by miniaturized flow systems enabling the safe processing of light- and heat sensitive reagents. Furthermore, the associated enclosed environment and reaction automation minimizes the operator's contact time with hazardous reagents. Finally, a paradigm shift has been seen in recent years for the initiation of chemical reactions by more sustainable approaches. The combination of inexpensive and traceless photons as both an energy source and as reagents with uniform irradiation and facile scalability of flow photochemistry offers a unique opportunity to develop more efficient and sustainable chemical processes.

Publications:

Consecutive photochemical reactions enabled by a dual flow reactor coil strategy, **R. Crawford,** M. Di Filippo, D. Guthrie and M. Baumann, *Chem. Commun***.** 2022, 58, 95, 13274-13277, DOI: 10.1039/D2CC05601A.

Telescoped Flow Synthesis of Azacyclic Scaffolds Exploiting the Chromoselective Photolysis of Vinyl Azides and Azirines, **R. Crawford** and M. Baumann, *Chem. Eur. J.*, e202401491, DOI: 10.1002/chem.202401491

Recent Advances Exploiting Reactive Intermediates Generated via Continuous Flow Chemistry, A. Bonner, P. Naik, **R. Crawford** and M. Baumann, *Curr. Opin. Green Sustain. Chem***.** 2024, 100907

Direct Photochemical Synthesis of Substituted Benzo[*b*]fluorenes, **R. Crawford**, Y. Ortin, B. Twamley and M. Baumann, *Org. Lett*. 2024, 26, 48, 10364-10368, DOI: 10.1021/acs.orglett.4c03978

Continuous Flow Technology Enabling Photochemistry, **R. Crawford** and M. Baumann, *Adv. Synth, Catal., 2025, ASAP,* DOI: 10.1002/adsc.202500133

Dominik Duleba

Research Title: *From fundamentals to applications: harnessing digital chemistry for nanopore sensor development*

Supervisor: Associate Professor Robert Johnson

Dominik's thesis seeks to explore how digital chemistry can be used in conjunction with experiments to further the understanding, development, and optimization of low technological readiness level ionic devices, such as ion current rectifying nanopore sensors. The development of these sensors is of great interest with applications in the medical, environmental, and forensic fields, however, the general fundamental understanding gained during the study of these devices can also advance the development of non-sensor ionic devices, such as salinity gradient energy harvesters and ionic photovoltaic cells. This project has been highly successful and resulted in 14 publications (two additional publications under peer-review) in high impact journals, such as Electrochimica Acta and Physical Chemistry Chemical Physics. The results of this work have also been presented at 10 conferences and was awarded the best poster prize at the Iontronics Faraday Discussions in Edinburgh.

Publications:

Duleba, D., Martínez-Aviñó, A., Revenko, A., & Johnson, R. P. (2025). Understanding Sensitivity in Nanoscale Sensing Devices. *ACS Measurement Science Au*.

Duleba, D., Dutta, P., Denuga, S., & Johnson, R. P. (2022). Effect of electrolyte concentration and pore size on ion current rectification inversion. *ACS Measurement Science Au*, *2*(3), 271-277.

Farrell, E. B., **Duleba**, D., & Johnson, R. P. (2022). Aprotic solvent accumulation amplifies ion current rectification in conical nanopores. *The Journal of Physical Chemistry B*, *126*(30), 5689-5694.

Duleba, D., & Johnson, R. P. (2022). Sensing with ion current rectifying solid-state nanopores. *Current Opinion in Electrochemistry*, *34*, 100989.

Duleba, D., & Johnson, R. P. (2024). Proton enrichment and surface charge dynamics in pH-responsive nanopipettes. *Electrochimica Acta*, *479*, 143838.

Almohammed, S., Finlay, A., **Duleba**, D., Cosgrave, S., Johnson, R., Rodriguez, B. J., & Rice, J. H. (2024). Piezoelectric Peptide Nanotube Substrate Sensors Activated through Sound Wave Energy. *ACS Materials Letters*, *6*(5), 1863-1869.

Farrell, E. B., McNeill, F., Weiss, A., **Duleba**, D., Guiry, P. J., & Johnson, R. P. (2024). The Detection of Trace Metal Contaminants in Organic Products Using Ion Current Rectifying Quartz Nanopipettes. *Analytical Chemistry*, *96*(15), 6055-6064.

Kidalov, V. V., Revenko, A. S., **Duleba**, D., Redko, R. A., Assmann, M., Gudimenko, A. I., & Johnson, R. P. (2024). Investigation of Mechanical Stresses in SiC/Porous-Si Heterostructure. *ECS Journal of Solid State Science and Technology*, *13*(11), 114003.

Duleba, D., Denuga, S., & Johnson, R. P. (2024). Reproducibility and stability of silane layers in nanoconfined electrochemical systems. *Physical Chemistry Chemical Physics*, *26*(21), 15452-15460.

Denuga, S., **Duleba**, D., Dutta, P., Macori, G., Corrigan, D. K., Fanning, S., & Johnson, R. P. (2024). Aptamer-functionalized nanopipettes: a promising approach for viral fragment detection via ion current rectification. *Sensors & Diagnostics*, *3*(6), 1068-1075.

Denuga, S., Dutta, P., **Duleba**, D., Macori, G., Fanning, S., & Johnson, R. P. (2025). Tuning Ion Current Rectifying Nanopipettes for Sensitive Detection of Methicillin-Resistant Staphylococcus aureus. *Analytical Chemistry*.

Gan, R., **Duleba**, D., Johnson, R. P., & Rice, J. H. (2025). p-Type Organic Semiconductor–Metal Nanoparticle Hybrid Film for the Enhancement of Raman and Fluorescence Detection. *The Journal of Physical Chemistry C*.

Farrell, E. B., McNeill, F., **Duleba**, D., Martínez-Aviño, A., Guiry, P. J., & Johnson, R. P. (2025). Determination of Enantiomeric Excess in Confined Aprotic Solvent. *ACS Electrochemistry*.

Alotaibi, A. F., Gan, R., Kume, E., **Duleba**, D., Alanazi, A., Finlay, A. Johnson, R. P., Rice, J. H. Flexible nanoimprinted substrate integrating piezoelectric potential and photonic-plasmonic resonances (2025). *Nanoscale Advances*