PAUL O’BRIEN

22 January 1954 — 16 October 2018

Elected FRS 2013

BY DAVID J. LEWIS¹,* AND RICHARD E. P. WINPENNY²,†

¹Department of Materials, The University of Manchester, Manchester M13 9PL, UK
²Department of Chemistry, The University of Manchester, Manchester M13 9PL, UK

Paul O’Brien, known affectionately as ‘POB’, was one of the most imaginative and creative materials chemists of his generation. He brought a deep understanding and knowledge of classical coordination chemistry to bear on routes to thin films and nanoparticles of technologically important materials, particularly metal chalcogenides. His development of molecular precursor chemistry as a method to produce very high quality materials safely, inexpensively and on a large scale laid the foundations for the successful technological exploitation of quantum dots. Paul had a compendious knowledge of science, particularly inorganic chemistry, and was passionate about the exploitation of science and engineering to improve society, both in the UK and around the world, most notably in Africa. He was a wonderful raconteur, and a great counsellor to his many friends, and a source of endless jokes (many of them bad). His greatest passion was science, yet somehow he also found time for other interests, including reading, hill-walking and camping, theatre and football. Paul was diagnosed with glioblastoma multiforme on his sixty-fourth birthday in January 2018, and this led to his retirement in July 2018 and his appointment as Emeritus Professor at the University of Manchester. He approached his illness with his usual scientific curiosity and optimism. He passed away peacefully with his beloved wife Kym by his side.

EARLY LIFE AND INTERESTS

Paul O’Brien (POB) was born in Ancoats, Manchester, in 1954, the son of Thomas O’Brien, a centre lathe turner at Ferranti, and his wife, Maureen (née Graham), who worked as a clerk.

*Email: david.lewis-4@manchester.ac.uk
†Email: richard.winpenny@manchester.ac.uk
His first home was the back bedroom in his grandparents’ home, but in 1955 Thomas, Maureen and baby Paul moved to a newly built council house on Coronation Road in Failsworth. Paul was an only child, but with a very large extended family, including fourteen uncles and aunts. Paul remembered both parents as highly intelligent but, due to family circumstances, neither had any formal education beyond the age of fourteen.

Paul attended the local primary school, Our Lady of the Immaculate Conception, where his first teacher, Miss Dwyer, described him as a ‘brick of common sense’. After Paul passed the 11-plus, his education continued at Cardinal Langley Grammar School in Middleton, Greater Manchester. He immediately excelled at science and decided at age eleven to become a scientist, despite having no role models to follow and no idea how to achieve his goal. He took his examinations early and was offered a place to read chemistry at the University of East Anglia. As he was only seventeen, he declined the offer and remained in the Sixth-Form at Cardinal Langley for a further year, during which time he studied biology, engaged in political debate, read widely in classical literature and poetry and began his life-long passion for theatre.

From an early age Paul developed a huge interest in amateur photography, starting with his childhood Box Brownie, even developing and printing his own film. He was an excellent photographer, often called upon to record family events, and at a later date became a semi-official photographer for the International Conference on Coordination Chemistry series (producing an excessive number of photographs of hairy-legged coordination-chemists in unfortunate shorts). Much later, Paul enjoyed the opportunity to photograph wildlife when on safari in Africa.

**Undergraduate days at the University of Liverpool**

Paul started as an undergraduate in the Department of Chemistry at the University of Liverpool in October 1972. At that time, the Department, reflecting its history, was divided into two parts:
Inorganic, Physical and Industrial chemistry (IPI), based in the Donnan Laboratories, and Organic Chemistry, based in the Robert Robinson Laboratories. The degree course was typical for the early 1970s. In years one and two students attended lectures in inorganic, organic and physical chemistry and in year three the students selected courses and final year project work in either IPI or Organic. The students were also required to study a second area of science in years one and two, and Paul chose physics. From his first year Paul displayed a clear enthusiasm for inorganic chemistry and a distinct lack of enthusiasm for his chosen second science subject; physics for chemists. Dr Mike Holmes, a contemporary at Liverpool, recalls that Paul found the concepts of experimental error, feedback loops and gain in solid state operational amplifiers particularly uninteresting. However, Paul fully embraced university life, joining many societies and regularly attending classical concerts given by Liverpool Philharmonic Orchestra, the latter developing his life-long interest in classical music.

In his third year at Liverpool, Paul had the opportunity to focus on inorganic chemistry by taking the IPI courses, and pursuing a final year undergraduate project supervised by Dr David Nicholls, the popular author of textbooks on coordination chemistry. He successfully completed his undergraduate studies in chemistry in the summary of 1975 with an upper second-class honours degree.

Paul remained very grateful to Liverpool throughout his life and was a strong supporter of the university. Among his many prizes, he was awarded the Potts Medal for chemistry by the University of Liverpool in 2001, and was absolutely delighted to receive this recognition as a distinguished alumni. The university subsequently awarded him an honorary degree in 2013 (figure 2).

**POSTGRADUATE STUDIES IN CARDIFF**

To the surprise of his friends Paul decided not to stay at Liverpool to study for a PhD, but rather to move to University College Cardiff to study the binding of metals such as copper and zinc to amino acids. These studies were pursued under the guidance of Professor R. D. Gillard and inspired a life-long interest in bio-inorganic chemistry. The research involved detailed investigations of the species present, considering the isomers of the amino acids bound and how binding to copper might cause racemization, which could be followed by the degree of optical rotation of light (1)* (figure 3). His PhD thesis, entitled ‘Catalysis and racemisation of amino acids’, was very successful, leading to seven papers from 1977 to 1980. The studies involved understanding the binding of metal ions to ubiquitous biological species rather than focusing on the synthesis of refractory target molecules. Characterization was always by spectroscopy rather than by X-ray diffraction.

Working on the bench to Paul’s right was Júlio Pedrosa de Jesus, who was at the beginning of an equally distinguished career. Later Júlio held senior roles in higher education in his native Portugal and is now involved in quality assurance in higher education throughout Europe. The friendship that developed was particularly important to Paul. At that time Júlio was beginning work on rhodium(III) coordination chemistry while Paul was embarking on his studies of optical activity of copper(II) complexes. Júlio recalls that ‘from the start we had a very enjoyable and fruitful exchange of views on scientific issues related with our work

* Numbers in this form refer to the Short Bibliography at the end of the memoir.
and possible developments. It was from this open and frank relationship with Paul that I became interested in starting work on the glucose tolerance factor, which I developed after coming back to Aveiro, in Portugal. This front of research was the basis of the PhD of a research assistant, with Paul being co-supervisor of the PhD’. Later, Júlio encouraged a junior colleague, Tito Trindade, to work with Paul at Imperial College on a project on nanomaterials; this project generated the first patents that led to Paul’s spin-out company Nanoco (vide infra). Júlio was also instrumental in obtaining an honorary doctorate for Paul from the University of Aveiro in 2015.

Paul’s PhD studies also led to a fascination with modelling the solution speciation of metal ions, which later fed into his research on the mechanisms by which nanoparticles and nanocrystals form. The studies were very much in the area of fundamental coordination chemistry and later Paul played a very active role in the International Conference in
Coordination Chemistry (ICCC), even after his main research line had moved towards materials science. His involvement with the ICCC also led to further great friendships with Professor Chris Orvig (University of British Columbia), Professor Ekke Hahn (Universität Münster) and Professor Will Rees (Los Alamos National Laboratory) (figure 4). Chris noticed two of Paul’s major character traits: ‘I marvelled at POB’s optimism and enthusiastic persuasive skills, regardless of the challenges, particularly in his early days at Manchester stickhandling (as we say in ice hockey) the infamous merger of Chemistry at UMIST [University of Manchester Institute of Science and Technology] and VUM [Victoria University of Manchester].’

At Cardiff Paul was an enthusiastic member of the mountaineering club which contributed to the most important event in Paul’s life. In the autumn of 1977, during the final year of his PhD, he met Kym for the first time at a club gathering (figure 5). Soon after they were dating and within weeks they were engaged. Paul had been applying for post-doctoral fellowships, but was now reluctant to leave Kym. As an alternative, Bob Gillard suggested Paul apply for a lectureship at Chelsea College before he submitted his PhD thesis. Perhaps unexpectedly, but thankfully, Paul succeeded at the interview.
First faculty position at Chelsea College, London (1978–1984)

Paul obtained a position at Chelsea College, London, directly from his PhD and at the tender age of 24. The chief technician had a nameplate made for Paul’s office which read ‘Paul O’Brien, BSc, BC’, where BC stood for ‘Boy Chemist’. (Paul had several nicknames and two- and three-letter abbreviations; he was almost always called ‘POB’, which is how he signed emails.) Friendships were forged with Jack Barrett, Peter Nunn, Sid Ross and others.

He returned to Cardiff in July 1979, where he and Kym graduated at the same degree ceremony. A few weeks later they were married in Porthcawl and bought their first home in Balham, refurbishing the dilapidated maisonette that had become theirs, helped by chemistry colleagues who replumbed the gas supply. Surplus college furniture found its way to Balham in the departmental van.

Work at Chelsea College was largely dedicated to bio-inorganic chemistry, including the binding of chromium(III) by amino acids and the observation of the formation of chromium(V) from the reduction of chromium(VI) by glutathione (2). During his time at Chelsea Paul secured a NATO research fellowship, which enabled him to spend summers with Professor Dwight Sweigart at Brown University. Here they studied metalloporphyrins, specifically focusing on how hydrogen-bonding of coordinated imidazoles influenced redox
potentials (3). Paul regularly returned to Brown throughout his life, becoming firm friends with Professor John O. Edwards and Professor Phil Rieger and their families. These visits also led to a love of the northeast of the USA; in later life Paul and Kym purchased a property in Maine and holidayed there annually.

**QUEEN MARY AND WESTFIELD COLLEGE, LONDON (1984–1995)**

In 1984 the University of London restructured, as universities are prone to do in the UK, and Paul moved to Queen Mary and Westfield College (QMWC), located in the East End of London. The major thrust of his research during the 1980s was into chromium toxicity, for example studying chromium(III) in erythrocytes and observing that chromium(V) complexes can generate hydroxyl radicals, and to the observation of damage to DNA during the reduction of chromium(VI) by glutathione (5). His chromium work led him to being one of three authors of the chromium chapter of the first edition of the authoritative *Comprehensive coordination chemistry*, published in 1987 (4). Paul also researched neurotoxicity in collaboration with a former colleague at Chelsea College, Dr Peter Nunn, who had moved to King’s College, London.

A key event in Paul’s professional career arose on moving to QMWC: he came ‘into the orbit of Professor Don Bradley FRS’, who, Paul recalled, had a group doing ‘materials things’. In Paul’s own words, Bradley ‘just cut out a corner and said “why don’t you look at that...
corner” — and that’s the corner I’ve worked on, and a bit wider, for the rest of my career’. It was typically gracious of Paul that he gave so much credit to Bradley; Paul had sufficient belief in his own worth to accept that no-one achieves much alone.

Professor Peter P. Edwards FRS had just started an independent career in Cambridge when he visited QMWC in the mid 1980s. Peter recalls Don and Paul being fascinated by not only the science of metal–ammonia (and other) solutions, but also the experimental details of how his group handled high vacuum and distillation techniques—particularly with the highly aggressive alkali metal, caesium. He recalls: ‘The level of kindness, generosity and interest in our work from both Don and Paul was truly overwhelming and, as you can imagine, most welcome gestures as I started to put my research group together at Cambridge.’ This began a life-long friendship between POB and Peter.

The materials corner Don Bradley suggested Paul look at was to examine precursors for thin films particularly of the metal chalcogenides. Paul’s first papers in this area appeared in 1989, which detailed the growth of highly orientated thin films of cadmium- and cadmium-zinc-sulfide by metal–organic chemical vapour deposition (MOCVD) using diethyldithiocarbamates (6). The key insight was that the chalcogenide can be introduced as part of an organic ligand that binds to the metal of interest. Early studies of preparation of materials from simple precursors also examined the use of basic zinc acetate as a route to ZnO.

This area of Paul’s research grew rapidly. The work also benefited from the outstanding crystallographic expertise of Professor Mike Hursthouse at QMWC; for the first time, POB’s papers contained X-ray single crystal structures. Paul’s approach was that of a coordination chemist: try any ligand that could contain the elements required in the final material. For deposition of II/VI materials, the POB group examined multiple nitrogen containing adducts of dimethylzinc, or thiolate complexes of cadmium. The chemistry revolved around dithiocarbamates and diselenocarbamates where the chalcogenide (S or Se) is included as part of the ligand, and the thermal decomposition of the precursors can be controlled by variation of alkyl groups. For example, the heteroleptic complexes [MeM(S2CNEt2)]2 (M = Zn or Cd) could be used to produce the corresponding metal sulfides (7). ZnSe could be made from a similar precursor but using diethyldiselenocarbamate. The alkyl group could also be varied to neo-pentyl or t-butyl to tune either decomposition temperature or solubility.

Cross-fertilization of ideas is very clear here, as dithiocarbamates—previously studied by Paul in the context of neurotoxicity—were now studied as ligands for single source metal–organic precursors. The materials targeted at this stage, which were generally thin films, were prepared by MOCVD.

This work showed that precisely defined molecular chemical precursors could be used to prepare a wide range of important functional materials as either thin films or isolated particles with critical dimensions of the order of nanometres. Relatively stable, safe and easy to handle compounds could be used to deposit and or prepare high quality functional materials. Paul’s background in reaction mechanisms, dating back to his PhD, led him to study the methods by which these precursors can be converted into useful functional electronic and or optical materials.

The period at QMWC led to life-long friendships with Alice Sullivan, Geoff Hawkes and Isaac Abrahams. Paul also made friends with Mark Faktor, Tony Jones and Barry Leese—a group of inventive scientists very interested in translating science into application, particularly in the area of chemical vapour deposition (CVD) of metal complexes. This led to Paul’s interest in entrepreneurship.
In 1995 Paul moved across London to Imperial College. The four years at Imperial were intense and set the outline of the work Paul would pursue for the following 20 years at Manchester. It was at Imperial that the key discoveries in Paul’s career regarding quantum dots would be made that would allow him to spin-out the work commercially.

Quantum dots are nanoscale semiconductor crystals whose critical diameters are below that of the parent bulk material’s exciton Bohr radius. The latter aspect gives rise to the phenomenon of ‘quantum confinement’, where only certain solutions of Schrödinger’s equation are possible. One of the results of this in crystalline semiconductors is that the band gap of the material at the nanoscale is typically increased compared with the bulk material; hence, by variation of nanocrystal diameter, the wavelengths of light at which the particle absorbs and emits can be tuned. This has some profound consequences in that a single material can be used to absorb and emit light over whole regions of the electromagnetic spectrum. This is in great contrast to bulk materials, where many different materials traditionally would have had to be used to achieve the same effect and where problems with interface incompatibilities from mismatched crystal lattices or simple corrosion effects previously dominated.

Because of the size of their band gaps and their tunability over the whole spectral range using quantum confinement, materials such as cadmium sulfide (CdS), and cadmium selenide (CdSe) became popular research topics for physicists, chemists and materials scientists during this period. Others had previously used a colloidal approach to make CdS and CdSe nanoparticles (NPs) requiring very toxic organometallic cadmium precursors such as dimethylcadmium combined often with H₂S. The previous studies also led to inclusion of oxides in the materials in anything but the most inert environments, with reactions requiring the use of a glovebox or vacuum. Clearly, a route requiring less stringent conditions would open up more possibilities for the mass manufacture of quantum dots. Owing to his background in inorganic coordination chemistry, and later materials science, Paul found himself extremely well placed to contribute to the nascent field.

The key paper that defined the materials processing route that became the cornerstone of Paul’s approach to producing quantum dots was entitled ‘A single source approach to the synthesis of CdSe nanocrystallites’ (8). The key principle defined in this paper is that a single precursor—methyl diethyldiselenocarbamato cadmium(II)—could be decomposed at 200°C in the presence of tri-n-octyl phosphine oxide (TOPO) and the growth of crystals of CdSe could be arrested in situ, and the resulting products were quantum confined (figure 6). The CdSe particles produced had diameters of ca 5 nm from transmission electron microscopy (TEM) images, with an absorption edge at 640 nm that was significantly blue-shifted compared with bulk CdSe (716 nm). This was also mirrored in luminescence emission spectra of the nanocrystallites, with emission peaks corresponding to the lowest energy band to band electronic transition significantly blue-shifted. Only a single peak was observed in the emission spectrum, suggesting that the nanocrystals had been stabilized by TOPO to remove surface defect states. It was also reported that the simple use of reaction temperature as a variable could control particle size and hence control the emergent properties of the quantum dots created using this pathway; CdSe nanocrystals produced at lower temperatures (120°C) had absorption edges at ca 460 nm, suggesting that they were even smaller in diameter. The paper ends with the profound statement that ‘the results reported here clearly show that
molecular compounds ... can be used as a single source precursor to prepare high quality semiconductor nanocrystallites’.

The POB group later used the single source precursors they had previously developed for MOCVD, such as bis[methyl(n-hexyl)di-thio or -seleno]carbamato metal complexes of the form \{M[E_2CNMe(C_6H_{13})]_2\} (M = Cd or Zn, E = S or Se), which were reacted in TOPO to produce highly mono-dispersed NPs of II–VI binary chalcogenides ME (M = Zn or Cd, E = S or Se). The particles were around 50 ± 2.5 Å in diameter (9). Using the same approach, the POB group reported the first core/shell particles synthesized from single source precursors (12). The synthesis is remarkably straightforward: [Cd\{Se_2CNMe(^n)Hex\}]_2] (^nHex = n-hexyl)
was heated at 250°C for 30 min in TOPO and then [Cd(S₂CNMeⁿHex)₂] was added and heated at 250°C for a further 30 min. These are technologically important composite semiconductors that can potentially produce different types of electronic heterojunctions within the same quantum dot, dependent on the band gap and work function of the two materials used. As a direct result of these key papers, patents were filed by Paul and others that became the basis of the successful company Nanoco (see below). Professor Matthew Rosseinsky (FRS 2008) commented: ‘Paul showed how elegant molecular synthetic chemistry could lead to scaleable production of functional nanomaterials, and realised this commercially. This success was based on excellence in fundamental materials chemistry.’

Paul also developed new ‘green’ deposition techniques that revolved around chemical bath deposition (CBD). The growth of thin films by CBD is, in general, a speciation problem and, given Paul’s background in mechanistic bio-inorganic chemistry, it was inevitable he would want to understand the processes underpinning CBD. In 1998 Paul used equilibrium models to show why formation of ZnS films by CBD was different from formation of CdS films (10). The group also performed an elegant study by GC-MS and EI-MS (electron ionization–mass spectrometry) of the vapour phase decomposition of M(Se₂CNEt₂)₂ and M(Se₂CNMeⁿHex)₂ (M = Cd or Zn) (13) (scheme 1). This showed that the diethyl-carbamates decompose, forming selenium clusters and significant quantities of Et₂Se, while this decomposition path is not found for the methyl n-hexyl carbamates. As a result, MSe films made from the former carbamates are contaminated with elemental selenium, while the latter carbamates give much better ZnSe or CdSe films. The work demonstrates that subtle changes in the precursor can have a major influence on the materials produced.

The other key family of semiconductors are the III–V materials, such as indium phosphide. As these materials do not contain cadmium, they have been suggested as next generation biological labels since initial work using CdSe quantum dots suggested that toxicity was an
issue. Quantum dots of InP were prepared from In(PtBu2)3 by refluxing in 4-ethylpyridine for 30 min (11). The ability to produce InP quantum dots in larger quantities allowed studies using them to replace organic dyes in luminescent concentrators, which suggested the possibility of using quantum dots within a transparent support as a means to increase the efficiency of photovoltaics. Further work to avoid cadmium came from the preparation of CuInS2 and CuInSe2 semiconductor quantum dots from single source precursors (14). With his PhD student, Mark Green, Paul also showed a similar approach could produce 8.6 ± 1.1 nm Au NPs, stabilized by a mixture of TOPO and octadecylamine (16). The use of heteroleptic zirconium and hafnium complexes of alkoxides and β-diketonates as precursors was also examined (15).

During this time, Paul was the Regents Appointed Visiting Professor at Georgia Institute of Technology, and later a distinguished Visiting Scholar. He was also a Royal Society Amersham International Research Fellow and the Sumitomo/STS Professor of Materials Chemistry. His work in Africa started in the University of Zululand in 1996.

Meanwhile Paul completed the Pennine Way and Coast to Coast walks, with his beloved dog Tris. This was quite a challenge as he could never take two consecutive weeks off work, so it had to be accomplished over a series of weekends. This involved many dashes north on a Friday evening, with Kym acting in a supporting role dropping him off at the point where he finished the weekend before and then picking him up 20 or so miles later, invariably at a grid reference on an unmade road.

THE UNIVERSITY OF MANCHESTER (1999–2018)

Paul arrived in Manchester in 1999 to a Chair of Inorganic Materials that was specially created for him; the post was joint between the School of Materials and School of Chemistry. He was immediately faced with a new challenge within the School of Chemistry as Professor C. David Garner FRS departed to the University of Nottingham, and so, rather unexpectedly, Paul became head of Inorganic Chemistry and set about recruiting new staff to rebuild the section. His recruits were of a very high calibre: Eric McInnes, Peter Skabara, Iain May, Richard Winpenny, Stephen Faulkner and Richard Layfield. The entire department was growing, and much of this was also due to the excellent leadership of the then head of department, Professor Jim Thomas. A major refurbishment of the building began under Jim’s leadership and continued throughout the following decade.

At the VUM, Paul was the research dean for three years, until 2002. He was highly active in the role, and many of the themes that continue to occupy the University of Manchester date from Paul’s time as research dean. He began to build the Centre for Nuclear Science and Engineering, Project Dalton, which, after the merger of VUM with UMIST, grew into the Dalton Nuclear Institute. The project was supported by British Nuclear Fuels and the Nuclear Decommissioning Authority and funded by a Higher Education Innovation Fund initiative. He also brought together a team from VUM, UMIST and the University of Sheffield to support outreach activities for the aerospace industry. He coordinated investment in nanotechnology leading to a new capability in the university, including the recruitment of Professor Sir Andre Geim (FRS 2007) from Nijmegen. The building that resulted, the Centre for Mesoscience and Nanotechnology, was where the key experiments on graphene were performed. Paul also began the discussions that led to the Organic Materials Innovation
Centre at Manchester, which began with funding from the Department of Trade and Industry.

He became head of chemistry at VUM in 2002. This period was very challenging as it coincided with the merger of VUM with UMIST. The future of chemistry at Manchester was one of the biggest challenges as there were large active chemistry departments within both institutions; moreover they had been competing for 20 years. Paul played a key role in bringing together the two departments. His vision, wisdom, humanity, common sense, immense patience and positive attitude were vital in breaking down barriers between the two groups of academics. He was the head of the School of Chemistry that resulted from the merger until 2009. Steve Faulkner, who witnessed the merger first-hand, said of Paul: ‘People mattered to him in Manchester as elsewhere, and none of us who were cajoled onto the paths of righteousness will ever forget the help and support he gave.’

From 2009 Paul took a short break from university leadership roles and was elected to a Visiting Fellowship at Magdalen College, Oxford. He very much took to the life of an Oxford college and enjoyed attending many events at Magdalen with Kym. Paul also became a member of the Development Trust of the College and was a significant benefactor. The Paul and Kym O’Brien Prize is awarded annually to the chemistry student at Magdalen who submits the best thesis on their final year research project. He was also a Distinguished Fellow at the Institute of Advanced Study at the University of Durham in early 2011. He returned to the fray as head of the School of Materials in Manchester from 2011 to 2015.

Paul had also discovered his favourite means of artistic expression: email. His Delphic emails gave immense pleasure to friends; one wonders what it did to recipients who were not one of the cognoscenti. When challenged on his tendency to send emails that were borderline incomprehensible, and which suggested he had only a passing acquaintance with English spelling and grammar, POB would explain:

- emails should not be taken seriously as they waste too much time;
- most emails are pointless but it is only polite to reply in some way, and anything will do.

If he sent an incorrect answer to an important question, he could always apologize and say he had been rushed, and he would then take the question seriously second time around. There is no doubt he had thought this all through, and also that occasionally he played up to the image, for example by signing emails ‘BOP’, but most often simply with a ‘Ta—POB’.

Paul’s outreach activities included working with the Manchester Literary and Philosophical Society to support a major annual competition for Manchester high schools to broaden interest in science among sixth formers. He was a regular contributor to Café Scientifique and, disturbingly, a disembodied head on a TV screen talking about nanoscience at the Museum of Science and Industry. He was also a patron and trustee of Catalyst in Widnes.

Paul received great scientific recognition while in Manchester: elected FRS in 2013 and FREng in 2016. He was also delighted to be made a CBE in 2016. He supported both the Royal Society and the Royal Society of Chemistry (RSC) with energy and enthusiasm, serving on countless committees and becoming a vice-president of the RSC.

The science pursued at Manchester exploited the breakthroughs made earlier in London in three distinct directions: first in examining how many other interesting materials could be made by CBD and how many new structures could result; second by looking at the physical
behaviour of these new materials, studies that involved close interactions with physicists; and third, attempts to understand how these new materials formed.

One natural target, given the success in making metal sulfides and selenides, was to produce metal telluride films from single source precursors. The challenge is that organic ligands such as ditellurocarbamates (R₂N-CTe₂)⁻ were either unknown or difficult to make. The solution was to use PNP ligands, i.e. [N(PR₂E)₂]⁻. The POB group showed that [N(PPPh₂Se)₂]⁻ ligands were good ligands for making metalloid chalcogenides and, based on synthetic work from the Chivers group, this was extended imino-bis(diisopropylphosphine tellurides) [N(P₂Pr₂Te)₂]⁻ (21). These are excellent ligands for a range of metals, including forming a beautiful hexamer with Ag(I). The compounds formed are frequently oligomers, and to deposit from vapour phase required aerosol-assisted CVD. Tellurides of cadmium, antimony, indium, copper and silver could all be prepared from these precursors, including truncated hexagonal plates of Ag₇Te₄.

The CBD route was used to produce mesocrystals of anatase TiO₂ via [NH₄][TiOF₃] (22). The intermediate mesocrystals of [NH₄][TiOF₃] were produced from reaction of [NH₄][TiF₆] and H₂BO₃ in surfactants based on polyoxyethylene ethers (e.g. C₁₆H₃₃(OCH₂CH₂)₂₀OH or C₁₈H₃₇(OCH₂CH₂)₁₀₀OH). Regular platelets are formed which are typically around 3.5 × 3.5 × 0.8 mm in dimensions with smoothly truncated corners (figure 7). Without the surfactant, the mesocrystals are irregular in shape and mainly TiO₂. The solution chemistry involves using boric acid as a fluoride scavenger, but using the surfactant to prevent complete hydrolysis of the [TiF₆]²⁻ precursor. The details of the reaction to form these mesocrystals were investigated and demonstrated the influence of the surfactant used, the reaction temperature, the concentration of boric acid used and even the rate of stirring. The mesocrystals can then be converted to anatase either by heating at 450°C or by reaction with further H₂BO₃.

A nickel complex of a PNP ligand, Ni[Pr₂P(S)NP(Se)Pr₂]₂, could be used to make either nickel phosphide or nickel selenide thin films (23), choosing which film is formed by control of the temperature of deposition. At 375 or 400°C, Ni₀.₈₅Se is formed. At 425°C a mixture of Ni₂P and Ni₅P₄, and at 450 and 475°C pure Ni₂P. The control is sufficient that multilayers can be deposited on indium tin oxide (ITO) by variation of temperature.

CBD was also used to produce truly alloyed PbSₓSe₁₋ₓ NPs of around 5 nm (figure 8). The key factor is the use of similar reagents as the source of sulfur and selenium. The POB group used (Me₃Si)₂E (E = S or Se) and reacted them with PbO dissolved in oleic acid mixed with octadecene at 130°C under an N₂ atmosphere (26). The composition was varied, with NPs produced with x = 0, 0.20, 0.33, 0.43, 0.50, 0.67, 0.80 and 1. The alloying within the NPs is demonstrated by energy dispersive X-ray (EDX) spectroscopy. The position of the photoluminescence from the NPs varies smoothly with composition, demonstrating that it is possible to tune the band gap in these NPs straightforwardly. The results are incredible given the simplicity of the chemical reaction used.

A further target was to produce objects involving the controlled assembly of different NPs. One report involves introducing amido- and azo-linkages between CdS NPs and Au or Ag NPs. For example, the amide-link involves reaction of an acid chloride, bound to the CdS NP, with an amine bound to the coinage group NP (25).

White light luminescence and room-temperature lasing throughout the visible was demonstrated for ZnO nanocolumns with an average nanocolumn length of ca 3 μm (18). The ZnO nanocolumns were grown directly onto Au-coated tin-oxide glass by CBD from a zinc carboxylate (e.g. acetate) dissolved in a solution containing hexamethylenetetramine. The
pH was then adjusted to 5.0 using glacial acetic acid and when colloid formation was observed the Au-coated substrate was immersed into the solution. The directionality of the emission, the lasing threshold and the observed mode spacing are all consistent with Fabry–Pérot lasing cavities. Scanning electron microscopy (SEM) shows formation of ZnO nanocolumns. This fascinating result from ZnO motivated a very detailed study of the factors that control the
Figure 8. (a) TEM image of PbS$_{0.5}$Se$_{0.5}$ nanocrystals; (b,c) zero loss images of selenium and sulfur, respectively. (From (26) with permission from the American Chemical Society.) (Online version in colour.)

formation of thin films of this material by CBD from aqueous solutions. To obtain good films, either the concentration of Zn$^{2+}$ ions has to be restricted, typically by adding chelating ligands, or the availability of OH$^-$ has to be controlled through pH (19).

Quantum dot–quantum well nanocrystals were also prepared by CBD using a three-step procedure (24). Initial ZnS NPs were grown from the single source precursor [Et$_3$NH]$_4$[Zn$_{10}$S$_4$(SPh)$_{16}$] in hexadecylamine. After these NPs were collected, they were coated with a CdSe layer by slow addition of [Et$_3$NH]$_4$[Cd$_{10}$Se$_4$(SPh)$_{16}$]. The UV–vis absorption and photoluminescence (PL) spectra were monitored while this shell was grown, and when the required emission wavelength was achieved no more CdSe precursor was added. The final ZnS shell was grown by alternate dropwise additions of 0.1 M solutions of diethylzinc and hexamethyldisilathiane in trioctylphosphine to a solution of the ZnS/CdSe NPs suspended in hexadecylamine. Detailed studies of these NPs show that the growth of a CdSe layer on top of ZnS nanocrystals leads to the formation of a graded ZnS/CdSe alloy in the core region, but that the final ZnS outer layer has a sharp interface. The PL observed from these nanostructures is tunable over the visible range and the PL efficiency can be as high as ca 60% (25).

A very typical and elegant POB investigation was to examine the growth of tetrapodal nanocrystals of cadmium chalcogenides (20). Paul was intrigued by the formation of these tetrapods—three legs about a spine—rather than growth of regular polyhedra. A straightforward arithmetic calculation of the number of surface atoms in tetrahedra against the number of surface atoms in a tetrapod predicted that the biggest difference occurs for particles between 2 and 4 nm. This is exactly the size of NPs when tetrapods are seen.

In the later years at Manchester the main focus of Paul’s research was to develop a range of ‘soft’ reactions to produce high quality semiconductor materials pertinent to renewable energy generation. He focused particularly on the use of metal xanthate ([M$_x$(S$_2$COR)$_y$]) complexes as single source precursors to give metal sulfides, and in particular realized that the low temperature of decomposition of xanthate powders can be used to make a range of polycrystalline metal chalcogenide semiconductor powders with scalability built in. In general, this would proceed by thermolysis of the solid state metal xanthate in inert atmospheres to leave the corresponding metal sulfide powder, and in many papers was referred to by POB as ‘solventless thermolysis’. The decomposition of metal xanthate precursors
proceeds via Chugaev elimination of the ligands, and for the short chain alkyl xanthates (e.g. ethyl xanthates, propyl xanthates), the side products are all gaseous, hence semiconductors without carbon contamination may be produced. The temperature at which the metal xanthates decompose is also typically below 200°C. This brings the exciting prospect of deposition onto polymer substrates leading to future applications in flexible electronics, for example in building-integrated thin film photovoltaics that could be mass produced by roll-to-roll printing. A typical example of a binary semiconductor produced by this route is the case of iron sulfide (29). Iron(III) xanthates of the form \([\text{Fe}(\text{S}_2\text{COR})_3]\) (where \(R = \text{n-butyl}, \text{2-butyl}, \text{2-methoxyethyl or 2-ethoxyethyl}\)) were used in solid state thermolysis reactions to produce powders and thin films of cubic pyrite at relatively low processing temperatures and short reaction times. What is striking is that in many cases the material is produced as a single phase (cubic \(\text{FeS}_2\) pyrite), which, given the complexity of the iron sulfide phase diagram, is an impressive achievement. Furthermore, from diffraction and electron microscopy the materials produced are nanostructured directly from the reaction.

The use of these types of reactions was extended to ternary metal sulfide alloys where two metals are combined with a chalcogenide atom, often with very different electronic properties as compared with the two binary materials. This is useful, for example, to access new materials where, by compositional tuning, a new band gap energy can be accessed. By mixing two metal xanthate precursors, and their subsequent solventless thermolysis, in inert atmospheres, these systems could be accessed at low temperature and in a relatively short time period. For example, Alqahtani et al. made the whole range of alloy powders in the \(\text{Bi}_{2-x}\text{Sb}_x\text{S}_3\) (0 \(\leq x \leq 1\)) solid solution by using a mixture of Bi and Sb ethyl xanthates as precursors with a reaction temperature of 250°C (28). These are useful materials for thermoelectric power generation as well as novel candidates for sustainable photovoltaics. Through the use of alloying, the band gap energy of \(\text{Bi}_{2-x}\text{Sb}_x\text{S}_3\) solids can be tuned as a function of the Sb mole fraction in a pseudo linear manner between \(ca. \) 1.6 and 2.2 eV. Further examples of this approach to ternary materials include the production of \(\text{M}_{2-x}\text{In}_{2x}\text{S}_3\) (where \(\text{M} = \text{Bi or Sb}\)) by the use of In xanthates in tandem with either the Bi or Sb xanthates (30). The latter systems may be useful for tuning carrier concentration for thermoelectric applications.

The use of three metal xanthates in tandem can be used for the production of quaternary metal chalcogenides from solventless thermolysis. For example, the POB group reported the synthesis of thin films, the photovoltaic absorber system \(\text{Cu}_2\text{ZnSnS}_4\) (kesterite CZTS) from thermolysis of a mixture of Sn, Zn and Cu xanthates (27). Remarkably, a single phase of the material can be produced, with optoelectronic properties measured that are suitable for use in solar devices. Using the same approach, and switching the zinc xanthate complex for iron xanthate, yields stannite \(\text{Cu}_2\text{FeSnS}_4\) (CFTS) (31). Both CZTS and CFTS are attractive for thin film solar cells as they have shown promising power conversion efficiencies (CZTS \(ca. 12\)%), comprise earth abundant, non-toxic elements and are extremely robust materials.

As mentioned previously, Paul spent time as a Fellow at the Institute of Advanced Study at Durham University, and from this time he decided that photovoltaic energy generation should be sustainable overall. His later research into low temperature routes toward new materials adhered to these principles.

Professor Phil Withers FREng FRS (Regius Professor of Materials in Manchester) said: ‘A curious and mischievous mind characterised Paul’s involvement in materials, aided by a special ability to apply basic chemistry principles to some really applied problems, from the role of lubricant additives to the hierarchical fracture behaviour of beetle cuticle. This
meant he connected with a very broad spectrum of researchers, shedding light on many knotty problems.’

**SCIENCE IN AFRICA**

Paul was passionate about science in Africa, campaigning for historically black institutions in South Africa in the post-apartheid period. Many African scientists obtained PhDs in his research group, before returning to academic positions in Ghana, South Africa, Tanzania
and Cameroon. The science he developed did not require costly sophisticated equipment, and therefore it transferred into less well-equipped laboratories in developing countries. His leadership and advocacy allowed African scientists to carry out materials science that competed with science from more developed countries. His advocacy led to funding from the Royal Society and from the Department for International Development, including current funding of over £1 million to make new materials for solar energy capture in three African countries. His research group always contained many young researchers from the developing world, who treasured the opportunity to work with a world-leading scientist. African scientists recognized his importance and he was awarded an honorary degree from Zululand (figure 9).

Professor X. A. Mtose, Vice-Chancellor of the University of Zululand, wrote on Paul’s passing: ‘Prof O’Brien was a supporting and caring friend of the university who not only was a distinguished honorary doctorate recipient at the University of Zululand but was a pioneer of projects in the Department of Chemistry. We cherish fond memories as he has always joined us when we celebrate and in times of grief and surely that would not have been possible if his wife was not supportive, to Kym we thank you for allowing us a piece of Prof and you shared him with us unreservedly.’

To his family, they say: ‘although we knew this day was going to come, nothing can diminish our sense of a profound and enduring loss. Prof’s good work is irreplaceable, he left a lasting legacy. His humility, passion and humanity, won us over.’

Emmanuel Onche, a Nigerian student studying for a PhD with Paul said simply: ‘An iroko tree has fallen in Africa’ (Buriak & Lewis 2018).

Kym arranged for Paul to wear his University of Zululand academic gown for his cremation. As Kym wrote: ‘His relationship with Africa was very important to him and I thought he would be pleased to wear his African gown one last time.’

**Honours and awards**

1990 Fellow of the Royal Society of Chemistry
1997 Royal Society Amersham International Research Fellow
2001 Potts Medal for chemistry, University of Liverpool (Distinguished Alumnus Award)
2001 Fellow of the Institute of Materials, Mining and Minerals (IOMMM)
2005 A. G. Evans Memorial Medal Lecturer, Cardiff University
2006 DSc (*hon. causa*), University of Zululand, KwaZulu-Natal, South Africa
2007 Kroll Medal, IOMMM
2009 Peter Day Award for Materials Chemistry, Royal Society of Chemistry
2009 Sir Colin Humphries Award, IOMMM
2013 Fellow of the Royal Society
2013 Honorary Doctorate, University of Liverpool
2015 Fellow of the Learned Society of Wales
2015 Honorary Doctorate, University of Aveiro
2016 Fellow of the Royal Society of Engineering
2016 Commander of the British Empire
2016 Longstaff Prize of the Royal Society of Chemistry
EDITORIAL DUTIES

Editor of the *Nanoscience Specialist Periodical Reports* from the Royal Society of Chemistry.

ACKNOWLEDGEMENTS

We are immensely grateful to Kym O’Brien for her huge assistance with this memoir and for providing photographs and anecdotes. We also thank Sir David Clary, David Collison, Pete Edwards, Steve Faulkner, Mike Holmes, Chris Orvig, Júlio Pedrosa de Jesus, Matt Rosseinsky and Phil Withers for their help in composing this memoir. Quotations attributed to POB are taken from private correspondence and discussions with the two authors. The frontispiece portrait photo was taken in 2013 and is from the Royal Society’s collection.

AUTHOR PROFILES

David J. Lewis

David Lewis (DJL) is Reader in Materials Chemistry and Deputy Head of the Department of Materials at the University of Manchester. He obtained both his MSc and PhD degrees in chemistry from the University of Birmingham. His research revolves around the synthesis of semiconductors and nanomaterials by chemical routes and he has published over 60 papers in the area. He worked closely with Paul O’Brien (POB) from 2013 to 2016, first as a post-doctoral research associate and later as research fellow. DJL acts as academic advisor for POB’s remaining PhD students at the Department of Chemistry at the University of Manchester, with Professor David Collison providing operational support, and now leads POB’s Royal Society DFID Africa Capacity Building Initiative programme grant with universities in South Africa, Cameroon and Ghana (2018–2021).

Richard E. P. Winpenny FLSW FRSC

Richard Winpenny (REPW) holds the Chair of Inorganic Chemistry at the University of Manchester. He obtained both his degrees from Imperial College, London; his PhD was carried out with Professor David Goodgame. His post-doctoral work was carried out with Professor John Fackler Jr at Texas A&M University, in 1988 and 1989, and involved the mass spectrometry of gold clusters. REPW joined the academic staff at Edinburgh in 1990 and moved to the University of Manchester in 2000 as the Chair of Inorganic Chemistry, working closely with POB for the following 18 years. He was awarded a Royal Society Wolfson Merit Award in 2009 and the RSC Tilden Medal in 2011. He was elected a Fellow of the Learned Society of Wales in 2016 (nominated by POB), was the winner of the Ludwig Mond Medal of the RSC in 2016 and
the recipient of the RSC Prize for Emerging Technologies in the area of materials in 2016. He was awarded an EPSRC Established Career Fellowship from January 2018 to December 2022 and a European Research Council Advanced Fellowship from September 2018 to August 2022.

REFERENCES TO OTHER AUTHORS

Buriak, J. M. & Lewis, D. J. 2018 Paul O’Brien: materials chemistry pioneer (Jan 22 1954–Oct 16 2018). *Chem. Mater.* **30**, 8113–8115. (doi:10.1021/acs.chemmater.8b04697)

Bibliography

The following publications are those referred to directly in the text. A full bibliography is available as electronic supplementary material at https://doi.org/10.6084/m9.figshare.c.5094963.

(1) 1978 (With R. D. Gillard) The isomers of α-amino acids with copper(II). Part IV: catalysis of the racemization of optically active alanine by copper(II) and pyruvate in alkaline solution. *J. Chem. Soc. Dalton Trans.* **1978**, 1444–1447. (doi:10.1039/DT9780001444)

(2) 1985 (With J. Barrett & F. Swanson) Chromium(V) can be generated in the reduction of chromium(VI) by glutathione. *Inorg. Chim. Acta* **108**, L19–L20. (doi:10.1016/S0277-5387(00)83664-5)

(3) (With D. A. Sweigart) Effect on redox potentials of hydrogen bonding from coordinated imidazole in metalloporphyrin complexes. *Inorg. Chem.* **24**, 1405–1409. (doi:10.1021/ic00203a028)

(4) 1987 (With L. F. Larkworthy & K. B. Nolan) Chromium. In Comprehensive coordination chemistry (ed. G. Wilkinson, R. D. Gillard & J. A. McCleverty), pp. 699–969. London, UK: Pergamon Press.

(5) 1989 (With A. Kortenkamp, Z. Ozolins & D. Beyersmann) Generation of PM2 DNA breaks in the course of the reduction of chromium(VI) by glutathione. *Mutation Res.* **216**, 19–26. (doi:10.1016/0165-1161(89)90019-8)

(6) (With D. M. Frigo & O. F. Z. Khan) Growth of epitaxial and highly oriented thin films of cadmium and cadmium zinc sulphide by low-pressure metalorganic chemical vapour deposition using diethylthiocarbamates. *J. Cryst. Growth* **96**, 989–992. (doi:10.1016/0022-0248(89)90662-3)

(7) 1991 (With M. B. Hursthouse, M. A. Malik & M. Motevalli) Mixed alkyl dialkylthiocarbamates of zinc and cadmium: potential precursors for II/VI materials. X-ray crystal structure of [MeZn(S2CNEt2)]2. *Organometallics* **10**, 730–732. (doi:10.1021/omom0049a036)

(8) 1996 (With T. Trinidad) A single source approach to the synthesis of CdSe nanocrystallites. *Adv. Mater.* **8**, 161–163. (doi:10.1002/adma.1996080214)

(9) 1997 (With T. Trinidad & X. M. Zhang) Synthesis of CdS and CdSe nanocrystallites using a novel single-molecule precursor approach. *Chem. Mater.* **9**, 523–530. (doi:10.1021/cm960363x)

(10) 1998 (With J. McAleese) Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS. *J. Mater. Chem.* **8**, 2309–2314. (doi:10.1039/A804692A)

(11) (With M. Green) A novel metalorganic route for the direct and rapid synthesis of monodispersed quantum dots of indium phosphide. *J. Chem. Soc. Chem. Commun.* **22**, 2459–2460. (doi:10.1039/A806419I)

(12) 1999 (With N. Revaprasadu, M. A. Malik & G. Wakefield) A simple route to synthesise nanodimensional CdSe-CdS core-shell structures from single molecule precursors. *Chem. Commun.* **16**, 1573–1574. (doi:10.1039/A901969C)

(13) (With M. Chunggaze & M. A. Malik) Studies of the thermal decomposition of some diselenocarbamato complexes of cadmium or zinc: molecular design for the deposition of MSe films by CVD. *J. Mater. Chem.* **9**, 2433–2437. (doi:10.1039/A905095G)

(14) (With M.A. Malik & N. Revaprasadu) A novel route for the preparation of CuSe and CuInSe2 nanoparticles. *Adv. Mater.* **11**, 1441–1444. (doi:10.1002/(SICI)1521-4095(199912)11:17&lt;1441::AID-ADMA1441>3.0.CO;2-Z)
(15) With K. A. Fleeting, D. J. Otway, A. J. P. White, D. J. Williams & A. C. Jones) Studies on mixed β-diketonate/isopropoxide compounds of zirconium and hafnium, the X-ray single-crystal structures of [M2(OPr)6(tmhd)2] (M = Zr, Hf): some chemistry important in the MOCVD of oxides. Inorg. Chem. 38, 1432–1437. (doi:10.1021/ic980690w)

(16) 2000 (With M. Green) A simple one phase preparation of organically capped gold nanocrystals. Chem. Commun. 3, 183–184. (doi:10.1039/A907532A)

(17) 2001 (With M. A. Malik & N. Revaprasadu) Air-stable single-source precursors for the synthesis of chalcogenide semiconductor nanoparticles. Chem. Mater. 13, 913–920. (doi:10.1021/cm0011662)

(18) 2002 (With K. Govender, D. S. Boyle, D. Binks, D. West & D. Coleman) Room-temperature lasing observed from ZnO nanocrystals grown by aqueous solution deposition. Adv. Mater. 14, 1221–1224. (doi:10.1002/1521-4095(20020903)14:17<1221::AID-ADMA1221>3.0.CO;2-1)

(19) 2004 (With K. Govender, D. S. Boyle & P. B. Kenway) Understanding the factors that govern the deposition and morphology of thin films of ZnO from aqueous solution. J. Mater. Chem. 14, 2575–2591. (doi:10.1039/B404784B)

(20) 2006 (With P. J. Thomas) A simple numerical calculation correctly predicts the observed size regime for growth of tetrapodal chalcogenide nanocrystals. J. Am. Chem. Soc. 128, 5614–5615. (doi:10.1021/ja076187c)

(21) 2007 (With J. S. Ritch, T. Chivers & M. Afzaal) The single molecular precursor approach to metal telluride thin films: iminobis(diisopropylphosphine tellurides) as examples. Chem. Soc. Rev. 36, 1622–1631. (doi:10.1039/B605535B)

(22) 2008 (With L. Zhou & D. Smyth-Boyle) A facile synthesis of uniform NH4TiOF3 mesocrystals and their conversion to TiO2 mesocrystals. J. Am. Chem. Soc. 130, 1309–1321. (doi:10.1021/ja076187c)

(23) (With A. Panneerselvam, M. A. Malik, M. Afzaal & M. Helliwell) The chemical vapor deposition of nickel phosphate or selenide thin films from a single precursor. J. Am. Chem. Soc. 130, 2420–2421. (doi:10.1021/ja078202)

(24) 2009 (With P. K. Santra, R. Viswanatha, S. M. Daniels, N. L. Pickett, J. M. Smith & D. D. Sarma) Investigation of the internal heterostructure of highly luminescent quantum dot–quantum well nanocrystals. J. Am. Chem. Soc. 131, 470–477. (doi:10.1021/ja8033075)

(25) 2010 (With W. Maneeprankorn & M. A. Malik) Developing chemical strategies for the assembly of nanoparticles into mesoscopic objects. J. Am. Chem. Soc. 132, 1780–1781. (doi:10.1021/ja910022q)

(26) 2011 (With J. Akhtar, M. Afzaal, M. Banski, A. Podhorodecki, M. Syperek, J. Misiewicz, U. Bangd, S. J. O. Hardman, D. M. Graham, W. R. Flavell, D. J. Binks & S. Gardonio) Controlled synthesis of tuned bandgap nanodimensional alloys of PbSxSe1−x. J. Am. Chem. Soc. 133, 5602–5609. (doi:10.1021/ja078202)

(27) 2017 (With M. Al-Shakban, P. D. Matthews, N. Savjani, X. L. Zhong, Y. Wang & M. Missous) The synthesis and characterization of Cu2ZnSnS4 thin films from melt reactions using xanthate precursors. J. Mater. Sci. 52, 12 761–12 771. (doi:10.1007/s10853-017-1367-0)

(28) 2018 (With T. Alqahtani, M. D. Khan, D. J. Kelly, S. J. Haigh & D. J. Lewis) Synthesis of Bi2−xSbxS3 (0 ≤ x ≤ 1) solid solutions from solventless thermolysis of metal xanthate precursors. J. Mater. Chem. C 6, 12 652–12 659. (doi:10.1039/c8tc02374c)

(29) 2019 (With L. Almanqur, F. Alam, G. F. S. Whitehead, I. Vitorica-yrezabal, & D. J. Lewis) Synthesis of iron sulfide thin films and powders from new xanthate precursors. J. Cryst. Growth 522, 175–182. (doi:10.1016/j.jcrysgro.2019.05.029)

(30) (With T. Alqahtani, R. J. Cernik & D. J. Lewis) Solid solutions of M2−xIxS3 (M = Bi or Sb) by solventless thermolysis. J. Mater. Chem. C 7, 5112–5121. (doi:10.1039/c9tc00148d)

(31) (With A. M. Alanazi, F. Alam, A. Salhi, M. Missous, A. G. Thomas & D. J. Lewis) A molecular precursor route to quaternary chalcogenide CFTS (Cu2FeSnS4) powders as potential solar absorber materials. RSC Adv. 9, 24 146–24 153. (doi:10.1039/c9ra02926e)