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PAPER

Concluding remarks: Harnessing non-covalent interactions for synthesis and catalysis

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An overview of the *Faraday Discussion* meeting on harnessing non-covalent interactions for synthesis and catalysis, is presented. This covers progress in the field across chemical biology, bioinspired catalysis using homogeneous coordination complexes, supramolecular approaches for catalysis, advanced diffraction and spectroscopic methods for the measurement of structure and the influence of non-covalent interactions, and how computational tools inform and start to predict the role of non-covalent interactions.

It is my privilege to write the closing remarks for this *Faraday Discussion* meeting on non-covalent interactions. The ambition of the organisers (myself, Paul Raithby, Anne Duhme-Klair, Neil Champness and Joost Reek) was to bring together researchers from across the physical and life sciences working in the areas of synthesis, materials and catalysis, for which non-covalent interactions (NCIs) are important to the mechanisms occurring in both solid-state and solution processes. A particular emphasis was on understanding and controlling the non-covalent intermolecular interactions that drive synthetic and catalytic processes across a range of length and timescales. Although a relatively small meeting (63 participants) the conference was a real success, due in large part to the excellent presentations from our speakers, the outstanding poster contributions and – most importantly – the high level of (often lively) scientific discussion from all attendees (whether presenting or not) that was conducted in a respectful but scientifically rigorous way. As well as a good number of UK participants, we welcomed colleagues from countries around the world, including Spain, France, Germany, the Netherlands, USA, Canada, Portugal, Belgium, Switzerland and Ireland. The North Yorkshire April weather almost held good for us as well, allowing people to enjoy in full our fine city of York. We also thank the excellent team from the Royal Society of Chemistry who looked after all the organisational and administrative aspects of the conference.

Over the three days of the meeting we, as a community, explored many aspects of what NCIs actually mean in synthesis and catalysis. Indeed, how we actually

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define NCIs led to some of the liveliest debate throughout the meeting! Contributions spanned chemical biology, bioinspired catalysis using homogeneous coordination complexes, supramolecular approaches for catalysis, advanced diffraction and spectroscopic methods for the measurement of structure and the influence of NCIs, and how computational tools (including data-driven tools such as machine learning) can be used to not only indicate the presence of NCIs in a wide variety of molecular settings, but also start to quantify and even predict their influence. These discussions were broadly grouped into themes of "Make", "Manipulate", "Model" and "Measure" but the discussion was free-ranging between all four and certainly not siloed into these, perhaps somewhat artificial, constraints.

We were delighted to start the meeting with our Spiers Memorial Lecture from Thomas Ward who elegantly showed us the power of NCIs in artificial metalloenzymes, especially the manipulation of the second coordination sphere (Ryan Peterson and Thomas Ward – Basel, **https://doi.org/10.1039/D3FD00034F**). The theme of NCIs in nature-inspired chemistry continued in the fine tuning of NCI interactions between polyoxometalates and proteins (Tatjana Parac-Vogt – Leuven, **https://doi.org/10.1039/D2FD00161F**), templated synthesis using linear oligoprolines (Bartosz Lewandowski and Helma Wennemers – Zurich, **https://doi.org/10.1039/D3FD00002H**), and detailed studies on bridged copper peroxido-complexes as tyrosinase mimics (Sonja Herres-Pawlis – Aachen, **https://doi.org/10.1039/D2FD00162D**).

The role of NCIs in catalysis by coordination compounds was covered by a number of contributors. Site-selective C–H activation processes were discussed using bioinspired Mn catalysts (Giorgio Olivo – Rome, and Miquel Costas – Girona, **https://doi.org/10.1039/D2FD00177B**). A substrate-descriptor approach was described to understand regioselective hydroformylation using encapsulated rhodium-based catalysts (Pim Linnebank and Joost Reek – Amsterdam, **https://doi.org/10.1039/D3FD00023K**). Supramolecular interactions in the second coordination sphere of Pd/Zn complexes were shown to boost activity in Mizooroki–Heck catalysis (Rafael Gramage-Doria – Rennes, **https://doi.org/10.1039/D2FD00165A**), while the role of second coordination sphere NCIs in the initiation of olefin metathesis has been studied using DFT methods (Naeimeh Bahri-Laleh – Tehran, and Albert Poater – Girona, **https://doi.org/10.1039/D2FD00163B**). Supported Rh-catalysis in which liquid confinement effects control regioselectivity in supported Rh-hydrosilylation catalysts (Michael Buchmeiser – Stuttgart, **https://doi.org/10.1039/D2FD00152G**), and the role of catalyst confinement (this time in a metal–organic framework) in nitrogen-atom transfer reactions as probed using detailed kinetic isotope experiments to probe substrate mobility (Thomas Cundari and David Powers – Texas, **https://doi.org/10.1039/D2FD00167E**), were presented. Rounding off the section on the influence of NCIs in catalysis, the pre-organisation of substrate, photosensitiser and supramolecular Pt_4 "square" catalysts for the photocatalytic dehalogenation of aryl halides was discussed (Sonja Pullen – Amsterdam, **https://doi.org/10.1039/D2FD00179A**).

Fundamental studies into structure and bonding as related to NCIs were an important topic of the *Discussion* meeting and included computational as well as experimental studies. Hydrogen and halogen bonding between N-heterocyclic carbene nickel fluoride complexes and donors such as indole and

iodopentafluorobenzene was discussed (Udo Radius – Würzburg, Torsten Beweries – Rostock, and Robin Perutz – York, https://doi.org/10.1039/D2FD00171C), while the unexpected role of π-backbonding from halogen bonds to a PF_3 promoter in the S_N2 self-exchange of geminal diiomethanes was presented (Pierre Kennepohl, – Calgary, https://doi.org/10.1039/D2FD00140C). Related studies reported on the use of chalcogen bonding in the second coordination sphere as a synthetic tool for the synthesis of copper(II) complexes (Antonio Frontera – Palma, Kamran Mahmudov and Armando Pombeiro – Lisbon, https://doi.org/10.1039/D2FD00160H). Machine learning tools were described that predict the strength of interactions between small organic molecules and solid-surfaces (Ian Rouse – Dublin, https://doi.org/10.1039/D2FD00155A). In a more applied contribution, the role of NCIs in reversible vapochromic and solvatochromic reactions at Pt-pincer complexes was presented (Paul Raithby – Bath, https://doi.org/10.1039/D3FD00025G). Two contributions that used computational methods to interrogate the bonding and stability of experimentally determined complexes with M···H–C bonds were discussed: the nature of the bonding in alkali-metal···methyl contacts in aluminates (Jorge Echeverría – Zaragoza, and Marta Mosquera – Madrid,https://doi.org/10.1039/D2FD00144F) and comparison of the influence of NCIs in the solid-state structures of two σ-alkane Rh complexes with very different stabilities (Stuart Macgregor – Edinburgh, https://doi.org/10.1039/D3FD00009E).

The development of advanced spectroscopic and diffraction (and related) methods is a key component of understanding, and thus manipulating, NCIs, and the *Discussion* meeting had a number of important contributions to this area. The photochemistry of cyclopentadiene was described in which ultrafast X-ray scattering data were simulated and experimental data predicted (Adam Kirrander – Oxford, https://doi.org/10.1039/D2FD00176D). Ultrafast infrared and X-ray absorption methods have also been used to understand the role of transient bonding in the photochemistry of homoleptic copper diimine complexes (Julia Weinstein – Sheffield, https://doi.org/10.1039/D3FD00027C). The role of NCIs on solid-state Pd-nitrito photoswitches was presented using a combined photocrystallography/charge density approach (Lauren Hatcher – Cardiff, https://doi.org/10.1039/D2FD00158F). Finally, the assessment of NCIs in temperature promoted structural transitions in bipyridinium squarate adducts using X-ray pair distribution functions was presented (Maria Diaz-Lopez – Didcot, https://doi.org/10.1039/D2FD00159D).

The conference was completed by an engaging "closing remarks" lecture from Dean Toste (Berkeley), summarising both the *Discussion* meeting and the role of NCIs in catalysis using supramolecular cages from his own research. A particular comment made, perhaps slightly tongue-in-cheek, was (and I paraphrase): "*We have been discussing the names of all different types of interactions, hydrogen bonds, halogen bonds, chalcogen bonds, π–π interactions…but at the end these are all just London dispersion interactions, so why not just stick to the old fashioned names*". This comment serves to demonstrate that while there is much debate still to be had on *how* we describe non-covalent interactions, that they are being increasingly recognised in their apparently many different forms as being important – even crucial – for a host of chemical transformations is beyond doubt. There is clearly still much to debate, discuss and discover in the field! In that spirit we very much hope that you enjoy, and are perhaps inspired by, reading the papers and of

course the transcripts of the *Discussion*, in the Make (**https://doi.org/10.1039/D3FD90012F**), Measure (**https://doi.org/10.1039/D3FD90016A**), Model (**https://doi.org/10.1039/D3FD90015K**), and Manipulate (**https://doi.org/10.1039/D3FD90013D**) themes.

Andrew Weller, York, July 2023.

Conflicts of interest

There are no conflicts to declare.

