

**Professor Howard M. Colquhoun**  
MA, ScD (Cambridge); PhD (London); FRSC

**Emeritus Professor of Materials Chemistry**

**Email:** h.m.colquhoun@rdg.ac.uk



**Biographical details:** Howard was born in County Durham in 1951 and attended Washington Grammar School. After degrees at the Universities of Cambridge (MA, St Catharine's College) and London (PhD, Westfield College), he carried out research at the ICI Corporate Laboratory in Cheshire before moving to Manchester University in 1994 as a Royal Society Industry Fellow. He was Professor of Inorganic Chemistry at the University of Salford from 1997 to 2000, before taking up the Chair of Materials Chemistry at the University of Reading.

His research has covered the fields of silicon chemistry, coordination chemistry, dinitrogen chemistry, supramolecular chemistry, and polymer chemistry.

Awards for his work include the RSC Medal and Prize for Materials Chemistry (2006), a Royal Society Leverhulme Senior Research Fellowship (2007), the Wilsmore Fellowship of the University of Melbourne (2007), the degree of Doctor of Science (ScD) of the University of Cambridge (2008), the MacroGroup UK Medal for achievement in polymer science (2012), and a Royal Society *Brian Mercer* Award (2013).

Howard retired in December 2018 and was awarded a Leverhulme Emeritus Research Fellowship, based in the University of Cambridge, where he worked from 2019 to 2020.

## Some Recent Publications

Sequence modification in copoly(ester-imide)s: a catalytic/supramolecular approach to the evolution and reading of copolymer sequence information. M. Knappert and H. M. Colquhoun. *Polym. J.* **2021**. in press.

Catechol-based macrocyclic aromatic ether-sulfones: Synthesis, characterization and ring-opening polymerization. F. Aricò and H. M. Colquhoun. *Arkivoc*, **2021**, in press.

Single-site binding of pyrene to poly(ester-imide)s incorporating long spacer-units: prediction of NMR resonance-patterns from a fractal model. M. Knappert, T. Jin, S. D. Midgley, G. Wu, O. A. Scherman, R. Grau-Crespo and H. M. Colquhoun. *Chem. Sci.*, **2020**, *11*, 12165-12177.

A thermotropic poly(ether ketone) based on the *p*-quaterphenyl unit: evidence for a smectic C phase. F. O. Oladoyinbo, D. F. Lewis, D. J. Blundell and H. M. Colquhoun. *Polym. Chem.*, **2020**, *11*, 75-83.

Supramolecular complexation between chainfolding poly(ester-imide)s and polycyclic aromatics: a fractal-based pattern of NMR ring-current shielding. M. Knappert, T. Jin, S. D. Midgley, G. Wu, O. A. Scherman, R. Grau-Crespo and H. M. Colquhoun. *Polym. Chem.*, **2019**, *10*, 6614-6650.

Elements of fractal geometry in the <sup>1</sup>H NMR spectrum of a copolymer intercalation-complex. J.S. Shaw, R. Vaiyapuri, M. P. Parker, C. A. Murray, K. J. C. Lim, C. Pan, M. Knappert, C. J. Cardin, B. W. Greenland, R. Grau-Crespo and H. M. Colquhoun. *Chem. Sci.*, **2018**, *9*, 4052-4061.

Trifluoromethylation of carbonyl groups in aromatic poly(ether ketone)s: formation of strongly polar yet surface-hydrophobic poly(arylenecarbinol)s. F. Leroux, R. A. Bennett, D. F. Lewis and H. M. Colquhoun. *Macromolecules*, **2018**, *51*, 3415-3422.

Quadruple stacking of macrocyclic viologen radical-cations. C. A. Murray, Z. Zhu, C. J. Cardin, H. M. Colquhoun and B. W. Greenland. *Supramol. Chem.*, **2018**, *30*, 751-757.

Mutual complexation between  $\pi$ - $\pi$  stacked molecular tweezers. M. P. Parker, C. A. Murray, L. R. Hart, B. W. Greenland, W. Hayes, C. J. Cardin, and H. M. Colquhoun, *Cryst. Growth Des.*, **2018**, *18*, 386-392.

Exchange reactions of poly(arylene ether ketone) dithioketals with aliphatic diols: formation and deprotection of poly(arylene ether ketal)s. I. Manolakis, P. Cross and H. M. Colquhoun, *Macromolecules*, **2017**, *50*, 9561-9568.

Controlled variation of monomer sequence-distribution in the synthesis of aromatic poly(ether ketone)s. K. J. C. Lim, P. Cross, P. Mills and H. M. Colquhoun, *High Performance Polymers*, **2016**, *28*, 984-992.

Molecular design of a discrete chain-folding polyimide for controlled inkjet deposition of supramolecular polymers. L. R. Hart, J. L. Harries, B. W. Greenland, H. M. Colquhoun and W. Hayes, *Polymer Chemistry*, **2015**, *6*, 7342-7352.

Mesomorphic behaviour in copoly(ester-imide)s of poly(butylene-2,6-naphthalate) (PBN). S. M. Jones, S. J. Meehan, S. W. Sankey, W. A. MacDonald and H. M. Colquhoun, *Polymer*, **2015**, *69*, 66-72.

Perylene as an electron-rich moiety in healable, complementary  $\pi$ - $\pi$  stacked, supramolecular polymer systems. L. R. Hart, N. A. Nguyen, J. L. Harries, M. E. Mackay, H. M. Colquhoun and W. Hayes, *Polymer*, **2015**, *69*, 293-300.

Supramolecular materials for inkjet printing: self-assembling polymer networks. L.R. Hart, J.L. Harries, B.W. Greenland, H.M. Colquhoun and W. Hayes, *ACS Applied Materials and Interfaces*, **2015**, *7*, 8906-8914.

Cocrystalline copolyimides of poly(ethylene 2,6-naphthalate). S. J. Meehan, S. W. Sankey, S. M. Jones, W. A. MacDonald and H. M. Colquhoun, *ACS Macro Letters*, **2014**, *3*, 968-971.

Information-containing macromolecules. H. M. Colquhoun and J. F. Lutz, *Nature Chem.*, **2014**, *6*, 455-456.

Multivalency in healable supramolecular polymers: the effect of supramolecular cross-link density on the mechanical properties and healing of noncovalent polymer networks. L. R. Hart, J. H. Hunter, N. A. Nguyen, J. L. Harries, B.W. Greenland, M. E. Mackay, H. M. Colquhoun and W. Hayes, *Polym. Chem.*, **2014**, *5*, 3680-3688.

Pairwise assembly of organopalladium(II) units with cyanurato(3-) and trithiocyanurato(3-) ligands: formation of chiral Pd<sub>12</sub>, Pd<sub>10</sub> and Pd<sub>9</sub> cage-molecules. C. A. Murray, C. J. Cardin, B. W. Greenland, A. Swift and H. M. Colquhoun, *Inorg. Chem.*, **2013**, *52*, 10424-10430.

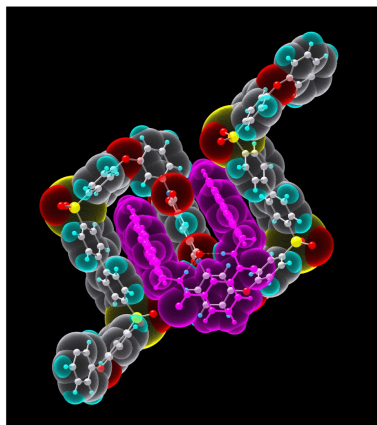
Molecular recognition between functionalized gold nanoparticles and healable, supramolecular polymer blends – a route to property enhancement. R. Vaiyapuri, B. W. Greenland, H. M. Colquhoun, J. M. Elliott and W. Hayes, *Polym. Chem.*, **2013**, *4*, 4902-4909.

Mutual binding of polymer end-groups by complementary  $\pi$ - $\pi$ -stacking: a molecular "Roman Handshake". B. W. Greenland, M. B. Bird, S. Burattini, R. Cramer, R.K. O'Reilly, J. P. Patterson, W. Hayes, C. J. Cardin and H. M. Colquhoun, *Chem. Commun.*, **2013**, *49*, 454-456.

A Microblock Ionomer in Proton Exchange Membrane Electrolysis for the Production of High Purity Hydrogen. D. W. Smith, F. O. Oladoyinbo, W. A. Mortimore, H. M. Colquhoun, M. S. Thomassen, A. Odegard, N. Guillet, E. Mayousse, T. Klicpera and W. Hayes, *Macromolecules*, **2013**, *46*, 1504-1511.

# Current Research Programme

## Information processing at the molecular level



**Figure 1.** Computational modelling of the interaction between a tweezer-type molecule (shown in purple) and an aromatic polyimide chain

Just as the information contained in a book is embodied in a linear sequence of letters, so the information needed for all living systems to function and reproduce is embodied in a linear sequence of chemical units – monomer residues – which make up the polymer chains of DNA and RNA. The digital information coded within the nucleic acids is read and acted upon by other molecules through *the recognition of specific monomer sequences* - the biological equivalent of reading a string of binary numbers from a magnetic tape. Our recent research has shown that information-processing at the molecular scale is not restricted to biological macromolecules, but can also be achieved, in principle, with entirely synthetic polymer systems. These new systems (copolymers based on aromatic polyimides) are unrelated to the nucleic acids and are vastly more stable. Figure 1 shows a computational model in which a tweezer-type molecule (in purple) binds to a specific, sequence of nine aromatic rings linked by ether, sulfone, biphenyl, and di-imide units within a designed copolyimide chain which folds tightly around the tweezer. We have obtained strong experimental evidence for this type of binding interaction from both solution NMR and from single-crystal X-ray studies in the solid state. The binding forces involved here are mainly associated with  $\pi$ - $\pi$  stacking interactions between the electron-rich tweezer arms and the electron-poor imide units in the polymer chain, but hydrogen bonding, identified in X-ray studies of model oligomer systems

also plays a significant role. Sequence-selectivity in binding is achieved through the introduction of minor variations in the environment of the di-imide tweezer-binding site. Such selectivity has been demonstrated by  $^1\text{H}$  NMR studies in which single resonances associated with specific sequences show very different responses to the presence of the tweezer-molecule. Striking changes in chemical shift are observed for "bound" sequences, but little effect is seen for more sterically-hindered sequences.

Current research in this area is aimed at understanding the emergence of fractal-based NMR spectra from complexes of random-sequence binary copolyimides with aromatic probe-molecules such as pyrene and perylene. Work with Dr Grau-Crespo has shown that the mathematical fractal underlying these spectra is the *fourth-quarter Cantor set*, and a graphical construction of this set is shown at right, indicating how it can be used to predict the  $^1\text{H}$  NMR spectrum of a random, binary copolymer in the presence of complexing pyrene molecules.

The construction involves dividing a line of unit length into four equal parts, discarding the fourth quarter, and repeating these operations on the remaining three segments. Iterating the construction an infinite number of times generates the final set. This type of analysis not only enables the pattern of chemical shifts to be predicted, but also their relative intensities. Moreover, it allows all resonances in the spectrum to be definitively assigned, as shown, to specific monomer-sequences or groups of sequences.

