

Editorial

# Supramolecular Chemistry in the 3rd Millennium

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The description of supramolecular chemistry as “chemistry beyond the molecule” (Jean-Marie Lehn, 1987 Nobel Lecture and Gautam R. Desiraju, *Nature*, **2001**, *412*, 397) encompasses the wide variety of weak, non-covalent interactions that are the basis for the assembly of supramolecular architectures, molecular receptors and molecular recognition, programmed molecular systems, dynamic combinatorial libraries, coordination networks and functional supramolecular materials. For this issue of *Chemistry*, the theme of “Supramolecular Chemistry in the 3rd Millennium” attracted eighteen contributions that cover a broad spectrum of supramolecular assemblies and exemplify the unity of contemporary multi-disciplinary science, in which organic, inorganic, physical and theoretical chemists work together with molecular biologists and physicists to develop a systems-level understanding of molecular interactions.

The issue features two reviews which focus, respectively, on supramolecular metallassemblies combining coordination and hydrogen bonds (Therrien) [1] and uranyl ion coordination compounds of polycarboxylates (Harrowfield and Thuéry) [2].

Supramolecular interactions are critical to selective binding within receptor molecules and host–guest chemistry, and several papers illustrate these principles using hydroquinone-based anion receptors (Gale and coworkers) [3], cucurbit[7]uril (Redshaw and coworkers) [4] and self-assembled *n*-alkyl-benzoureido-15-crown-5-ethers as selective ion-channels for K<sup>+</sup> cations (Barboiu and coworkers) [5]. Dalgarno and coworkers contribute with a fascinating investigation of cage assembly using *p*-<sup>t</sup>Bu-calix[4]arene building blocks [6]. Catalysis carried out within the confines of molecular or supramolecular cages is a topical area, and Ward and his coauthors describe a beautiful example exploiting a cubic M<sub>8</sub>L<sub>12</sub> coordination cage [7]. The assembly of highly symmetric metal–cyclo-tricathylene cages supported within a three-dimensional cubic hydrogen-bonded network is described by Abrahams and coworkers [8].

The introduction of sulfur atoms into ligands often leads to interesting supramolecular interactions. For example, close S...S contacts. Carballo, Belén Lago and coworkers illustrate the different supramolecular interactions that predominate in the structures of the copper(II) coordination compounds of two flexible bis-tetrazole organosulfur ligands [9]. Copper(II) coordination compounds containing Schiff base ligands have been designed by Marques Netto and coworkers as model systems to realize allosteric behavior by regulating the equilibrium between monomeric and dimeric species [10].

Supramolecular interactions play a vital role in the assembly of molecular helicates, and it is therefore fitting that this area of chemistry is represented in this themed issue – the assembly of enantiopure M<sub>4</sub>L<sub>4</sub> helicates is described in a study from Turner and coworkers [11]. Moving from multinuclear helicates to coordination polymers takes us on to contributions that describe supramolecular assemblies containing trinuclear copper(II)–pyrazolato units (Raptis, Boudalis, Herchel and coworkers) [12] and chloro-substituted pyrazin-2-aminocopper(I) assemblies featuring hydrogen bond and halogen bond interactions (Mailman, Rissanen and coworkers) [13]. Halogen bonds are a relatively new addition to the array of supramolecular interactions and also feature in the assembly of architectures comprising tetrakis(4-(iodoethynyl)phenyl)methane and 1,3,5,7-tetrakis(4-(iodoethynyl)phenyl)adamantane building blocks (Aakeröy and coworkers) [14]. This



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work nicely illustrates the potential for halogen bonding in the assembly of porous molecular solids. Bourne and coworkers report a series of cobalt- or zinc-based metal organic frameworks (MOFs) containing pyridylbenzoate linkers [15]. The three-dimensional assemblies comprise non-interpenetrated frameworks that retain their structure upon activation under vacuum, and the study extends to the sorption capacity of the assemblies and their selectivity for volatile organic compounds (VOCs).

Cocrystallization and polymorphism, respectively, are the topics of articles from Merz and coworkers [16] and from Baisch, Vella-Zarb and coworker [17]. This latter article presents an interesting holistic crystallographic study of the antiviral ganciclovir. Baisch and Vella-Zarb also present the crystal structure of *N,N',N'',N'''*-tetraisopropylpyrophosphoramidate and compare the supramolecular interactions with those found in the solid-state structures of other pyrophosphoramidates [18].

The range of topics in this themed issue of *Chemistry* illustrates the diverse nature of the research areas which depend upon supramolecular interactions, and I am grateful to all the authors who contributed to this issue.

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## References

1. Therrien, B. Combining Coordination and Hydrogen Bonds to Develop Discrete Supramolecular Metalla-Assemblies. *Chemistry* **2020**, *2*, 565–576. [[CrossRef](#)]
2. Harrowfield, J.; Thuéry, P. Uranyl Ion Complexes of Polycarboxylates: Steps towards Isolated Photoactive Cavities. *Chemistry* **2020**, *2*, 63–79. [[CrossRef](#)]
3. McNaughton, D.; Fu, X.; Lewis, W.; D'Alessandro, D.; Gale, P. Hydroquinone-Based Anion Receptors for Redox-Switchable Chloride Binding. *Chemistry* **2019**, *1*, 80–88. [[CrossRef](#)]
4. Xu, W.; Zhu, X.; Bian, B.; Xiao, X.; Tao, Z.; Redshaw, C. A Study of the Interaction between Cucurbit[7]uril and Alkyl Substituted 4-Pyrrolidinopyridinium Salts. *Chemistry* **2020**, *2*, 262–273. [[CrossRef](#)]
5. Li, Y.; Zheng, S.; Wang, D.; Barboiu, M. Selective Proton-Mediated Transport by Electrogenic  $K^+$ -Binding Macrocycles. *Chemistry* **2020**, *2*, 11–21. [[CrossRef](#)]
6. Coletta, M.; Palacios, M.; Brechin, E.; Dalgarno, S. A Brucite-Like Mixed-Valent Cluster Capped by  $[Mn^{III}p\text{-}t\text{-}Bu\text{-}calix[4]arene]^-$  Moieties. *Chemistry* **2020**, *2*, 253–261. [[CrossRef](#)]
7. Mozaceanu, C.; Taylor, C.; Piper, J.; Argent, S.; Ward, M. Catalysis of an Aldol Condensation Using a Coordination Cage. *Chemistry* **2020**, *2*, 22–32. [[CrossRef](#)]
8. Holmes, J.; Russell, S.; Abrahams, B.; Hudson, T.; White, K. Complementarity in Cyclotricatechylene Assemblies: Symmetric Cages Linked within 3D Cubic Hydrogen Bonded Networks. *Chemistry* **2020**, *2*, 577–590. [[CrossRef](#)]
9. Gómez-Paz, O.; Carballo, R.; Lago, A.; Vázquez-López, E. Metallosupramolecular Compounds Based on Copper(II/I) Chloride and Two Bis-Tetrazole Organosulfur Ligands. *Chemistry* **2020**, *2*, 33–49. [[CrossRef](#)]
10. Castro, C.; Silveira, R.; Colombari, F.; de Moura, A.; Nascimento, O.; Marques Netto, C. Solvent Effect on the Regulation of Urea Hydrolysis Reactions by Copper Complexes. *Chemistry* **2020**, *2*, 525–544. [[CrossRef](#)]
11. Boer, S.; Cao, W.; Glascott, B.; Turner, D. Towards a Generalized Synthetic Strategy for Variable Sized Enantiopure  $M_4L_4$  Helicates. *Chemistry* **2020**, *2*, 613–625. [[CrossRef](#)]
12. Shi, K.; Mathivathanan, L.; Herchel, R.; Boudalis, A.; Raptis, R. Supramolecular Assemblies of Trinuclear Copper(II)-Pyrazolato Units: A Structural, Magnetic and EPR Study. *Chemistry* **2020**, *2*, 626–644. [[CrossRef](#)]
13. Mailman, A.; Puttreddy, R.; Lahtinen, M.; Svahn, N.; Rissanen, K. Hydrogen and Halogen Bond Mediated Coordination Polymers of Chloro-Substituted Pyrazin-2-Amine Copper(I) Bromide Complexes. *Chemistry* **2020**, *2*, 700–713. [[CrossRef](#)]
14. Gunawardana, C.; Sinha, A.; Reinheimer, E.; Aakeröy, C. From Frustrated Packing to Tecton-Driven Porous Molecular Solids. *Chemistry* **2020**, *2*, 179–192. [[CrossRef](#)]
15. Ndamyabera, C.; Zacharias, S.; Oliver, C.; Bourne, S. Solvatochromism and Selective Sorption of Volatile Organic Solvents in Pyridylbenzoate Metal-Organic Frameworks. *Chemistry* **2019**, *1*, 111–125. [[CrossRef](#)]
16. Komisarek, D.; Schauerte, C.; Merz, K. Controlled Stepwise Synthesis and Characterization of a Ternary Multicomponent Crystal with 2-Methylresorcinol. *Chemistry* **2020**, *2*, 93–100. [[CrossRef](#)]
17. Spiteri, L.; Baisch, U.; Vella-Zarb, L. Understanding Conformational Polymorphism in Ganciclovir: A Holistic Approach. *Chemistry* **2021**, *3*, 126–137. [[CrossRef](#)]
18. Micallef, D.; Vella-Zarb, L.; Baisch, U. Exploring the Structural Chemistry of Pyrophosphoramidates: *N,N',N'',N'''*-Tetraisopropylpyrophosphoramidate. *Chemistry* **2021**, *3*, 149–163. [[CrossRef](#)]