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Two-Dimensional Supramolecular Chemistry on Surfaces

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Supramolecular chemistry represents one of the central themes of modern chemical sciences. Crossing traditional boundaries of chemistry, materials science, biology, and physics, the field of supramolecular chemistry affords opportunities to create new molecules and materials, with far reaching implications for many and diverse applications. The significance of supramolecular chemistry lies behind two Nobel Prizes, 1987 [1] and 2016 [2–4], and is now not only a field in its own right but is also a central underpinning theme in almost any area of chemistry. The primary principle of supramolecular chemistry is the use of non-covalent interactions to create and control self-assembled structures. A large range of interactions is available to the supramolecular chemist to influence and control self-assembly processes. From hydrogen bonds [5–7] and halogen bonds [8, 9] to π-interactions [10, 11], coordination bonds [12, 13] and the mechanical bond [2, 3, 14–16], interactions of different strengths and varying degrees of geometrical preferences are available to design and create structures. When in its infancy, supramolecular chemistry focussed predominantly on synthetic strategies in combination with understanding the fundamental properties of the non-covalent interactions employed. Over recent years, the field has developed to such an extent that it is now commonplace to focus effort towards applications and these range across a vast spectrum. Supramolecular chemistry is so wide-ranging that its relevance can be applied to diverse fields, from biology [17, 18] and medicine [18, 19] to new materials [20, 21] and energy-related applications [22, 23].

The origins of supramolecular chemistry lie in solution-based systems, using intermolecular interactions to create supermolecules. From these origins, supramolecular chemistry is now observed in most phases, notably in the solid-state, through crystal engineering [24, 25], in liquid crystals [26] and ionic liquids [27], and even in the gas phase [28]. It was only natural that supramolecular chemistry strategies would come to be applied to the two-dimensional (2D) environment of surfaces (Figure 1.1). This seemingly natural progression also raised a number of challenges to practitioners of the subject, not least in terms of appreciating this quite different

environment and perhaps most importantly the different techniques that are used to characterise and interpret surface-based molecular systems.
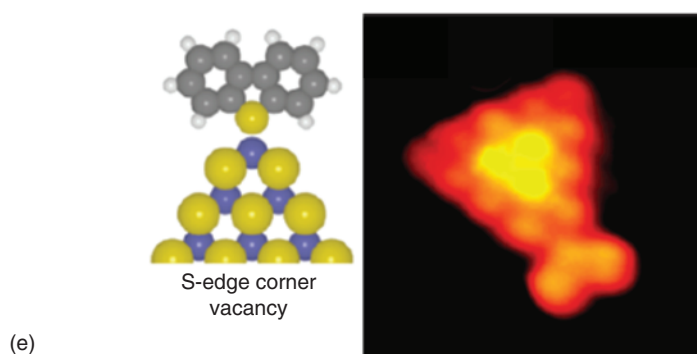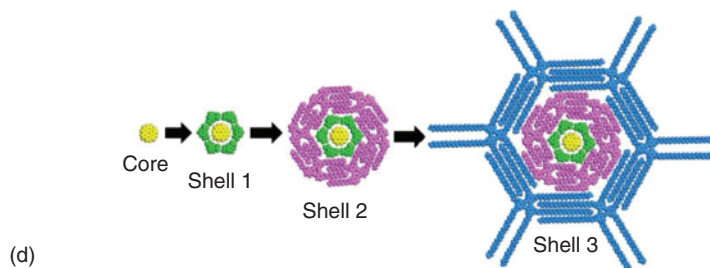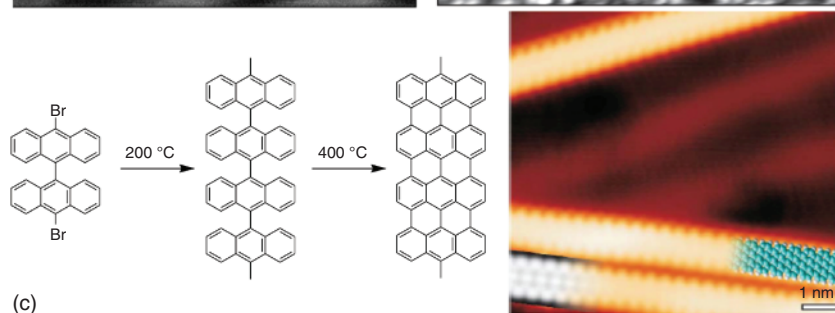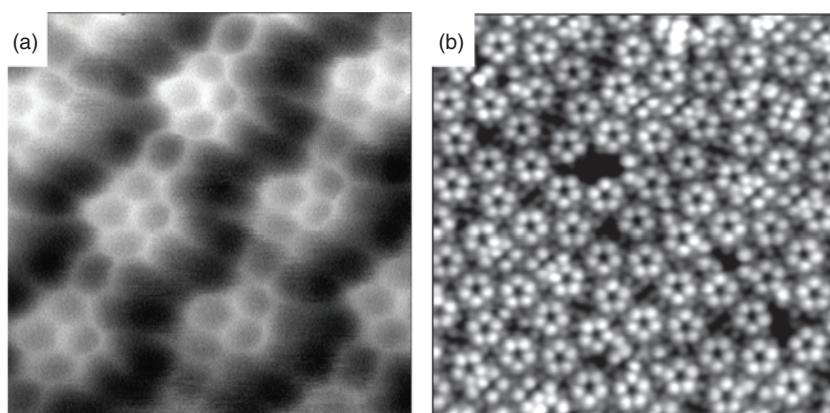

(a)

(b)

(c)

200 °C

400 °C

1 nm

(d)

Core

Shell 1

Shell 2

Shell 3

(e)

S-edge corner vacancy

Figure 1.1 Examples of two-dimensional supramolecular chemistry on surfaces discussed within this volume. (a) ncAFM image of a hydrogen-bonded naphthalene-1,4:5,8-tetracarboxylic diimide (NTCDI) island on a Ag:Si(111) − ($\sqrt{3} \times \sqrt{3}$) R30° surface acquired at 77 K. The image reveals sub-molecular details of the self-assembled structure; (b) STM image of self-assembled arrays of ferrocene-carboxylic acid (FcCOOH); each bright feature represents a separate FcCOOH molecule, which then assemble into pentamers highly reminiscent of a Penrose tiling arrangement; (c) Surface-assisted C−C coupling reaction used to prepare straight graphene nanoribbons from bianthryl monomers, including a STM image of nanoribbon, following cyclodehydrogenation at 400 °C, with partly overlaid molecular model (right in blue) and a density-functional theory model (bottom left in grey); (d) Schematic representation of a strategy used to prepare a multicomponent system using a 'core−shell' approach. Each colour represents a different molecular building block; (e) Schematic representation and STM image showing dibenzothiophene bound to the corner vacancy of a S-edge-terminated MoS_2 nanocluster. Source: Images reproduced with permission as follows: (a) Sweetman et al. [29]; (b) reproduced with permission from Springer Nature from Wasio et al. [30]; (c) reproduced with permission from Springer Nature from Cai et al. [31]; (d) Mali et al. [32]; (e) reprinted and adapted with permission from Tuxen et al. [33]. Copyright (2010) American Chemical Society.

Whereas the techniques applied to characterising solution phase, or solid-state, supramolecular systems are common across synthetic chemistry, for example, NMR spectroscopy, mass spectrometry, and X-ray diffraction, characterisation of surface-bound molecules is a quite distinct domain. The most common approaches to characterising molecular species on surfaces are scanning probe microscopies (SPM). Specifically, techniques such as scanning-tunnelling microscopy (STM) [34] and atomic force microscopy (AFM) [35] represent the dominant characterisation methods used in the analysis of surface-based supramolecular systems. These imaging microscopies can be, and often are, supplemented by other approaches, such as X-ray photoelectron spectroscopy (XPS), but SPM approaches provide invaluable insight into specific molecular arrangements allowing determination of the geometric structure of organic molecules with molecular resolution. More recently, the development of noncontact atomic force microscopy (ncAFM) [36] allows the characterisation of supramolecular systems with sub-molecular resolution [37]. The use of SPM characterisation techniques in itself presents opportunities, which are rarely available to those working in other phases, not least because such microscopies function at the molecular, or even sub-molecular, level and as a result information, both structural and electronic, can be gathered for individual molecules and defined self-assembled arrays. In comparison, techniques such as NMR spectroscopy or X-ray diffraction rely upon the signal from comparatively large numbers of molecules. Thus, the characterisation of surface-based supramolecular systems can give a detailed picture of the structures and even transformations between different arrangements with a high degree of resolution. The complexities, challenges, and advantages of different SPM techniques are discussed in more detail by Sweetman, Champness, and Saywell in this volume.

A further aspect of the detailed imaging with molecular resolution is that this allows characterisation of structures that would prove extremely challenging by any other technique. Using SPM techniques allows ready identification of defects within supramolecular arrays but intriguingly allows the study of extended structures,

which do not possess long-range order, with molecular resolution. This approach has been applied to the study of random, entropically stabilised, rhombus tilings [29, 38, 39], a molecular Penrose tile [30], quasicrystalline structures [40], and fascinating assemblies that exhibit the structure of Serpiński triangles [41]. The complex issues with studying and characterising quasicrystalline 2D arrays are discussed in detail by Kandel in this book.

The study of supramolecular chemistry on surfaces probably began with early studies of hydrogen-bonded assemblies [42–44] but has spread to employ other non-covalent interactions including coordination bonds [45, 46] and weaker van der Waals interactions [47–49]. The use of different intermolecular interactions is discussed throughout chapters in this volume. In particular, Mali, Teyssandier, Bilbao, and De Feyter discuss the use of hydrogen bonds and van der Waals interactions to create complex structures whereas the application of coordination bonds is presented by Lin and Liu. It will become clear to the reader that the choice of intermolecular interaction influences the choice of experimental conditions used, including deposition conditions, use of ultra-high vacuum (UHV) or studies at the solid–solution interface, and even the nature of the surface employed for surface self-assembly. The interactions between surface, substrate, solution, and self-assembled array are all important in determining the subtle energetic balance between different products [50].

These studies have now developed further to create covalently linked structures including nanographenes [51, 52] and covalent-organic frameworks (COFs) [53]. All of these strategies present their own distinct advantages, and disadvantages, but importantly represent a broad palette for researchers to employ and explore. Weaker interactions such as hydrogen bonds, van der Waals interactions, and even coordination bonds, form reversibly and therefore facilitate the formation of well organised, and relatively defect-free, supermolecule structures over comparatively large areas. Creating larger defect free structures can be more challenging using covalent bonds although the use of reversibly-formed bonds such as imines [54] has been developed to aid in this respect. Nanographenes, where carbon–carbon bonds are an absolute requirement, present quite different challenges but remarkable advances have been made in this area. In this volume Peng, Xing, and Wu discuss the use of intermolecular interactions to control on-surface reactions and Wang, Zhang, and Chi present developments in the field of on-surface reactions to create covalently bonded systems.

Another major challenge that requires thought when one considers surface-based supramolecular chemistry are the reaction environment and conditions. Firstly, it is typical to use a surface that is atomically flat or at least close to atomically flat. This rather stringent requirement facilitates the use of SPM characterisation and simultaneously controls the introduction of surface-based reactive sites to the self-assembly process. Even though atomically flat surfaces are commonly used, it would be a mistake to consider the surface as an innocent bystander in the self-assembly process. Indeed, adsorption between the surface and the molecules involved in self-assembly is essential to allow the formation of a surface-bound or surface-supported, supramolecular structure [50]. A range of surfaces are available to researchers

investigating such systems but some are more common than others, notably highly-oriented pyrolytic graphite (HOPG) and Au(111). However, in some areas of study, the surface plays an integral role in the reaction process providing active sites, such as metal atoms, which catalyse the formation of a specific product [55].

The other major aspect that influences the self-assembly process is the experimental conditions of the experiment. SPM techniques can be used in both UHV conditions or at the interface between surface and solution. These quite different conditions present both advantages and disadvantages depending on the specific molecules and reaction processes being investigated. For example, studying molecules and self-assembled aggregates in UHV conditions can lead to higher resolution imaging, in part because lower temperatures (below the freezing point of solvents) can be accessed. Additionally, ncAFM imaging specifically requires UHV conditions. However, the introduction of molecules to the surface typically involves sublimation, and hence heating of the sample. Sublimation is not always possible and thermal degradation is a significant impediment for complex molecules. Milder electrospray deposition techniques have been developed [56] but the use of this approach is not yet widespread. In contrast, studies at the solution-solid interface directly image self-assembled structures in the presence of solvent. In terms of preparative conditions, this approach is quite straightforward, simply imaging at the interface between a drop of solvent containing the molecules of interest and the substrate. Although this approach offers many advantages the choice of solvent, which is limited by the requirements for imaging, can clearly influence the self-assembly process, potentially with solvent molecules interacting or even co-adsorbing with the target species. Although images tend to have lower resolution than UHV studies, this is not always the case and remarkable examples of molecular resolution with AFM have been reported [49].

Ultimately, the possibilities that arise from the various approaches to create supramolecular structures suggest the possibility of creating molecular level devices and the application of 2D materials. The advances in this area are illustrated in the chapter by Huang and Wee where they discuss the rapidly advancing field that studies 2D transition metal dichalcogenides and their potential integration with organic molecules for multifunctional flexible devices.

This book brings together perspectives from research leaders in the field. It can be seen that across the breadth of the subject, there are many fascinating examples of applying supramolecular chemistry to the development of surface-based arrays. Whether through the direct implementation of hydrogen bonds, coordination bonds, or well-designed van der Waals interactions, or through the controlled formation of covalently-bonded arrays, it is clear that strategies for creating 2D arrays on surfaces are well developed. A theme that commonly arises throughout the contributions is that of complexity. It is not a surprise that this subject has become prominent in the field of surface-based supramolecular arrays when one considers the specificity of the SPM characterisation techniques employed for characterisation. When one applies a technique that affords molecular resolution, allowing detailed appreciation of extended frameworks, their complexity becomes all the more apparent, drawing the attention of researchers and hence becoming a

focus for investigation. Remarkable discoveries have been made across the field and in turn, spur new endeavours. An emerging aspect of the field is the implementation of synthetic strategies towards new applications with electronic properties of new structures receiving notable attention. However, other directions of research are also emerging at the solid–solution interface, for example, applying the chirality of surface arrays. Exploiting the interplay between surface-based arrays and solution chemistry promises to be of significance in applications ranging from sensing to the interface with biological processes.

In summary, as is common for new areas of science, the field now stands at a crossroads. The origins of the field have been based on developing an underpinning methodology for both synthesis and characterisation and an appreciation of the many factors that affect surface-based supramolecular assembly. Increasingly, there is a focus on developing these fascinating 2D materials for specific applications and for their incorporation into devices. I am confident that all the authors of the other chapters will agree that there is a promising and bright future for the area of 2D chemistry on surfaces.

References

1 Lehn, J.-M. (1988). *Angew. Chem. Int. Ed. Engl.* 27: 89–112.
2 Stoddart, J.F. (2017). *Angew. Chem. Int. Ed.* 56: 11094–11125.
3 Sauvage, J.-P. (2017). *Angew. Chem. Int. Ed.* 56: 11080–11093.
4 Feringa, B.L. (2017). *Angew. Chem. Int. Ed.* 56: 11060–11078.
5 Li, Z.T. and Wu, L.Z. (eds.) (2015). *Hydrogen Bonded Supramolecular Materials*. Heidelberg: Springer.
6 Prins, L.J., Reinhoudt, D.N., and Timmerman, P. (2001). *Angew. Chem. Int. Ed.* 40: 2382–2426.
7 Gonzalez-Rodriguez, D. and Schenning, A.P.H.J. (2011). *Chem. Mater.* 23: 310–325.
8 Metrangolo, P., Meyer, F., Pilati, T. et al. (2008). *Angew. Chem. Int. Ed.* 47: 6114–6127.
9 Gilday, L.C., Robinson, S.W., Barendt, T.A. et al. (2015). *Chem. Rev.* 115: 7118–7195.
10 Hunter, C.A. and Sanders, J.K.M. (1990). *J. Am. Chem. Soc.* 112: 5525–5534.
11 Bauzá, A., Deyà, P.M., and Frontera, A. (2015). Anion-π interactions in supramolecular chemistry and catalysis. In: *Noncovalent Forces, Challenges and Advances in Computational Chemistry and Physics*, vol. 19 (ed. S. Scheiner), 471–500. New York: Springer.
12 Chakrabarty, R., Mukherjee, P.S., and Stang, P.J. (2011). *Chem. Rev.* 111: 6810–6918.
13 Lanigan, N. and Wang, X. (2013). *Chem. Commun.* 49: 8133–8144.
14 Stoddart, J.F. (2009). *Chem. Soc. Rev.* 38: 1802–1820.
15 Bąk, K.M., Porfyrakis, K., Davis, J.J., and Beer, P.D. (2020). *Mater. Chem. Front.* 4: 1052–1073.

16 Mena-Hernando, S. and Pérez, E.M. (2019). *Chem. Soc. Rev.* 48: 5016–5032.

17 Peng, H.-Q., Niu, L.-Y., Chen, Y.-Z. et al. (2015). *Chem. Rev.* 115: 7502–7542.

18 Williams, G.T., Haynes, C.J.E., Fares, M. et al. (2021). *Chem. Soc. Rev.* 50: 2737–2763.

19 Smith, D.K. (2018). *Chem. Commun.* 54: 4743–4760.

20 Stupp, S.I. and Palmer, L.C. (2014). *Chem. Mater.* 26 (1): 507–518.

21 Amabilino, D.B., Smith, D.K., and Steed, J.W. (2017). *Chem. Soc. Rev.* 46: 2404–2420.

22 Griffin, S.L. and Champness, N.R. (2020). *Coord. Chem. Rev.* 414: 213295.

23 Cordova, K.E and Yaghi, O.M. (2017). *Mater. Chem. Front.* 1: 1304–1309.

24 Desiraju, G.R. (2013). *J. Am. Chem. Soc.* 135: 9952–9967.

25 Aakeröy, C., Champness, N.R., and Janiak, C. (2010). *CrystEngComm* 12: 22–43.

26 Saez, I.M. and Goodby, J.W. (2005). *J. Mater. Chem.* 15: 26–40.

27 Hayes, R., Warr, G.G., and Atkin, R. (2015). *Chem. Rev.* 115: 6357–6426.

28 Schalley, C.A. (2000). *Int. J. Mass Spectrom.* 194: 11–39.

29 Blunt, M.O., Russell, J., Giménez-López, M.C. et al. (2008). *Science* 322: 1077–1081.

30 Wasio, N.A., Quardokus, R.C., Forrest, R.P. et al. (2014). *Nature* 507: 86–89.

31 Cai, J., Ruffieux, P., Jaafar, R. et al. (2010). *Nature* 466: 470–473.

32 Mali, K.S., Pearce, N., De Feyter, S., and Champness, N.R. (2017). *Chem. Soc. Rev.* 46: 2520–2542.

33 Tuxen, A., Kibsgaard, J., Gøbel, H. et al. (2010). *ACS Nano* 4: 4677–4682.

34 Binnig, G., Rohrer, H., Gerber, C., and Weibel, E. (1982). *Appl. Phys. Lett.* 40: 178–180.

35 Binnig, G., Quate, C.F., and Gerber, C. (1986). *Phys. Rev. Lett.* 56: 930–933.

36 Gross, L., Mohn, F., Moll, N. et al. (2009). *Science* 325: 1110–1114.

37 Sweetman, A.M., Jarvis, S.P., Sang, H. et al. (2014). *Nat. Commun.* 5: 3931.

38 Stannard, A., Russell, J.C., Blunt, M.O. et al. (2012). *Nat. Chem.* 4: 112–117.

39 Steeno, R., Minoia, A., Gimenez-Lopez, M.C. et al. (2021). *Chem. Commun.* 57: 1454–1457.

40 Urgel, J.I., Écija, D., Lyu, G. et al. (2016). *Nat. Chem.* 8: 657–662.

41 Shang, J., Wang, Y., Chen, M. et al. (2015). *Nat. Chem.* 7: 389–393.

42 Barth, J.V., Weckesser, J., Cai, C. et al. (2000). *Angew. Chem. Int. Ed.* 39: 1230–1234.

43 Griessl, S., Lackinger, M., Edelwirth, M. et al. (2002). *Single Mol.* 3: 25–31.

44 Theobald, J.A., Oxtoby, N.S., Phillips, M.A. et al. (2003). *Nature* 424: 1029–1031.

45 Stepanow, S., Lingenfelder, M., Dmitriev, A. et al. (2004). *Nat. Mater.* 3: 229–233.

46 Dong, L., Gao, Z., and Lin, N. (2016). *Prog. Surf. Sci.* 91: 101–135.

47 Elemans, J.A.A.W., Lei, S., and Feyter, S.D. (2009). *Angew. Chem. Int. Ed.* 48: 7298–7332.

48 Elemans, J.A.A.W., De Cat, I., Xu, H., and De Feyter, S. (2009). *Chem. Soc. Rev.* 38: 722–736.

49 Tobe, Y., Tahara, K., and De Feyter, S. (2021). *Chem. Commun.* 57: 962–977.

50 Song, W., Martsinovich, N., Heckl, W.M., and Lackinger, M. (2013). *J. Am. Chem. Soc.* 135: 14854–14862.

51 Narita, A., Wang, X.-Y., Feng, X., and Müllen, K. (2015). *Chem. Soc. Rev.* 44: 6616–6643.

52 Song, S., Su, J., Telychko, M. et al. (2021). *Chem. Soc. Rev.* 50: 3238–3262.

53 Jin, Y., Hu, Y., Ortiz, M. et al. (2020). *Chem. Soc. Rev.* 49: 4637–4666.

54 Xu, L., Zhou, X., Yu, Y. et al. (2013). *ACS Nano* 7: 8066–8073.

55 Judd, C., Haddow, S.L., Champness, N.R., and Saywell, A. (2017). *Sci. Rep.* 7: 14541.

56 Saywell, A., Magnano, G., Satterley, C.J. et al. (2010). *Nat. Commun.* 1: 75.