# Universal aspects of self-assembly: The wide domain of weak interactions

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**Supramolecular self-assembly in organic and inorganic molecular systems, occurring through weak interactions such as hydrogen bonding, is well-documented. Self-assembly of low-dimensional structures generates three-dimensional structures in some of the complex inorganic systems. More importantly, self-assembly of objects occurs over a wide range of sizes, from a nanometer to several millimeters, although the process appears to occur over limited areas or volumes in large mm-sized objects. What appears to be universal about self-assembly in these disparate systems is the dominance of weak interactions.**

## Introduction

Supramolecular chemistry based on the self-assembly of molecular units has provided a powerful means for designing molecular systems with novel structures and properties[1,2]. Hydrogen bonding is, by far, the most common interaction encountered in supramolecular organic structures, but van der Waals and such weak interactions play an important role as well, as exemplified by nitro ... iodo and iodo ... iodo type interactions. While hydrogen bond energies are generally around 3–5 kcal mol$^{-1}$, van der Waals interaction involves even smaller energies, of the order of 1 kcal mol$^{-1}$. We show two typical supramolecular organic systems in Figures 1 and 2 to exemplify the nature of interactions in these materials. Supramolecular organic chemistry has matured to the extent that one is able to recognize basic structural units or synthons responsible for the assembly[3]. Supramolecular inorganic systems are also being discovered constantly[2]. The formation of complex supramolecular inorganic structures such as the zeolites and other open-framework structures is likely to involve self-assembly, accompanying other processes. It is, however, difficult to pin down the basic structural units involved in the building of these structures[4,5]. There has been some success recently in unravelling the building-up process in open-framework metal phosphates[6]. It is noteworthy that the phenomenon of self-assembly is not restricted to molecular systems alone. It occurs in colloidal systems with particles in the size range of 1–2000 nm. Self-assembly of millimeter-sized objects also yields two- and three-dimensional ordered arrangements[7]. The occurrence of self-assembly in a large variety of objects of varied dimensions between 0.1 and $10^7$ nm reflects the universal nature of the phenomenon. That self-assembly over the entire range of sizes is governed by weak interactions makes the phenomenon even more fascinating (see Table 1). We shall examine certain of these universal aspects of self-assembly in this article.

## Extended inorganic structures

Let us first examine the role of self-assembly in the formation of complex inorganic structures. Müller and
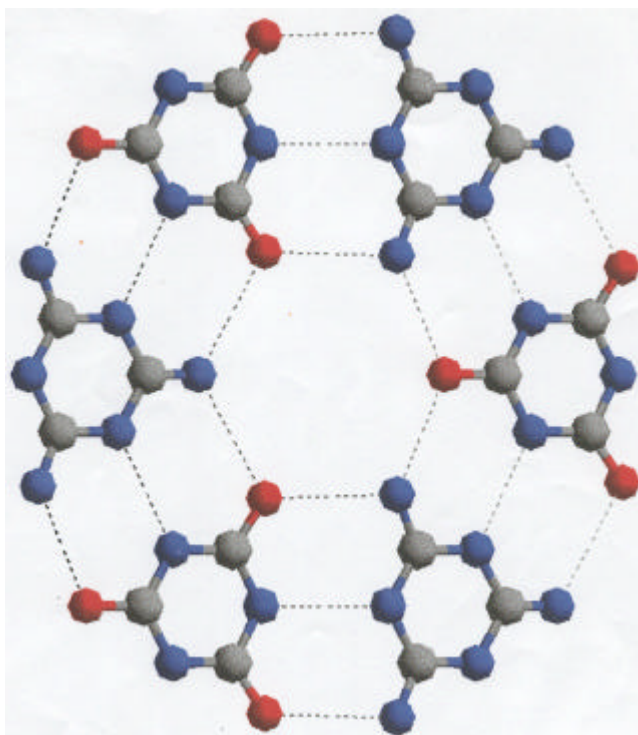


**Figure 1.** The rosette structure of the hydrogen-bonded adduct of cyanuric acid and melamine. Notice that all hydrogen bonding possibilities have been exploited in forming the structure (from Ranganathan, Pedireddi and Rao, *J. Am. Chem. Soc.*, 1999, **121**, 1752).
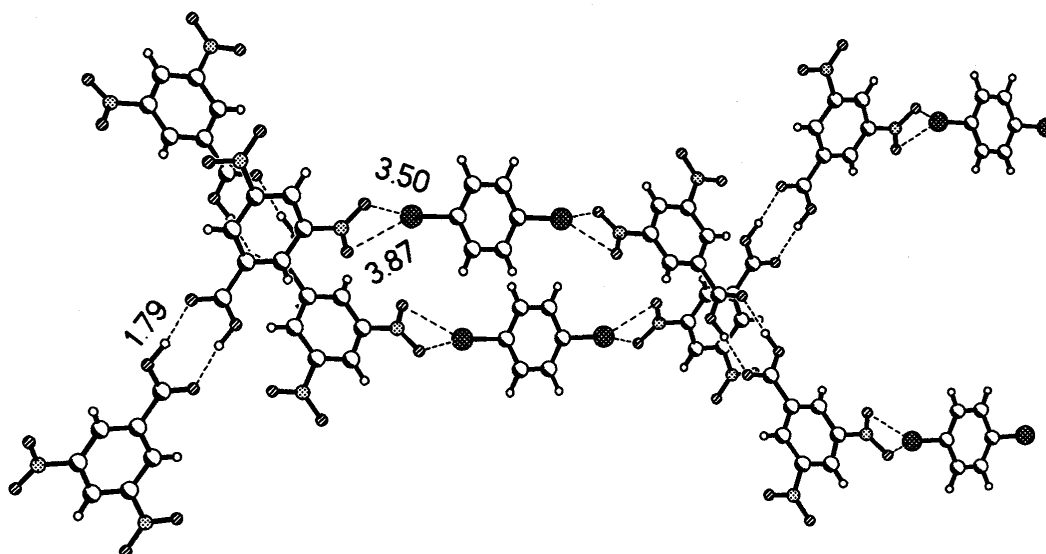
**Figure 2.** Arrangement of molecules in a complex of 3,5-dinitrobenzoic acid and 4-diiodobenzene (from Ranganathan and Pedireddi, *Tetrahedron Lett.*, 1998, **39**, 1803).
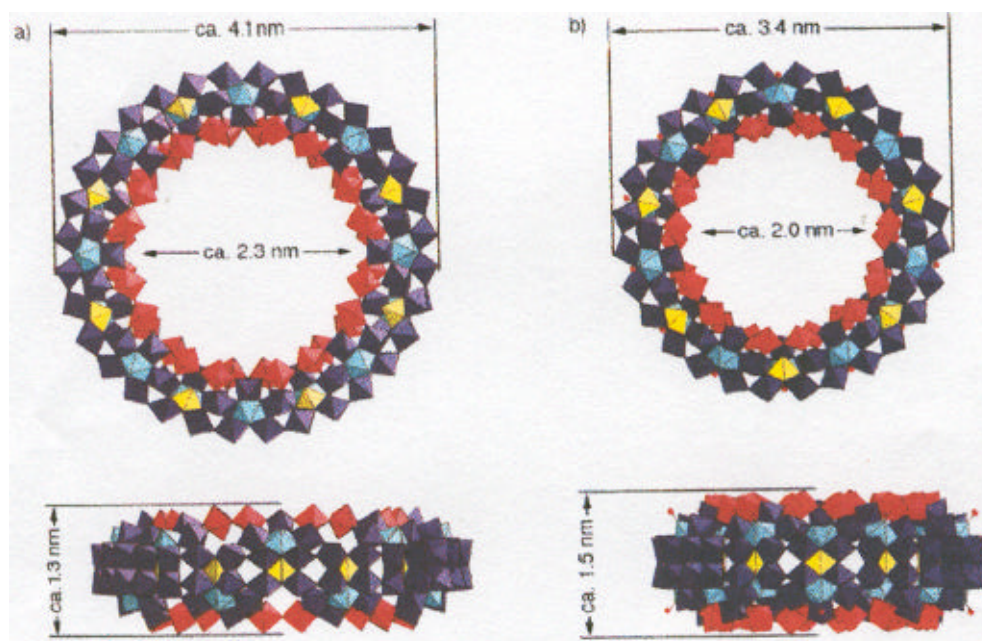


**Figure 3.** Polyhedral representation of the oxomolybdates, *a*, $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$; *b*, $[Mo_{154}(NO)_{14}O_{448}(H_2O)_{70}H_{28}]$ (ref. 14). Views from the top and the side are both shown (from Müller *et al.*[4b]).

coworkers[8] have reported polyoxomolybdates forming giant wheel-clusters of 3–4 nm diameter (Figure 3). These fascinating structures are not likely to be formed by conventional mechanisms involving the making and breaking of one bond at a time. Then, is there a basic building unit which transforms or/and self-assembles to produce these structures? There is no clear answer to such a question. A system which has shown some promise in this direction is the family of open-framework metal phosphates. A large number of these phosphates

have been prepared and characterized in recent years[9]. They occur with different dimensionalities, the three-dimensional (3D) structures with channels being the most common (Figure 4). The one-dimensional (1D) phosphates generally exist as chains or ladders formed by four-membered rings. These materials are generally prepared under hydrothermal conditions in the presence of an organic amine which acts as a template or a structure-directing agent. The amine may also directly participate in the formation of open-architectures through
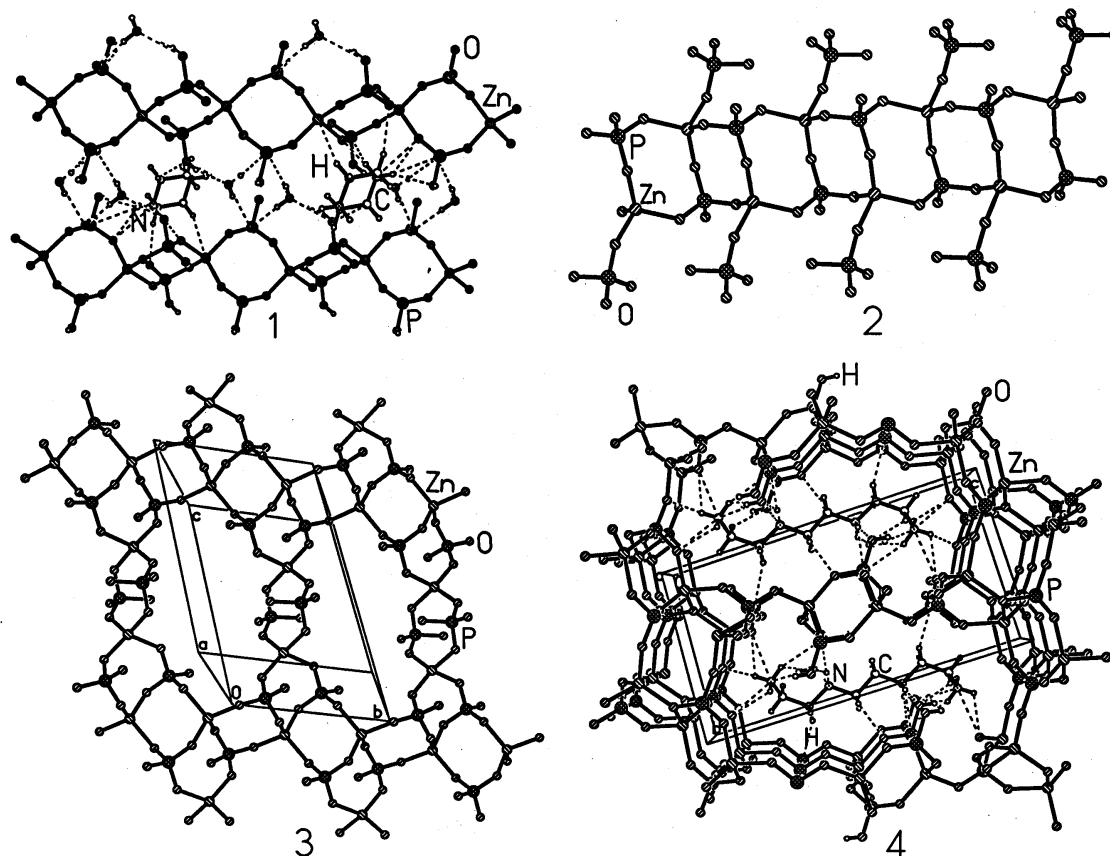
**Figure 4.** Open-framework zinc phosphates of different dimensionalities: 1, 1D (linear chain); 2, 1D (ladder); 3, 2D (layer); 4, 3D (with channels) (from Rao et al.[6a]).
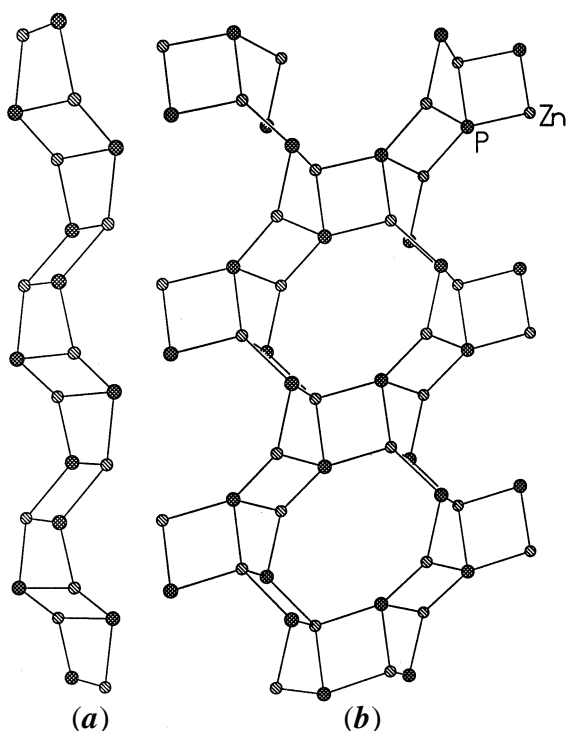


**Figure 5.** This figure illustrates how a zinc phosphate with a one-dimensional ladder structure (*a*), can transform to a three-dimensional open frame-work zinc phosphate with gismondine structure (*b*).

**Table 1.** Ranges of sizes and interaction energies in self-assembling systems

| Unit (size range) | Interaction | Interaction energy (kcal mol$^{-1}$) |
|---|---|---|
| Molecules (≤ 1 nm) | Hydrogen bond | 3–5 |
| | van der Waals | 1 |
| | dipolar | 1 |
| Metal/semiconductor nanocrystals (nm) | Capillary (van der Waals) | 1 |
| Long-chain molecules (nm) | Hydrophobic | 1 |
| PMMA or silica spheres (nm–μm) | Capillary | 1 |
| Carbon nanotubes (nm–μm) | van der Waals | 1 |
| Millimeter sized objects | van der Waals hydrophobic | 1 |

amine phosphate intermediates[10]. It is not uncommon to obtain several open-framework phosphates in the same synthesis and with the same amine. Zero-dimensional monomeric phosphates comprising a four-membered ring (formed by the metal and phosphorus atoms) have been isolated recently, and there is some evidence to indicate that the zero-D or/and 1D phosphates may be the basic building units of the complex open architectures[6]. Accordingly, the zero-D and 1D structures transform under simple reaction conditions and at moderate

temperatures to the 2D and 3D structures. The observation of such a building-up process from low-dimensional (0D/1D) structures to 3D structures in the open-framework phosphates appears to be the first example of its kind in supramolecular chemistry. Although the building-up process may involve steps such as hydrolysis, deprotonation of phosphoric acid, insertion of metal ions and bond rotation, there is reason to believe that self-assembly occurs in the building-up process. Thus, the 3D structures obtained as products often possess elements of the 1D structure as illustrated in Figure 5.

*In-situ* synchrotron X-ray diffraction studies have shown evidence for the occurrence of spontaneous assembly of a precursor state (possibly a 0D or a 1D structure) to yield a 3D open-framework phosphate[11]. It is plausible that a similar assembly of basic building units occurs in aluminosilicates as well. Considering the nature of these inorganic structures, it appears unlikely that the organized assembly of complex structures occurs starting from simple polyhedral units such as the $SiO_4$ and $PO_4$ tetrahedra and metal–oxygen octahedra. It is more likely that the starting point of the self-assembly is a chain, a ladder or some such unit formed by the polyhedra. The formation of several open-framework structures in the same synthesis as well as the self-assembly of basic building units may be favoured by the comparable energies of the different structures and by the kinetic control of the transformations. Self-assembly also appears to occur in the formation of open-framework metal oxalates and the presence of a hierarchy of structures, from monomer (0D) and chain (1D) structures to the 3D structure, has been established[12]. Self-assembly in these extended inorganic
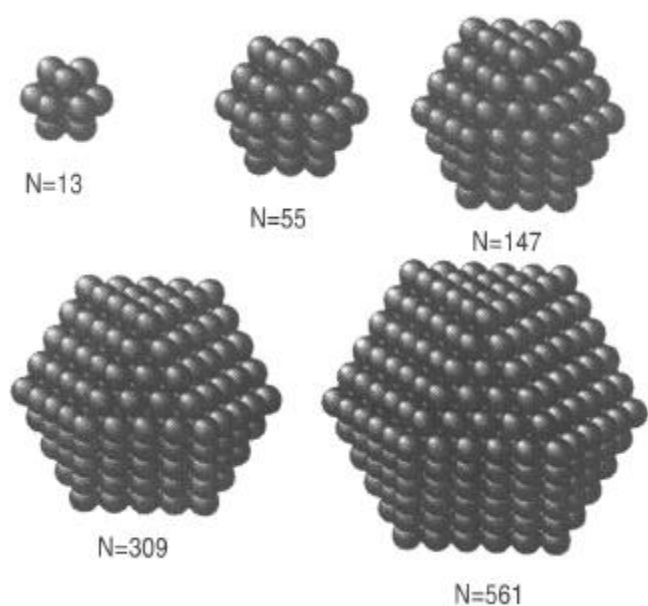
structures is, however, not as straight-forward as in supramolecularly organized molecular compounds
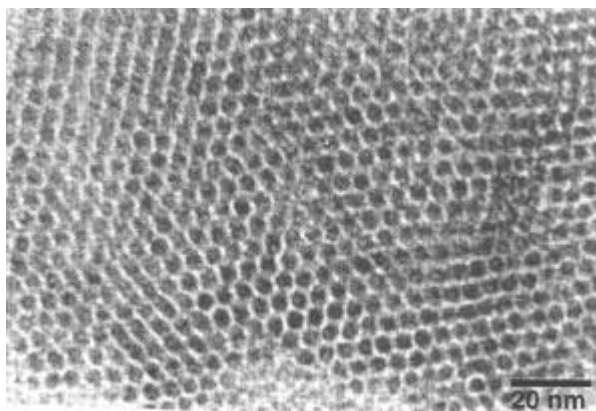


**Figure 7.** Crystalline array of thiolized Pd nanocrystals of 3.2 nm diameter containing 1415 atoms (from Rao *et al.*[16a]).
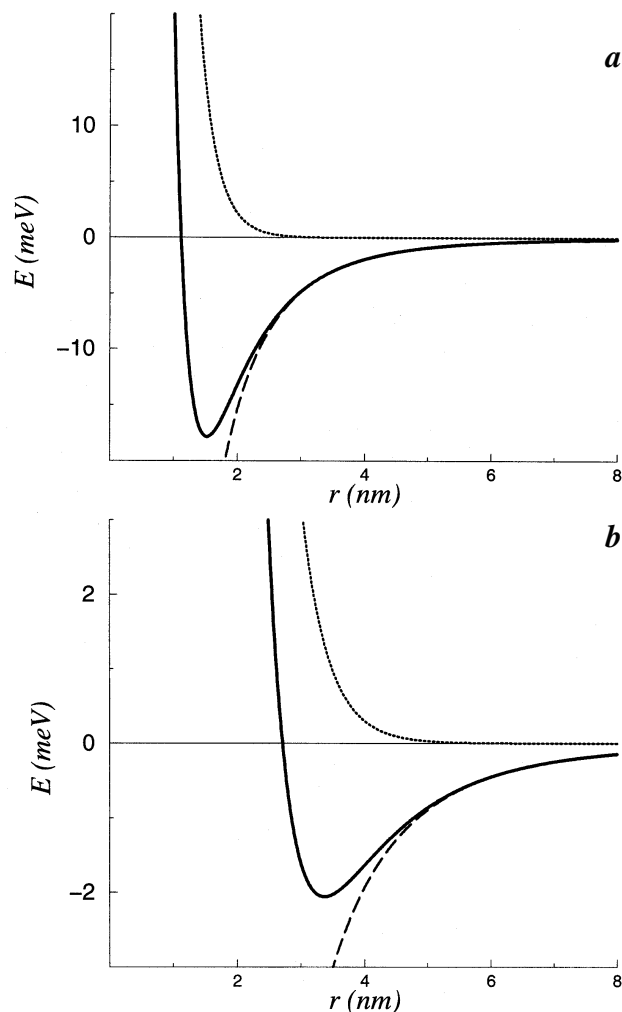




**Figure 8.** Potential energy curves for the interaction of 4.5 nm nanocrystals with (*a*) octanethiol and (*b*) dodecanethiol as spacers. The attractive and repulsive parts are also shown (from Thomas *et al.*[16a]).
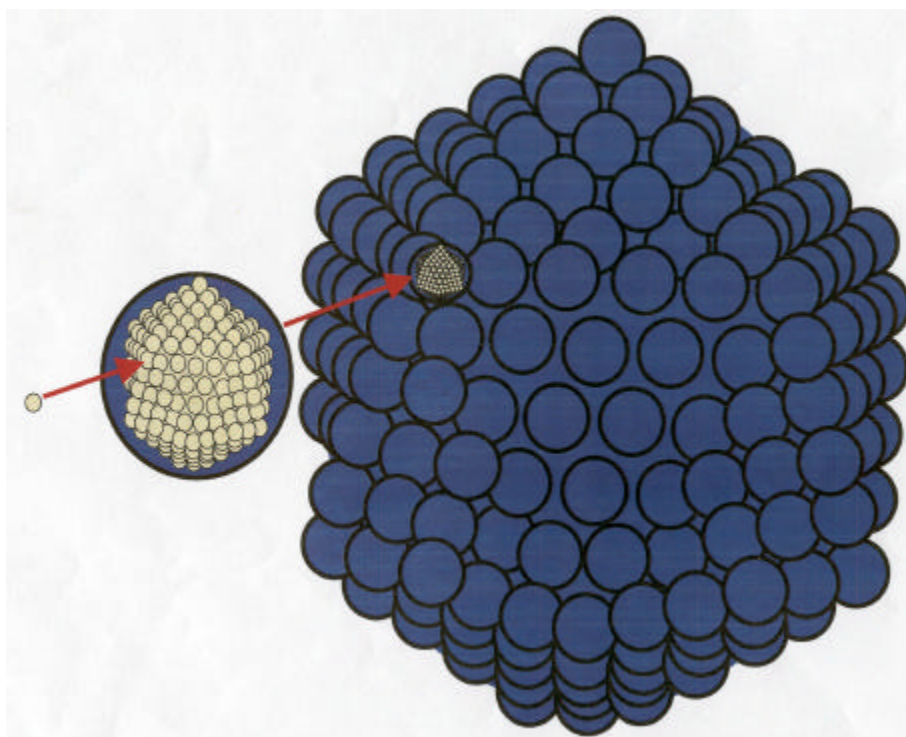


**Figure 6.** Clusters containing magic numbers of particles.

**Figure 9.** Figure showing how a $Pd_{561}$ nanocrystal (~ 2.5 nm dia) is formed starting from Pd atoms and how the $Pd_{561}$ nanocrystals then aggregate to give a giant nanocrystal containing 561 $Pd_{561}$ nanocrystals.

wherein hydrogen bonding or some other form of weak interaction binds the different molecular units.

The open-framework metal phosphates discussed above belong to the family of nanoporous solids with pores or channels of 0.6–2 nm diameter. Mesoporous solids with pores of 2–20 nm obtained by surfactant templating[13], are examples of self-assembly and biomimicry. The diameter of the channels in hexagonal mesoporous solids can be increased by adding hydrocarbons to the surfactants during the synthesis. Supramolecular organization of linear alkanes with respect to the surfactant molecules has been found to be responsible for the expansion of pore size[14]. The structure of the mesoporous solid (layered, hexagonal or cubic) itself depends on the concentration of the surfactant and the nature of its organization[15].

## Metal nanocrystals (0.1–100 nm regime)

We can learn much about the nature of the self-assembly of objects, by examining some of the recent results in the case of metal nanocrystals. It is well known that metal atoms aggregate to form clusters or nanocrystals with magic numbers of atoms, depending on the number of shells of close-packed atoms in the nanocrystal[16]. The magic numbers 13, 55, 147, 309 and 561 correspond to closed shells of 1, 2, 3, 4 and 5 respectively (Figure 6). Clusters of the type shown in

Figure 6 are formed by argon and fullerene $C_{60}$ as well, suggesting a commonality in the nature of interactions responsible for the formation of clusters of spherical objects. The metal nanocrystals tend to possess the icosahedral structure, and the detailed atomic arrangements in them are revealed by high-resolution electron microsocopy. Nanocrystals of metals and semiconductors form crystalline 2D arrays when they are treated with alkanethiols or alkanecarboxylic acids[17]. In Figure 7, we show a 2D array formed by thiolized Pd nanocrystals of 3.2 nm diameter (containing 1415 atoms). The stability of the 2D array of such monodisperse nanocrystals depends on the diameter of the nanocrystal, $d$, and the length of the spacer, $l$. The observed stability regime ($d$–$l$ phase diagram) is explained satisfactorily by a simple model wherein the thiolized nanocrystals are treated as soft spheres[16b]. In this treatment, the total potential energy, $E$, is taken as the sum of a repulsive, $E_r$, and an attractive term, $E_a$, the latter representing van der Waals interactions. These terms are as follows:

$$E_a = \frac{A}{12}\left\{\frac{d^2}{t^2-d^2}+\frac{d^2}{t^2}+2\ln\left(\frac{t^2-d^2}{t^2}\right)\right\}$$

$$E_r = \frac{50dl^2}{(t-d)\boldsymbol{ps}_a^3}kTe^{-\boldsymbol{p}(t-d)}.$$
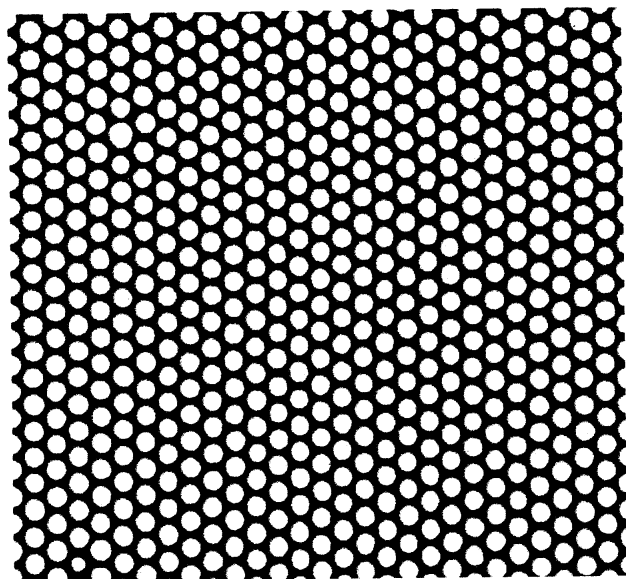
**Figure 10.** Crystalline array of polymethylmethacrylate spheres (1.5 μm diameter) (from the webpage of D.A. Weitz).
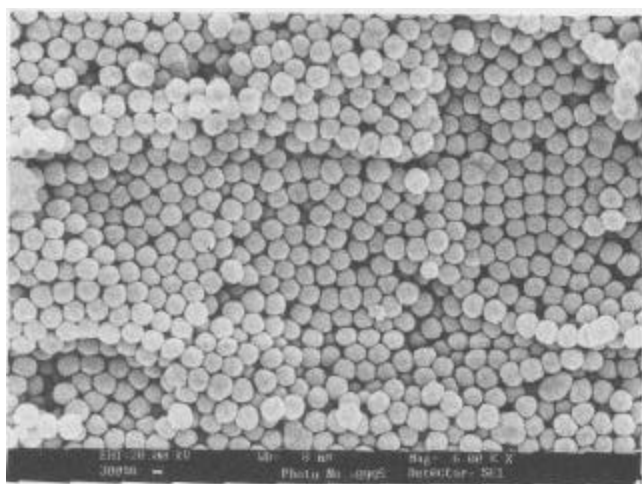


**Figure 11.** An arrangement of silica spheres (625 nm diameter) (from Gundiah and Rao, *Mater. Res. Bull.*, 2001, **36**, 1751).

Here, *t* is the interparticle distance, $s_a$ is the area occupied by the spacer molecules (thiol) and *A* is the Hamaker constant. In Figure 8, we show typical potential energy curves for nanocrystals of 4.5 nm diameter, separated by two different alkane thiols. Such calculations suggest that the nanocrystal arrays get disordered for *d/l* ratios smaller than 1.5 and greater than 4.0, in agreement with experiment[16b].

When monodisperse Pd nanocrystals of 2.5 diameter (containing ~561 atoms) are coated with polyvinylpyrrolidone and left standing in water, they aggregate to form giant nanocrystals[16c]. Interestingly, the giant nanocrystals contain magic numbers of the initial nanocrystals. Thus, giant nanocrystals containing 561 and 1415 nanocrystals of Pd, each of which contains 561

atoms, have been observed and characterized. Self-assembly in the metal nanocrystals covers a wide range of sizes, starting with an atom (~ 0.2 nm dia) and ending with a giant nanocrystal (~ 30–50 nm dia), with 150–250 orders of magnitude change in size. Yet, weak forces suffice to cause the assembly. In Figure 9, we schematically show the two stages of self-assembly of metal particles.

## Colloidal particles (nm–μm regime)

Chemists, by and large, are mainly familiar with the self-assembly of molecular units. These molecular units are generally small with diameters close to a nm. In actuality, however, self-assembly occurs in systems of considerably larger sizes. For example, spheres of polymethylmethacrylate, polystyrene, latex and silica self-assemble or crystallize into highly ordered structures[18]. In Figures 10 and 11, we show the crystalline assembly polymethylmethacrylate and silica spheres respectively. The diameters of the spheres can be anywhere between 100 and 2000 nm (2 μm). Self-assembly of these colloidal particles occurs through weak interactions (capillary forces) with an energy comparable to that in van der Waals interactions. Alignment of micron-length carbon nanotubes to form bundles would also involve such weak interactions (Figure 12).

## Self-assembly of mm-sized objects

Self-assembly does not stop at the nm–μm scale. Whitesides and coworkers[7,19] have investigated the mesoscale self-assembly of large mm-sized objects by means of capillary forces wherein shape recognition and minimization of liquid–liquid interfacial free energy play a role. In order to accomplish such self-assembly, they cover the desired surfaces of the shaped objects with
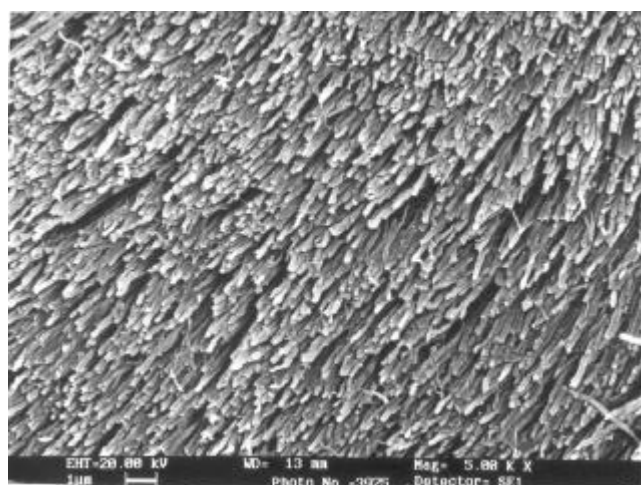


**Figure 12.** Self-assembled carbon nanotube bundles (from Rao, Govindraj and Sen, *Chem. Commun.*, 1998, 1525).
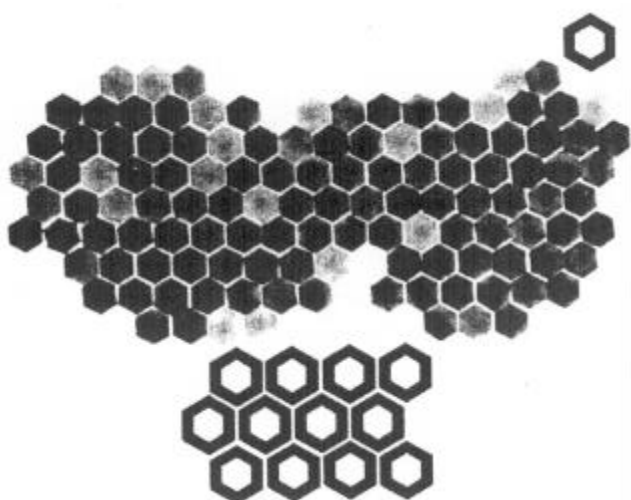
**Figure 13.** Close-packed array formed by the self-assembly of hexagons of polydimethylsiloxane (5.4 mm dia) coated with hydrophobic layers on all the six sides (from Choi et al.[19b]).
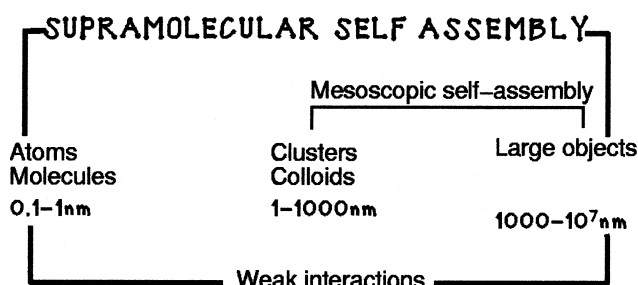


**Figure 14.** The wide range of self-assembly of objects.

films of hydrophilic or hydrophobic materials, the objects themselves being made of polydimethylsiloxane or polyurethane. By such a strategy, they have accomplished the self-assembly hexagonal plates wherein lateral capillary forces are operative. In Figure 13, an example of such a self-assembly is illustrated. Shape-selective recognition and self-assembly is favoured in objects suitably designed to act as receptor–ligand pairs. There appears to be a hierarchy of interactions in these self-assemblies. Mesoscale self-assembly also occurs in three-dimensional objects such as mm-sized cubes. Well-organized three-dimensional crystals with open structures have been obtained by covering faces of the objects with thin metallic films. A limitation in the self-assembly of large mm–sized objects appears to be that the process does not extend to large areas or volumes as revealed in Figure 13. This is to be contrasted to the self-assembly of molecules or small objects in the molecular or the nm regime where the process involves a large number of units comparable to the Avogadro number.

## Concluding remarks

The above discussion should suffice to convince oneself that self-assembly based on weak interactions occurs in different ways and forms, in a variety of objects, encompassing a wide range of sizes (Table 1). Although it is customary to refer to the self-assembly of nm–mm objects as mesoscopic, in contrast to molecular self-assemblies encountered in supramolecular chemistry, we should recognize that the term 'supramolecular' (beyond the molecule), as defined by Lehn, embraces, literally and in spirit, all size scales. One may consider the wide range in sizes between atoms (molecules) and macroscopic objects (mm scale) to represent a continuum[20], wherein self-assembly occurs by making use of weak interactions (Figure 14). In the process of assembly, the potential energy curve for the interaction between two objects is described satisfactorily by a suitable choice of attractive and repulsive terms as in Figure 8. van der Waals interactions, which are generally considered weak (and often ignored), could provide the stability and strength of many of the self-assembled structures, specially in the mesoscopic regime. Clearly, in these systems, *weak is strong*. No wonder, the strong grip of a lizard on a smooth wall is through van der Waals interaction[21]. There is every reason to believe that self-assembly of systems will be exploited in the near future as a means of putting together a wide variety of objects for use in devices and machines. Whether self-assembly over relatively large dimensions is limited to small nanometer-sized objects and does not apply to the millimeter-sized objects is an aspect that needs to be fully explored.

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20. Similar continua that one recognizes in condensed matter science are relevant to the subject of this article. For example, between atoms/molecules and extended solids, there is a continuum, with clusters and nanomaterials coming in between. There is also a continuum between molecular solids and extended solids.

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