



## Soft Supramolecular Materials

D.V. SOLDATOV

*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Ac. Lavrent'ev Av. 3, Novosibirsk, 630090 Russia and Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Dr., Ottawa, ON, K1A 0R6 Canada; E-mail: Dmitriy.Soldatov@nrc.ca*

(Received: 29 July 2003; in final form: 22 August 2003)

**Key words:** functional materials, metal-organic frameworks, molecular crystals, soft materials, supramolecular stabilization, smart materials, weak interactions

### Abstract

Soft Supramolecular Materials (SSM) are multicomponent materials formed by the bulk supramolecular assembly/aggregation of building units into a regular structure, with stronger bonding within building units and weaker bonding between them. The nature of the building units may vary from simple molecules to nanoparticles, and the forces linking the units together may vary from coordinative to van der Waals. Recently SSM have attracted a great deal of attention due to their wide variability, easy conversion from one structure to another, and active response to external stimuli. It seems evident that the progress in the chemistry of SSM predestines the appearance of a new generation of functional and “smart” materials.

**Abbreviations:** SSM – Soft Supramolecular Materials;  $[MA_4X_2]$  – Octahedral Werner complexes, M = M(II), A = amine, X = X<sup>-</sup>; DBM – Dibenzoylmethanate, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub><sup>-</sup>;  $\alpha$  and  $\beta$  forms – dense and porous crystalline forms of a compound, respectively.

### Introduction

The definition of SSM, as given in the first two sentences of the Abstract, is rather wide. The purpose of this short review is not so much as to cover all known types of materials which fall under this definition, but rather to emphasize those properties of SSM that make them attractive in light of a general tendency of today's materials science to move towards innovation and design [1]. Supramolecular chemistry tremendously extended our view on how new matter can be created, and the significance of these new ideas was emphasized with a Nobel Prize. [2] Since the first materials having supramolecular organization were identified half a century ago [3], whole generations of such materials have been purposefully created [4, 5, 6], and new findings of conceptual importance were made, including, to mention just few, coordination compounds of alkali metal cations [7], compounds containing helium [8] and other noble gases [9] in their chemical formula, new insight into chemical stoichiometry [10], relation of crystal packing, symmetry and stability [11], stabilization of chemical species in supramolecular environment [12, 13], supramolecular control of reactivity in the solid state [14, 15], new understanding of some well-known inorganic materials [16], supramolecular approach to the engineering of organic solids [17], isolation of the crystals with the lowest ever-known density [18], the development of “molecular machines” [19], microporous [20], mesoporous [21, 22], functional [23, 24, 25] and smart

[26] materials. All these achievements raised an increasing interest in weak interactions as well as in materials whose composition and structure are determined by weak interactions. Comprehensive study and purposeful design of such materials is becoming one of priority directions in modern chemistry.

### Range of SSM

The range of SSM embraces a variety of crystalline supramolecular compounds [27], organic-inorganic nanocomposites [28], partially crystalline or glassy low-dimensional organic polymers [29], dendrimers [30], materials formed by nanoparticles and self-assembled supramolecular layers [31], liquid-like systems such as gels [32], liquid crystals and liquid clathrates [33], and biomaterials [34, 35, 36].

A great number of SSM have been created for scientific, industrial and daily living needs, while many were found in nature. An example of SSM of great practical interest are the naturally occurring clathrate hydrates, a huge reservoir of hydrocarbon fuel deposited in the world's permafrost regions and offshore on the continental margins [37]. Another example is hemoglobin, one of the most studied proteins functioning as the carrier of the molecular oxygen between lung alveoles and tissues capillaries [38].

The most important distinguishing feature of all SSM is their supramolecular organization with a prominent hier-

archy of covalent, specific and weak non-specific interactions among components. In clathrate hydrates, the water molecule, a species containing two covalent bonds, forms a host hydrate framework linking water molecules to each other by hydrogen bonds, while guest hydrocarbon molecules are retained in the cavities of the framework due to van der Waals forces. In hemoglobin, four molecular porphyrin complexes of Fe(II) (hemes) are included in four subunits of a protein (globin) preventing Fe(II) from oxidation. The whole unit containing four porphyrin complexes and 574 aminoacid residues has a highly organized structure which makes it possible the fixation of molecular oxygen due to coordinative and van der Waals interactions spatially controlled by a specific supramolecular environment within the unit.

Crystalline inclusion compounds are among the best studied SSM [4, 27]. The nature of the host component varies from purely inorganic (e.g., clathrate hydrates, graphite intercalates and clays), through metal-organic (Hofmann, Werner and porphyrin-based clathrates), to organic (inclusion compounds of hydroquinone, phenol, "hexahosts", Dyanin's compound, cyclodextrins, calixarenes) and bioorganic (urea, deoxyholic acid, gossypol). Crystalline inclusion compounds give a good illustration of how similar structural topologies may be achieved using very different matter. For example, trigonal (hexagonal) inclusion lattices, with channels of similar shape and dimensions, were found among the Werner clathrates [39, 40], porphyrin-based frameworks [41],  $\beta$ -diketonate complexes [42], Dyanin's compound clathrates [43] and "trigonal symmetry" organic hosts [44, 45], with hydrogen bonds, coordinative interactions or van der Waals forces combining host molecules of these different types into the channel-type architecture.

### Variability of SSM

Weaker bonding among the building units in SSM allows for the variation of the units within the same type of material. This property makes it possible to modify each material into a family of analogs where a sought property will change by small steps over a wide range. A good illustration of this was given by the studies on Werner complexes [46, 47]. About ten different metals (M), 15 anionic groups (X) and >100 organic ligands (A) were incorporated successfully into this host of general formula  $[MA_4X_2]$  to give hundreds of new host receptors, each able to include a variety of guest components. Detailed studies made it evident that for every guest a characteristic host receptor, specifically selective towards the particular guest, could be found (Table 1) [47].

The variability of SSM provides a basis for their rational design. A good illustration of intentional design by the systematic variation of a component was given by the guanidinium disulfonates [48]. The sulfonates in the pillars (Figure 1a) form a two-dimensional hydrogen-bonded network with guanidinium cations (Figure 1b), the pillared interlayer space being available for the hydrophobic inclusion of guest aromatics (Figure 1c). A library of pillars controlling the interlayer space from 3 to 17 Å with  $\sim 1$  Å

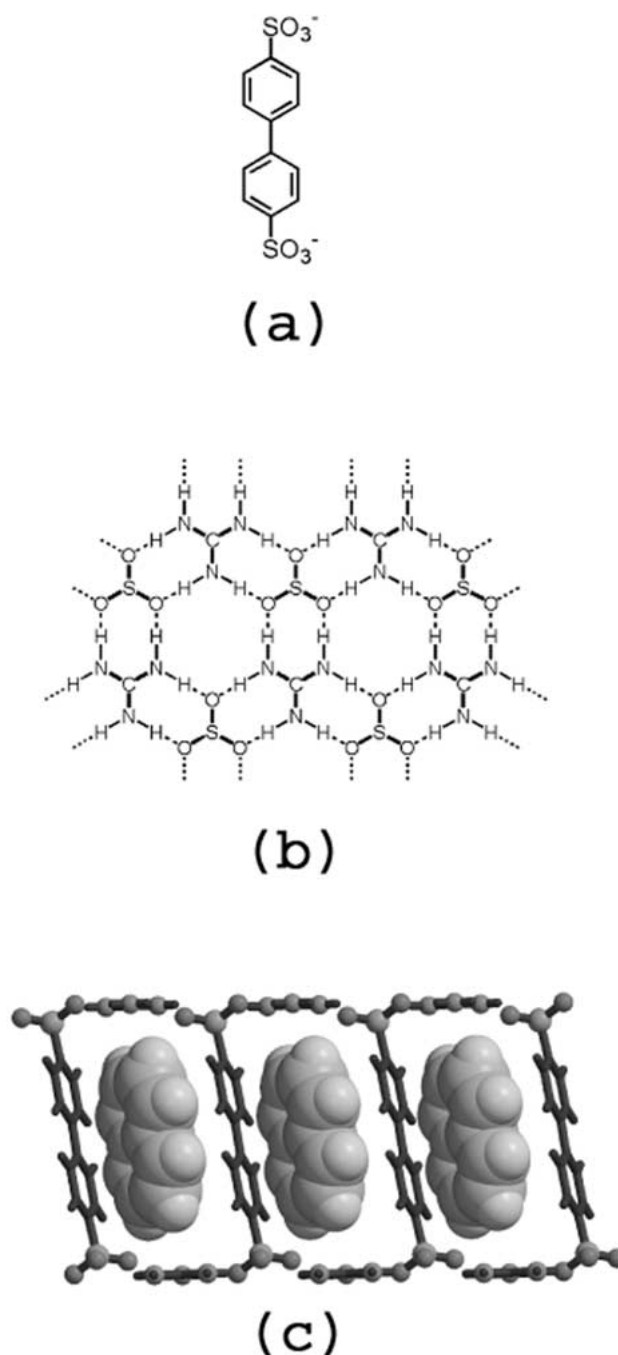


Figure 1. Inclusion compound  $(C(NH_2)_3)_2(SO_3C_6H_4C_6H_4SO_3) \cdot (C_{10}H_8)$  [49]. (a) Disulfonate dianion pillar. (b) Hydrogen-bonded layer of guanidinium cations and sulfonate groups. (c) Guest naphthalene (van der Waals dimensions) included in the interlayer space of the guanidinium disulfonate host framework.

increment provides a diverse set of soft organic frameworks with systematically adjustable pore characteristics.

Variation of the host components turned out to be one of most useful strategies in generation of new SSM, especially applicable for metal-organic hosts, such as polymeric cyanometallates [50], metal-tetraarylporphyrins [51] and modified metal dibenzoylmethanates [52, 53, 54].

Table 1. Selected data on inclusion of various isomers by  $[\text{Ni}(\text{Y}-\text{C}_6\text{H}_4-\text{CHR}-\text{NH}_2)_4(\text{NCS})_2]$  [47]

Guest isomers	Host		Percentage of isomers ( <i>o</i> , <i>m</i> , <i>p</i> )						Selectivity
	Y	R	Feed			Extract			
Xylenes	<i>p</i> -Br	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	34	32	34	86	11	3	<i>o</i>
	<i>p</i> -F	C <sub>6</sub> H <sub>13</sub>	34	33	33	6	84	10	<i>m</i>
	<i>m</i> -Cl	CH <sub>3</sub>	32	34	34	10	7	83	<i>p</i>
Ethyltoluenes	<i>p</i> -Cl	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	34	33	33	97	3	0	<i>o</i>
	H	C <sub>6</sub> H <sub>13</sub>	34	32	34	8	84	8	<i>m</i>
	<i>m</i> -Br	C <sub>2</sub> H <sub>5</sub>	34	33	33	5	10	85	<i>p</i>
Bromotoluenes	H	C <sub>4</sub> H <sub>9</sub>	33	32	35	87	13	0	<i>o</i>
	H	C <sub>5</sub> H <sub>11</sub>	45	40	15	7	88	5	<i>m</i>
	<i>m</i> -Br	CH <sub>3</sub>	33	32	35	2	6	92	<i>p</i>

## Reversible transformations and functionality of SSM

Functionality of a material implies implementation of the material in a specific process. Molecular magnets [55], catalysts [24], chemical sensors [56], materials displaying useful optical and conductivity effects, [25] colloidal transporters for bioactive molecules [57, 58] are examples of supramolecular materials that may be utilized as functional.

In many cases the presence of functionality in a material implies change. The existence of several energetically similar forms for the same compound, transforming to each other at certain conditions, is a typical feature of SSM. This property is a result of the weak linkage between building units and the variety of ways the units can assemble into a structure. A small change in external conditions can lead to another thermodynamically stable form, or, a little change in preparative conditions can lead to another kinetically stable product. Water exemplifies such a structural diversity, giving rise to dozens of ice and hydrate frameworks, each appearing under specific conditions of temperature and pressure with different guest types, and transforming into each other as the conditions change [59, 60]. The ability of SSM to respond to changing external conditions with dramatic structural reorganization reveals a tremendous potential for their applications. Liquid crystals already have been utilized extensively in liquid crystal displays and thermometers, optical imaging and recording.

Metal complexes are very good candidates in the design of functional materials including those that undergo a desired reversible transformation as a result of externally controlled environmental change. The properties that can change range from those originating from molecules (color, dia/paramagnetism, chemical reactivity) to those solely attributable to macroscopic structure (microporosity, heterogeneous catalysis, ferromagnetism).

An example of a reversible transformation of a bulk material followed by the reorganization on molecular level is given by nickel(II) dibenzoylmethanate [61]. The complex may exist both in monomeric and trimeric forms (Figure 2).

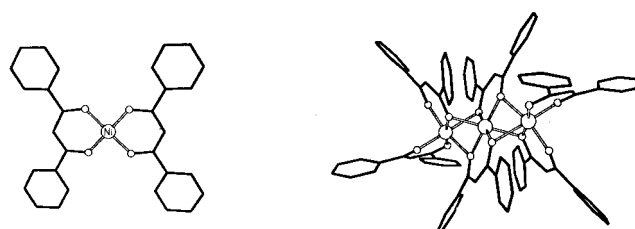
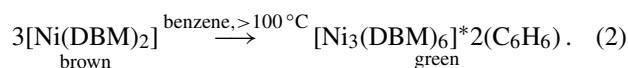


Figure 2. Monomeric  $[\text{Ni}(\text{DBM})_2]$  (brown, diamagnetic) (left) and trimeric  $[\text{Ni}_3(\text{DBM})_6]$  (green, paramagnetic) (right) forms of nickel dibenzoylmethanate [61].

The monomeric form is a brown diamagnetic solid while the trimeric form is a green paramagnetic material. At room temperature the brown form is stable and the green form is metastable. The brown  $\rightarrow$  green transformation is induced by heating (occurring as a polymorphous transition at 202 °C) while the reverse green  $\rightarrow$  brown transformation is catalyzed by some organic solvents (room temperature):



Alternatively, the trimerization can be accomplished under very mild conditions using a suitable template: with benzene, a brown  $\rightarrow$  green transformation takes place at room temperature with an inclusion compound  $[\text{Ni}_3(\text{DBM})_6] \cdot 2(\text{benzene})$  as a product:



The inclusion compound contains the trimeric nickel dibenzoylmethanate species existing at room temperature as the main component of a thermodynamically stable phase. This example illustrates a dramatic but reversible and totally predictable response of SSM on slight changes in external conditions.

An important class of SSM are microporous solids made up on weaker interactions. These sorbents mimic physico-

chemical behavior of zeolites while exhibiting considerable advantages for purposes of design as well as other useful properties such as easily controlled assembly-disassembly. Microporous solids of this kind were prepared out of organic molecules [62–64], metal complexes [65–74] and low-dimensional organic polymers [75–80]. Recently special efforts have been applied to create sorbents which respond to the sorption process with slight structural modifications in the host matrix. In many cases these modifications cause drastic changes in bulk properties of the material. Such sorbents are able to “sense” the presence of guest species and to “recognize” them responding to each type of guest in a different way.

This new tendency is especially apparent in the evolution of microporous metal-organic frameworks. Three generations of frameworks have been distinguished [81]: (1) “unstable to the loss of included guest”; (2) “stable frameworks, reversibly losing and re-adsorbing guest species without undergoing a change in phase or morphology”; (3) “dynamic structures, which change their frameworks responding to external stimuli”. This last type of “third generation”, or “dynamic”, frameworks is also referred to, by other authors, as “soft” [48] or “flexible” [13] frameworks. Several sorbents of this kind have been already reported [53, 82–90].

### Smart sorbents

“Smart” materials is an example of functional materials possessing two functions: to sense external signals and to respond to the signals with a useful response [26]. Examples of SSM that are “smart” as they interact physically with the environment are available [25, 91]. More complicated systems, where the interaction involves a chemical process, also have been reported [85, 92].

“Smart” sorbent [13, 93] is a material that can switch between dense and porous forms, with the process of switching being defined by the sequence of applied external conditions. Once in the porous form, the material acquires the ability to function as a sorbent as long as required; being transformed back into the dense form, the materials becomes “inert” waiting for the next cycle. The act of switching may be accomplished by an operator or automatically, as a part of a programmed process.

The phase interconversion scheme for a smart sorbent is shown in Figure 3 [53, 94]. The whole process was realized for a material based on a copper  $\beta$ -diketonate [13, 93]. The complex may exist in either dense  $\alpha$  form which is thermodynamically stable, or in microporous  $\beta$  form which shows kinetic stability [95, 96]. The  $\beta$ -form behaves as a typical zeolite-type sorbent with approximate pore diameter of 6 Å, pore volume of 20%, and specific surface area of  $\sim 380 \text{ m}^2/\text{g}$ . However, unlike for zeolites and other common sorbents, this sorbent may be “switched off” by being temporarily transformed into the dense ( $\alpha$ ) form at any time. This property gives the material an unprecedented potential as a programmable, smart sorbent. The generation of microporosity in the material was performed in two steps

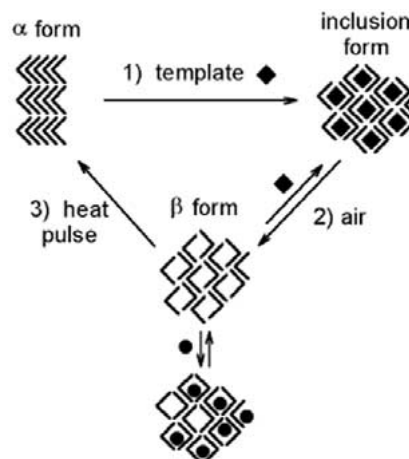


Figure 3. The phase interconversion scheme for a smart sorbent [53, 94].  $\alpha$  and  $\beta$  are the dense and porous forms of the sorbent, respectively. The  $\alpha \rightarrow \beta$  conversion proceeds in two steps: The transformation of the  $\alpha$  form into inclusion form (1) is driven by a guest template (“diamonds”). The empty  $\beta$  form is available after the guest template is removed from the pores (2). The  $\beta \rightarrow \alpha$  conversion (3) is a collapse of the metastable empty  $\beta$  form into the  $\alpha$  form. Note that the material can act as a sorbent only while in  $\beta$  form. Sorbate species are shown as circles.

(Figure 3): (1) The dense  $\alpha$  form was transformed into inclusion form in a flow of gas containing methylene chloride as a guest template. (2) Removal of methylene chloride in a flow of inert gas yielded the microporous  $\beta$  form of the material. The switching off the sorbent functionality was performed by the application of a temperature pulse (3); the disappearance of the microporosity was observed due to collapse of the metastable  $\beta$ -form back into the stable  $\alpha$  form. Each step of the process was performed *in situ* under complete control and with direct monitoring of the structure and microporosity [93].

The above example shows that SSM, with their high sensitivity to external conditions and easy response to environmental changes, possess the qualities that make their implication as smart materials a matter of an appropriate engineering solution. An essentially endless variability of SSM, arising from the vast variability of their organic and inorganic components and multitude of ways that these components can be assembled to form a 3D structure, allows that it should be possible to create a proper material for any particular task, and provides an area where the rational design of such materials can be foreseen. The above reasons provide convincing evidence that progress in the chemistry of SSM predestines the appearance of a new generation of functional and smart materials.

### Stabilization of chemical species in SSM

Stabilization of certain chemical species, their different forms and assemblies in a particular supramolecular environment is an attractive area where SSM may be extensively utilized. The phenomenon plays an important role in stabilizing drugs and may be useful in separation, purification and the development of new approaches to chemical and biological research.

Stabilization of chemical species may be caused by either kinetic or thermodynamic reasons. Kinetic stabilization increases the lifetime of highly reactive species by increasing the activation barrier for the reactions of their decomposition. This may be achieved by the isolation of reactive species from each other or from other possible issues of their instability such as oxygen, water, light and radiation. The  $\beta$ -cyclodextrin inclusion compound of nitroglycerine is extremely stable and cannot be exploded even with an initiator [97]. The lifetime of photosensitive drugs may be significantly increased by inclusion in a cavity of a suitable host receptor [98].

Thermodynamic stabilization may favor formation of "unusual" species which become a part of a thermodynamically stable supramolecular phase. Such species exist as long as they reside inside this supramolecular phase and decompose, change, or equilibrate with alternative forms once brought out of their "stabilizing" environment. Stabilization of conformational isomers in molecular crystals [99], different polymorphs [100] and inclusion compounds [53, 101–105] is well known. Stabilization of both *cis* and *trans* spatial isomers for the same molecule may be achieved using an appropriate templating agent; the range of such templating species exemplified in the literature varies from inorganic ions [106], through polar molecules like water [107], to typical organic molecules like substituted benzenes [95, 108]. Oxonium and other ions of biological significance may be stabilized in calixarenes or coordination polymers, such as  $\text{H}_3\text{O}^+$  [109],  $\text{H}_5\text{O}_2^+$  [110],  $\text{H}_7\text{O}_3^+$  [111],  $\text{N}_2\text{H}_7^+$  [112].

Of special interest are chemical reactions which occur at the expense of thermodynamic stabilization of the forming chemical species in a new supramolecular environment. The appearance of a blue color on contact of iodine with some naturally occurring polymers such as starch has been known for a long time as "blue reaction" of iodine [113]. Structural studies of the blue complex of iodine with amylose (the linear fraction of starch) showed that the guest iodine molecules undergo a significant change when included in the helix formed by amylose [114]. Inside this helix, iodine molecules form a polymeric chain with a periodicity of 3.1 Å which is shorter than the non-bonded distance between iodine atoms (4.3 Å) but greater than the bond distance in the  $\text{I}_2$  molecule (2.7 Å) [115]. The polyiodide chain is stabilized by favorable van der Waals contacts with the atoms of the helix and dissociates outside this "stabilizing" environment. The cleavage of a polymeric copper(I) complex driven by a guest template was reported; the reaction was followed by the disappearance of blue emission and the appearance of yellow emission because of the formation of tetrameric complexes acting as host in a new phase [116]. One example of trimerization induced by template was mentioned above (see Equation (2)) [61]. Some complex molecules may exist only in certain clathrate matrices while decomposing upon removal of the guest template; this phenomenon, referred to as "contact stabilization", was observed in a number of systems [12, 117–121].

## Conclusion

To a great degree, the interest in SSM has been dictated by the interest in weak interactions and by the intention to take control over weak interactions in the design of new materials of academic and practical importance. In the past, most SSM were obtained by chance and most their modifications were performed by analogy and intuition. Today, many approaches have been developed to the purposeful engineering of materials bearing desired properties and functions. An intrinsic feature of SSM is their resemblance of biological matter with its complex supramolecular organization, high sensitivity to environmental conditions and the ability to change in concordance with the conditions of the outer world. The future of SSM may be seen in creation of libraries of the materials that exhibit various useful functions including those peculiar to living organisms. Smart materials is one of such ultimate targets in the engineering of new SSM while the further development may include materials with a learning or tuning functions, materials that become smarter with age, and materials able to choose and make correct decisions where multiple choices exist.

## Acknowledgement

The author thanks all whose comments were useful in the preparation of this manuscript: A.B. Burdukov, G.N. Chekhova, V.Yu. Komarov, J.A. Ripmeester and others.

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