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Review

Spin crossover in soft matter

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ABSTRACT

This review article is devoted to the study of the spin crossover phenomenon in soft matter. Spin crossover compounds, though known for decades, bear the potential for practical applications in switching, sensing and display devices. Having arrived at a reasonable understanding of the spin transition process in solid and liquid states, one trend in this research field is to extend the knowledge into soft matter. The review begins with a brief description of Langmuir–Blodgett thin films based on Fe^{II} coordination compounds since it represents the first study of the spin crossover phenomenon in soft matter. The following section illustrates the Fe^{II}, Fe^{III} and Co^{II} complexes reported so far and the interplay-synergy observed between the spin crossover or valence tautomerism phenomenon and the crystal–liquid crystal or crystal–liquid phase transitions. The spin crossover phenomenon in gels is subject of another chapter, where it is described the development of thermochromic gels making use of the change of color associated with the spin transition in Fe^{II} coordination compounds. The last sections encompass the study of dendrimer and lipid complexes that undergo thermally induced spin crossover properties as well as a particular case of amphiphilic Fe(III) complexes exhibiting cooperative spin transition in solution.

1. Introduction

The spin crossover (SCO) or spin transition (ST) phenomenon is known as the inter-conversion between the electronic spin states occurring in coordination compounds of 3d elements with electron configurations d^4–d^7. In the high spin (HS) and low spin (LS) configurations the compounds present distinct metal-donor atom distance (molecular volume), magnetic, dielectric and optical properties [1]. Switching between the spin states can be induced by an external perturbation such as variation of temperature [2], application of pressure [3], magnetic field [4], light irradiation [5] or electron pumping [6].

In the solid state, the type of the SCO transition, continuous, abrupt with hysteresis, two-step or incomplete, and the critical temperature at which it occurs depends on the inherent variables and the structure-determined parameters [2b]. The type of the ligand, its substituents, type of the anion, crystal solvent and dimensionality define the chemical nature of the compound. These are the

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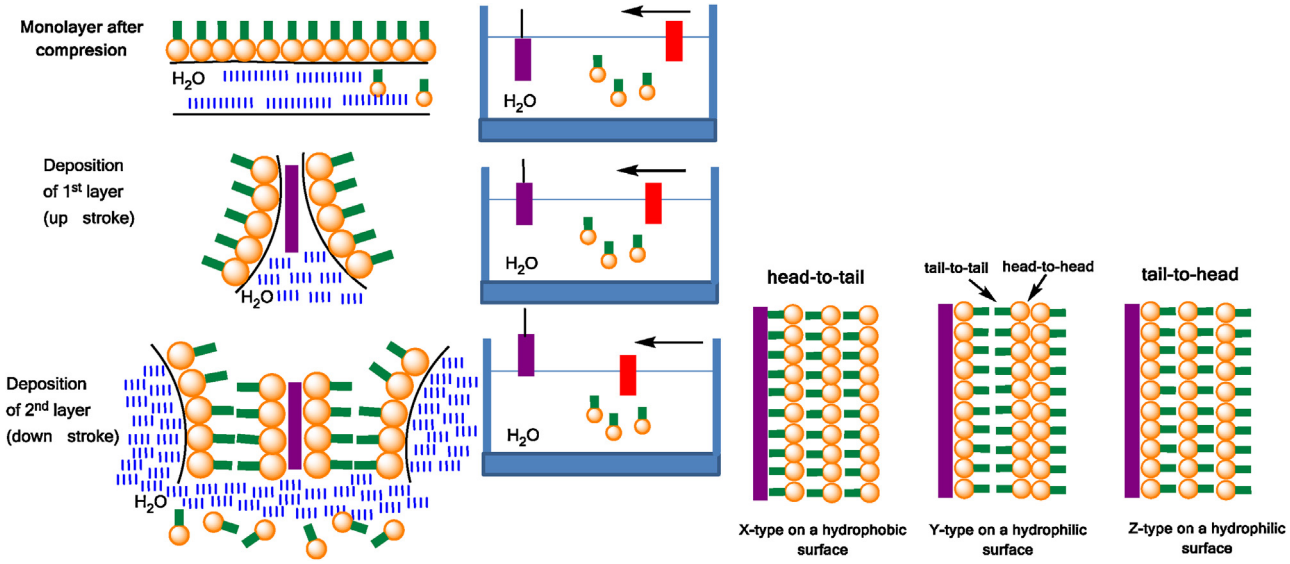

Fig. 1. Schematic illustration of the Langmuir–Blodgett technique (left) and the different types of layers (right). The method simply consists of dipping and pulling a solid substrate, oriented vertically, through the coating monolayer while keeping the surface pressure constant. The transfer of monolayer film occurs via hydrophobic interactions between the alkyl chains and the substrate surface or the hydrophilic interaction between the head groups of the molecules and the hydrophilic substrate surface. Subsequent dipping or pulling deposits a second layer on top of the first, the process simply being repeated until the desired number of layers has been deposited.

inherent variables while hydrogen bonds, π–π, electrostatic and van der Waals interactions constitute the structure-determined parameters [1c,2b]. During the course of the spin state phase transition the intermolecular contacts in the crystal can vary as a consequence of a structural phase transition or a structural reorganization. The spin state phase transition refers to the switch of spin state, which can be of the first order when accompanied by hysteresis or of the second order for continuous spin transitions [2b]. Strong intermolecular contacts between complex molecules or rigid connectivity between metal centers in polymers are the source of cooperative SCO [1c,1f, 2b, 7]. The magnetic, optical, structural and dielectric properties drastically change in a narrow range of temperature or pressure for cooperative SCO. These first order spin transitions exhibiting hysteresis give rise to a memory effect. The potential applications of SCO materials as molecular switches, sensors or memory devices are based on this bistability [8].

The origin of the term "spin crossover" lies in the crossover of the energy vs field strength curves for the possible ground state terms for ions of particular d^n configurations in Tanabe–Sugano and related diagrams. The term "spin transition" is used almost synonymously with "spin crossover" but the latter has the broader connotation, incorporating the cooperative effects, spin transition tending to refer to the actual physical event [2b]. The study of the SCO phenomenon dates back to 1930 when Cambi et al. observed for Fe^{III} dithiocarbamates the interconversion between the electronic spin states induced by a change of temperature [9]. Three decades later a temperature dependent $^5T_{2g}(O_h) \leftrightarrow {}^1A_{1g}(O_h)$ spin transition was reported for the Fe^{II} compound $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline) [10]. Since then very active research on the spin crossover phenomenon both in the solid state [1,7,11] and in solution [12] have been undertaken.

During the last years attention has been focused on the study of SCO phenomenon in soft matter [13,14]. The aim was twofold: to obtain materials gathering additional properties and to explore pathways for the processibility of bulk SCO compounds into thin films [1d,1g, h, 11a].

In soft matter, a modest external stimulus (electric, magnetic, chemical) can bring about a strong perturbation of the properties of the material. Therefore, incorporation of SCO centers in a liquid crystalline matrix could lead to a material where the SCO properties are induced by external electrical or magnetic fields. On the other hand by exploiting the fluid nature of the liquid crystals or the solubility of dendrimers and lipids in organic media thin films of SCO compounds could be obtained by slow evaporation or spin coating. Gels can response to specific chemical environment. Indeed, gelation provoked by the addition of a chemical substrate could enhance or inhibit the SCO properties of the gel.

Liquid crystals, gels, dendrimers, lipids, polyelectrolyte amphililes and Langmuir–Blodgett films exhibiting SCO by the incorporation of Fe^{II} or Co^{II} coordination centers have been synthesized and studied [11b,14,15]. The aim of this review article is to give an overview of the last achievements in this new research topic.

2. Langmuir–Blodgett thin films based on Fe^{II} spin crossover coordination compounds

The Langmuir–Blodgett (LB) technique is one of the most promising techniques for preparing thin films as it enables, (i) the precise control of the monolayer thickness, (ii) homogeneous deposition of the monolayer over large areas and (iii) the possibility to make multilayer structures with varying layer composition. An additional advantage of the LB technique is that monolayers can be deposited on almost any kind of solid substrate. The most common choices are glass, silicon, mica or quartz which can be coated to provide different hydrophobicity.

The growth of films takes place as follows: first, a single layer of molecules is organized on a liquid surface (water) and is termed a Langmuir monolayer; secondly it is transferred onto a solid support to form a thin film with the thickness of a constituent molecule called a Langmuir–Blodgett film. The multi-layered films are obtained by repeating the process [16] as it is illustrated in Fig. 1.

Coordination compounds can be chemically modified by grafting alkyl chains on the organic ligand in order to obtain amphiphilic complexes. The LB technique can be employed to prepare thin films of these complexes. Similar physical properties to those of the three dimensional systems (solid state) can be conferred on the two-dimensional polar planes. The first report on a Langmuir–Blodgett thin film of a SCO compound dates back to 1988. Kahn and co-workers deposed the compound $[Fe(\mathbf{1})_2(NCS)_2]$ onto CaF_2 and