DYNAMIC CONSTITUTIONAL MATERIALS.
CRYSTALLIZATION- AND SOL-GEL-DRIVEN SELF-SORTING
OF FUNCTIONAL SUPRAMOLECULAR ARCHITECTURES

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In this review we describe some of most representative examples of **metallosupramolecular architectures** and **dynamic hybrid materials** recently published by our group in which supramolecular functional devices are **constitutionally self-sorted** by crystallization or by sol-gel polymerization. The self-selection is based on constitutional interactions resulting in the dynamic amplification of self-optimized architectures. The **dynamic constitutional materials** reported here therefore illustrate the convergence of the combinatorial self-sorting of dynamic combinatorial libraries (DCLs) with the specific self-optimized functions, extending the application of **constitutional dynamic chemistry**[2] from materials science to **functional constitutional devices**.

Mihail D. Barboiu was born in Paşcani, Roumania in 1968. In 1993 he became Assistant Professor of Chemistry at University "Politehnica" in Bucharest. He received his PhD in 1998 from University of Montpellier II before spending 2 years as Associate Professor at College de France, with Professor Jean-Marie Lehn at the Supramolecular Chemistry Laboratory, University Louis Pasteur, Strasbourg. Since 2001, he has been CNRS Research Fellow and EURYI Group Leader at the Institut Européen des Membranes in Montpellier, France.
His research on hybrid supramolecular membrane materials began in 1994 with the development of molecular recognition based-membranes. Subsequently, basic working principles of self-organized membranes are developed, in order to design functional biomimetic hybrid membrane materials. Finally, the constitutional self-adaptation of the membrane material, producing a specific response in the presence of its solute represents a nice example of the dynamic adaptative membranes where a solute induces the upregulation of (prepares itself) its own selective membrane.
Author of about 100 papers and 6 reviews and book chapters, Dr. Barboiu has received in 2004 EURYI Award in Chemistry.

INTRODUCTION

The design and construction of supramolecular architectures has attracted intense interest not only for their potential applications as new functional materials but also for their fascinating structural and superstructural diversity. It is based on the structural organization and functional integration within a molecular or supramolecular architecture of components presenting features such as photo-, electro- or iono-activity.[1] Self-organization of supramolecular entities may be directed by **design** or by **constitutional evolution** of **dynamic combinatorial systems**.[2-5]

The **self-organization by design** is based on the implementation of compounds containing specific molecular information stored in the arrangement of suitable binding sites and of

external or internal stimuli (ions, molecules, etc.) reading out the structural information through the algorithm defined by their interactional preferences. The selection of one or more components occurs as function of either internal (such as the nature and the geometry of the binding subunits, the stoichiometry, etc.) or external factors (such as the nature of the medium, the presence of specific molecules or ions, etc).

In view of the lability of the supramolecular bonds (H-bonding, van der Waals, coordinative bonds, etc.) numerous supramolecular processes may present a number of novel features such as cooperativity, diversity, selection or adaptation. Thus, this might allow the generation of dynamic libraries (mixtures) of supramolecular entities presenting features such as self-selection, solid-state selection of a constituent of an equilibrating collection of complexes, reversible switching between different arrays.[2-9] Starting with seminal publications by groups of Lehn[2] and Sanders[3] **dynamic combinatorial chemistry** has emerged as a powerful tool for the development of new receptors, drugs, catalysts and materials.

The dynamic features of supramolecular devices can also serve to bring into play the **constitutional evolution** of such species and during the last years several groups made an important advancement and they provided useful insights in this field. [5-9]

Dynamic combinatorial libraries (DCLs) are mixtures of different compounds/architectures that exist in a dynamic equilibrium yielding a set of interconverting constituents from which the selection of one or more components occurs. One of the key issues in designing complex DCLs is the choice of reversible processes that can interconvert the constitutional components. A number of such reactions have been tested including imine-, thiol-disulfide-, esterification- or ligand-exchange in coordination complexes.[2-7] Combination of two such reversible reactions in double-level dynamic combinatorial libraries using "orthogonal"[7a,b] and "communicative"[7c] exchange processes have been reported. More precisely, if the reversible processes occur independently, they might be addressed as **orthogonal.** When two levels of dynamic exchange cross over, they are considered as **communicative.**

Crystallization processes may allow the amplification from the dynamic mixtures of very specific supramolecular architectures with a unique network topology.[8] Several types of supplementary features, such as coordination behaviour and geometry, stacking interactions, inter- and intra-molecular space hindrance, are some of the

parameters identified as being responsible for the amplification of topologically favoured architectures in equilibrium of the DCLs. Indeed, such complicated topologies have attracted tremendous interest because of their simple one-pot synthesis from simple molecular components. Examples presenting features such as structural self-selection (self-sorting),[4-6] reversible switching between different coordination arrays[7-8] or solid-state selection[9,10] are becoming increasingly feasible.

Many research groups have demonstrated that the supramolecular self-organization can be readily transcribed into functional nanostructures by using a polymerization process.[9] Supramolecular self-organization can be an advantageous choice to reinforce the controlled communication between interconnected "**dynamic supramolecular**" and "**fixing polymerisable**" components. Accordingly, we have reported a synthetic route for preparing self-organized ion-channels systems which have been "frozen" in a polymeric matrix, as a straightforward approach for the design of a novel class of solid hybrid membranes.[11,12]

We therefore decided to review in this paper some of most representative examples recently published by our group, in which specific functional devices are **constitutionally self-sorted** by crystallization or by sol-gel polymerization.[10-12] The self-selection is based on constitutional interactions resulting in the dynamic amplification of self-optimized architectures. The systems reported in this paper therefore illustrate the convergence of the combinatorial self-sorting of DCLs strategy and the constitutional self-optimized function.

CRYSTALLIZATION-DRIVEN DCL CONSTITUTIONAL SELF-SORTING

Self organization of metallosupramolecular entities may be directed by design and is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry. The design of the ligand is crucial and bipyridine, terpyridine, etc. derivatives are extensively used. The synthesis of such-former ligands is very challenging and other simple procedures were sought. That may provide a more direct access to these systems by using imine and hydrazone mimics which are useful bulding blocks for the generation of grid-type, cage, helical architectures.[13]
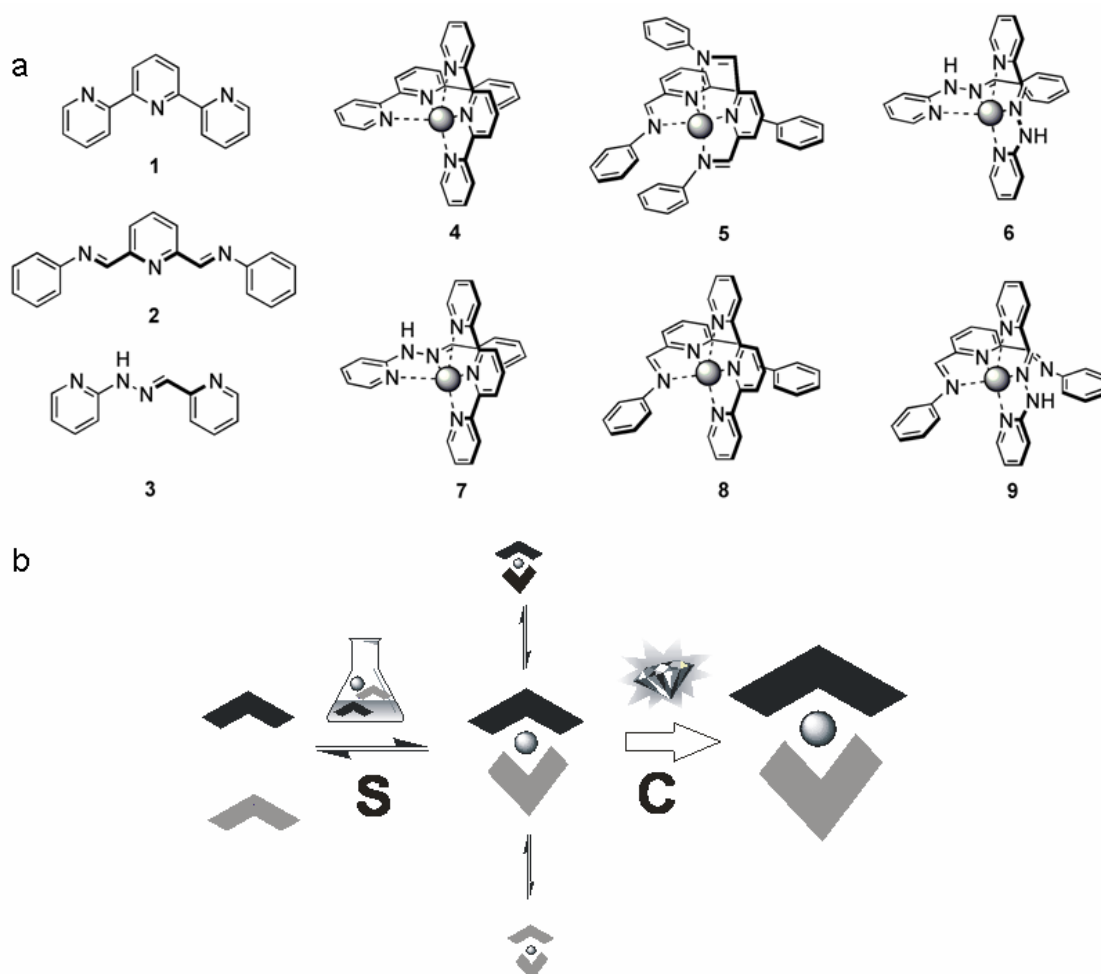
Fig. 1 – a) Structures of the terpyridine-type ligands **1-3** and the DCL library of resulted homo- (**4-6**) and heteroduplex (**7-9**) metallosupramolecular complexes; b) Statistical pre-amplification in solution (**S**) and solid state selection process (**C**) of the heteroduplex complexes **7-9**.

Of special interest are coordination complexes based on terpyridine-type ligands **1** and octahedrally coordinated metal ions, revealing a range of interesting structural and physicochemical properties. We have recently reported[10a] the terpyridine-type (terpy) tridentate ligands like the bis-Schiff-base **2** and the hydrazone bis-pyridine **3** giving easy synthetic access to similar systems (Figure 1a). Addition of Zn^{2+} to the binary mixture of terpy-type ligands **1-3** should cause the appropriate recruitment of two ligands in a pairwise mode and might be controlled by coordination behaviour and internal interactions between different aromatic moieties of these compounds. Specifically, it was of interest to investigate whether the coordination behaviour of these systems on the addition of octahedral Zn^{2+} ions could be selectively expressed in the formation heteroduplex ternary complexes. In term of specific self-assembly the homo- and heteroduplex Zn^{2+} complexes of the terpyridine-type ligands **1-3** self-organize in the solid state in 1D- or 2D- stacked

layers (**4**, **7**, **9**), double-helix (**5**) or dimeric (**8**) architectures as a function of synergetic intra- and intermolecular π-π stacking interactions between different ligands. In term of specific self-organization the heteroduplex architectures **7-9** represent an attractive example of solid-state structures resulted by a synergistic effects of statistical (**7**, **9**) and constitutional-driven (**8**) binding of two different ligands by the Zn^{2+} metal ions. Layering the solutions of stoichiometric binary mixtures of homoduplex complexes **4-6** in acetonitrile with the non-solvent, resulted in a unique set of crystals for each experiment. The X-ray structural determinations of the selected single-crystals resulted from these stoichiometric binary mixtures revealed that such complexes present unique **heteroduplex superstructures 7-9** in the solid state. Redissolution of the crystals in CD_3CN results in regeneration of the reaction mixture prior to crystal growth. These features are similar with other dynamic processes operating mixtures of

coordination complexes from which a single member may be trapped by crystallization.[10d-f] The heteroduplex Zn^{2+} complexes **7-9** are quantitatively crystallized in the solid state by statistical (**7**, **9**) and structural (**8**) driven selection in solution from a binary mixture of the terpyridine-type complexes and then be trapped by crystallisation in the solid state (Figure1b).

Conformational and configurational equilibria are also typical reversible processes.[10c] For each combination, the recognition function determine a distinct geometry of space available in order to amplify (optimise) the interactional algorithms between the library conformational components.
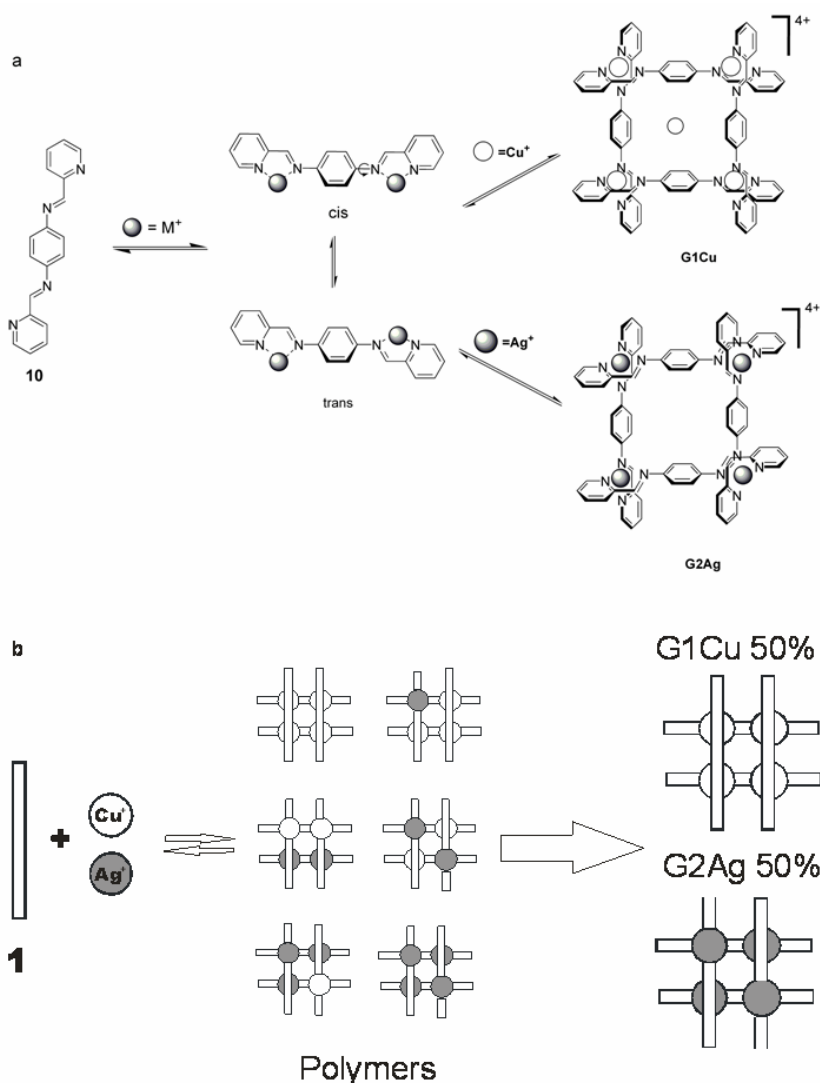

Fig. 2 – a) Two-level metal-ion coordination/conformational exchange processes and
b) generation of a dynamic library of the [2x2] grids from mixtures of **10** : Cu^+: Ag^+, 2 : 1 : 1 (mol : mol : mol).

Recently we have generated a double-level combinatorial library based on metal-ion coordination and *cis-trans* conformational processes. The simple building block **10** [10c] carrying two 2-iminopyridine functionalities was chosen as synthetic precursor for the double level-library (Figure 2a). The simultaneous metal-ion coordination/ conformational interconversion between the *cis* and *trans* arrangements around the central phenyl moiety of the

chelating sites of **10** are expected to act simultaneously, leading to the exchanging species in solution. Our strategy was to employ ligand **10** and different tetrahedral Cu^+ and Ag^+ metal ions in order to generate the interconversion of all possible stoiechimetries, thereby forming a double-level dynamic library of hetero- and homonuclear grids complexes (Figure 2b).
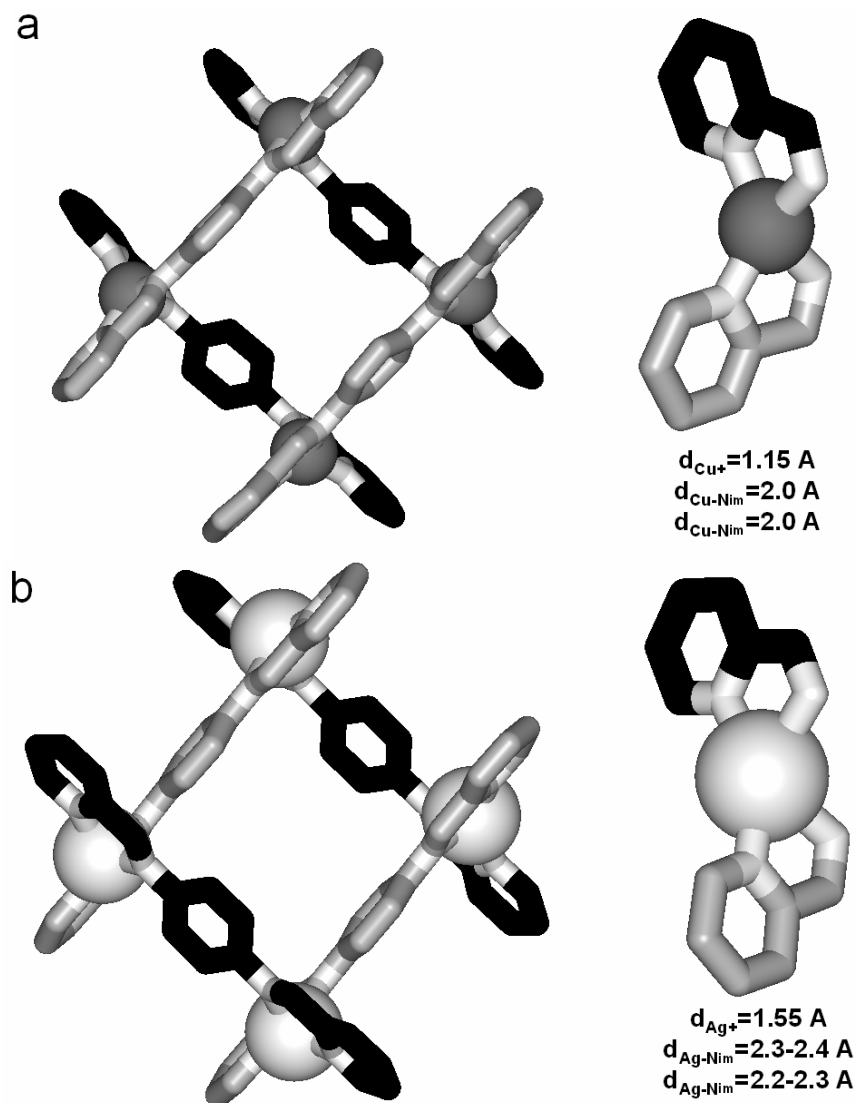
a

d_{Cu+}=1.15 A
d_{Cu-Nim}=2.0 A
d_{Cu-Nim}=2.0 A

b

d_{Ag+}=1.55 A
d_{Ag-Nim}=2.3-2.4 A
d_{Ag-Nim}=2.2-2.3 A

Fig. 3 – Crystal structure and coordination geometries (stick representation) of (a) **G₁Cu** and (b) **G₂Ag** grid complexes.
Cu^+ and Ag^+ ions are represented as grey and white spheres, respectively.

The present system is able to select the appropriate conformation of the ligand, required by the metal ions to form quantitatively an equimolar mixture of the **homonuclear** grid-type complexes **G₁Cu** and **G₂Ag** (Figure 2b). The heteronuclear grid compounds combining different metal ions require to adapt the conformation of their ligands to the very different coordination geometries of Cu^+ and Ag^+ (Figure3). The symmetrical (Cu^+/iminopyridine) (Figure3a) and the unsymmetrical (Ag^+/ iminopyridine) (Figure 3b) coordination geometries may be unfavourably associated within the same grid entity. The homocomplexation process represents the best compromise of combination of ligand **10** with Cu^+ and Ag^+ metal ions resulting in the kinetical formation of the symmetrical **G₁Cu** grid and in the thermodynamical evolution of the interwoven

G₂Ag grid. These results representing a new and original example, use a rationally designed ligand of different conformational geometries, different metal ions and a simple chemical mechanism-**quantitative parallel amplification** and show that it is possible to select the metal-adapted geometry of the ligand in order to amplify the **homonuclear** grid architectures within a double-level DCL by constitutional self-selection.

A further step toward processes of increasing complexity involved the ligands of different dimensionality or the library diversification by ligands undergoing structural reversible interconnections by chemical exchange. Thus we were interested in the possibility to use DCLs in order to self-sort specific metallosupramolecular architectures of specific based functions.
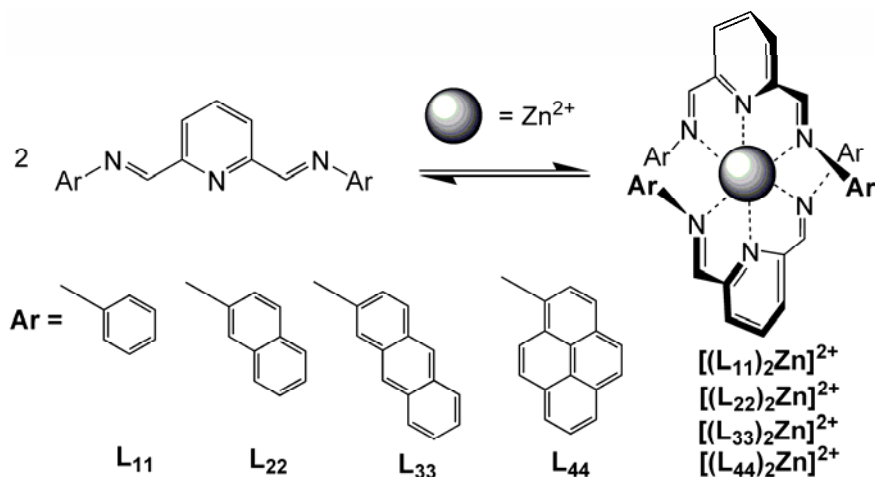
Fig. 4 – Synthesis of homoduplex complexes $[(L_{ii})_2Zn]^{II}$ i=1-4.

We therefore decided to synthesize and to study an extended series of 2,6-(iminoarene)pyridine-type Zn^{2+} complexes $[(L_{ii})_2Zn]^{2+}$ which were surveyed for their ability to self-exchange their aromatic arms and to form different homoduplex and heteroduplex complexes aggregates in solution.[10f] Then they are self-sorted based on intramolecular interactions, and which ultimately show and improved charge transfer energy function by virtue of dynamic amplification of self-optimized heteroduplex architectures. These systems therefore illustrate the convergence of the combinatorial self-sorting of DCLs strategy and the constitutional self-optimized function. For the reasons mentioned above, simple 2,6-(iminoarene)pyridine building blocks L_{11}-L_{44}, carrying two iminoarene chromophores, were chosen as synthetic precursors to constitute the double level DCLs. We restricted our studies to benzene L_{11}, naphthalene L_{22}, antracene L_{33} and pyrene L_{44} groups, common aromatic groups (Figure 4).
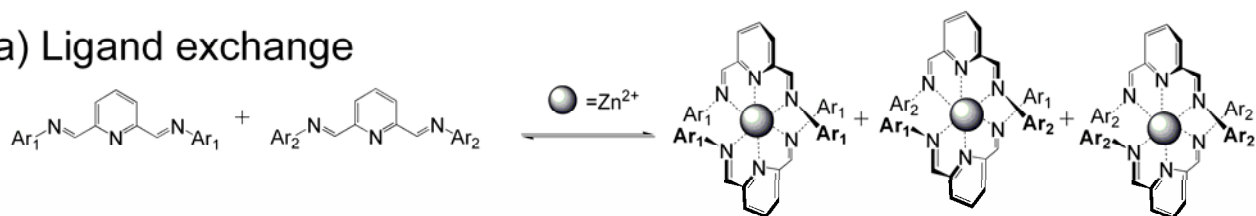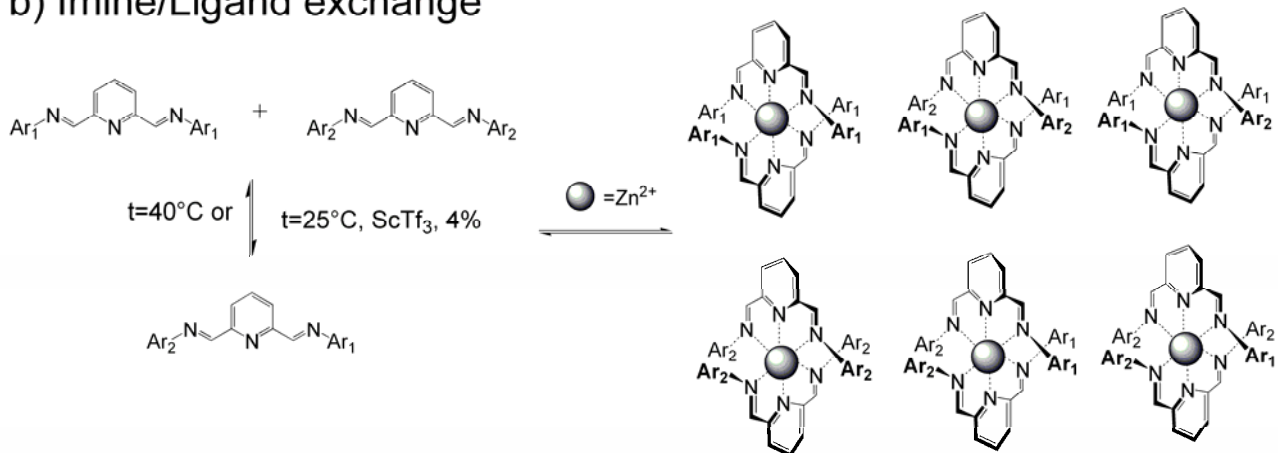

Fig. 5 – a) Single level ligand-exchange and b) double level imine/ligand exchange DCLs.

We have then demonstrated that single level ligand- (Figure 5a) and double level ligand /aromatic-imine (Figure 5b) exchanges around a metal-center within terpyridine-type architectures lead to the preferential formation of mixtures of heteroduplex complexes instead of the amplification of pure compounds. Within these mixtures, the complexes of pairs of two homoligands $[(L_{ii}L_{jj})Zn]^{2+}$ or those formed by the heteroligand L_{ij}: $[(L_{ij}L_{jj})Zn]^{2+}$, $[(L_{ij}L_{ij})Zn]^{2+}$ and $[(L_{ii}L_{ij})Zn]^{2+}$ are preferentially amplified. In addition, the octahedral metal ion complexation is positioning the aromatic chromophores moieties and the pseudo-terpyridine unity of the second ligand in close proximity, so that charge transfer energy from the choromophore and pseudo-terpyridine units occurs.

From a conceptual point of view, the **constitutional evolution** of the dynamic coordination systems toward the selection of **mixtures of heteroduplex architectures** instead of a specific amplified architecture is of special interest for the improvement of their specific charge transfer energy function. For each combination of two homoduplex complexes the fluorescence intensity of initial compounds systematically decreases for single level ligand-exchange mixtures and then for double level imine/ligand heterocomplexes. Such collective reorganization of the system allows the self-sorting of specific heterocomplex architectures presenting an intrinsic property of energy transfer specifically amplified under the pressure of internal structural factors. Similar examples of self-sensing[14a] or self-extracting[14b] structurally complex systems, self-optimizing their function through their constitutional self-assembly have been recently reported. The self-sorting processes are very common in selective-functional self-assembly of multi-component biological[14a], polymeric[14b-d] or DCLs[5] systems. Such systems represent a nice example of **dynamic instructed mixtures** of coordination compounds, where the concept of constitutional self-sorting and a specific function (charge transfer energy) might be in principle associated.[10f]

SOL-GEL-DRIVEN DCL CONSTITUTIONAL AMPLIFICATION-NEW HYBRID FUNCTIONAL MATERIALS

Hybrid organic–inorganic materials produced by sol-gel process are the subject of various investigations, offering the opportunity to achieve nanostructured materials firstly from robust organogel systems and secondly from self-organised supramolecular silsesquioxane systems. Of special interest is the structure-directed function of biomimetic and bioinspired hybrid materials and control of their build-up from suitable units by self-organisation. Our main interest focus on functional biomimetic materials in which the recognition-driven properties could be ensured by a well-defined incorporation of receptors of specific **molecular recognition and self-organization** functions, incorporated in a hybrid solid dense or the mesopourous materials.[12] Moreover, the different interconverting outputs resulting from such supramolecular systems may form by self-organization a dynamic polyfunctional diversity from which we may "extract selectively" a constitutional preferend architecture by sol-gel polymerization in solid state, under the intrinsic stability of the system.

Considerable challenges lie ahead and the more significant one is the "**dynamic marriage**" between **supramolecular self-assembly** and the **polymerization process**, which kinetically and sterochemically might communicate in order to converge to supramolecular self-organization and functions in hybrid materials. The weak supramolecular interactions (H-bonds, coordination or van der Waals interactions, etc.) positioning of the molecular components to give the supramolecular architectures are typically less robust than the cross-linked covalent bonds formed in a specific polymerization process. Accordingly, the sole solution to overcome these difficulties is to improve the binding (association) efficiency of molecular components generating supramolecular assemblies. At least in theory, an increased number of interactions between molecular components and the right selection of the solvent might improve the stability of the templating supramolecular systems, communicating with the inorganic siloxane network.

Nucleobases oligomerization can be an advantageous choice to reinforce the controlled communication between interconnected "**supramolecular**" and "**siloxane**" systems. Moreover, the different interconverting outputs that nucleobases may form by oligomerization define a dynamic polyfunctional diversity which may be "extracted selectively" by sol-gel polymerization in solid state, under the intrinsic stability of the system. In this context, alkoxysilane nucleobases form in solution different types of hydrogen bonded aggregates which can be expressed in the solid state as discrete higher oligomers. After the sol-gel process, the

constitutional preference for compact geometries in hybrid materials is most likely dictated by hydrophobic interactions and Hoogsteen

H-bonding self-assembly. These examples unlock the door to the **self-organized constitutional hybrid materials**.
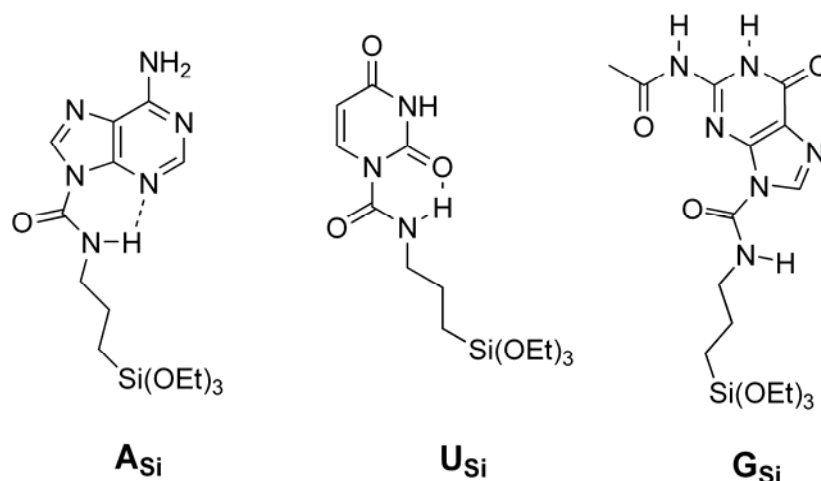

Fig. 6 – Molecular structures of nucleobase ureido-silsesquioxanes A_{Si}, U_{Si}, G_{Si}.

Three heteroditopic nucleobase ureido-silsesquioxanes A_{Si}, U_{Si}, G_{Si} receptors have been recently reported by our group[11g-i] (Figure 6). They generate self-organized continual superstructures in solution and in the solid state based on three encoded features: (1) the molecular recognition, (2) the supramolecular H-bond directing interactions and (3) the covalently bonded triethoxysilyl groups. The inorganic precursor moiety allows us, by sol-gel processes, to transcribe the solution self-organized dynamic superstructures in the solid heteropolysiloxane materials.

The A_{Si} and U_{Si} compounds were designed as rigid H-bonding modules. For instance, introducing bulky blocking alkoxysilanepropylcarboxamide groups in N9 (A) and N1 (U) positions we limit only the Watson-Crick and the Hoogsteen interactions as preferential H-bonding motifs. The A_{Si} and U_{Si} precursors generate self-organized superstructures based on two encoded features: 1) they contain a nucleobase moiety which can form ribbon-like oligomers *via* the combination of H-bond pairings; 2) the nucleobase moiety is covalently bonded to siloxane-terminated hydrophobic groups packing in alternative layers and allowing by sol-gel process to transcribe their self-organized superstructures in the solid hybrid materials.

The dynamic self-assembly processes of such supramolecular systems undergoing continous reversible exchange between different self-organized entities in solution, may in principle be connected to kinetically controled sol-gel process in order to extract and select an amplified

supramolecular device under a specific set of experimental conditions. Such "**dynamic marriage**" between supramolecular self-assembly and in sol-gel polymerization processes which sinergistically might communicate leads to "**constitutional dynamic hybrid materials**".

The generation of hybrid materials M_A, M_U and M_{A-U} can be achieved using mild sol-gel conditions. X-ray powder diffraction experiments show that well-defined long-range order is present in the precursors A_{Si} and U_{Si}, but also in the hybrid materials M_A, M_U and M_{A-U} after the sol-gel polymerization step. As a general rule, as proved by the differences between the values of interplanar Bragg diffraction distances, d_{Si-Si}, the condensation process between the ethoxysilane groups during the sol-gel process results in the formation (extraction) of the **more compact hybrid materials M_A, M_U and M_{A-U}** compared with the unpolymerized **A**, **U** and AU_{mix} powders (Figure 7).

G-quartets, formed by the hydrogen-bonding self-assembly of four guanosine and stabilized by alkali cations play an important role in biology, particularly in nucleic acid telomers of potential interest to cancer therapy.[15] The role of cation templating is to stabilize by coordination to the eight carbonyl oxygens of two sandwiched **G-quartets**, the **G-quadruplex**, the columnar device formed by the vertical stacking of four G-quartets. The **G-quadruplex** with a chiral twisted supramolecular architecture represents a nice example of a dynamic supramolecular system, when guanine and guanosine molecules are used.
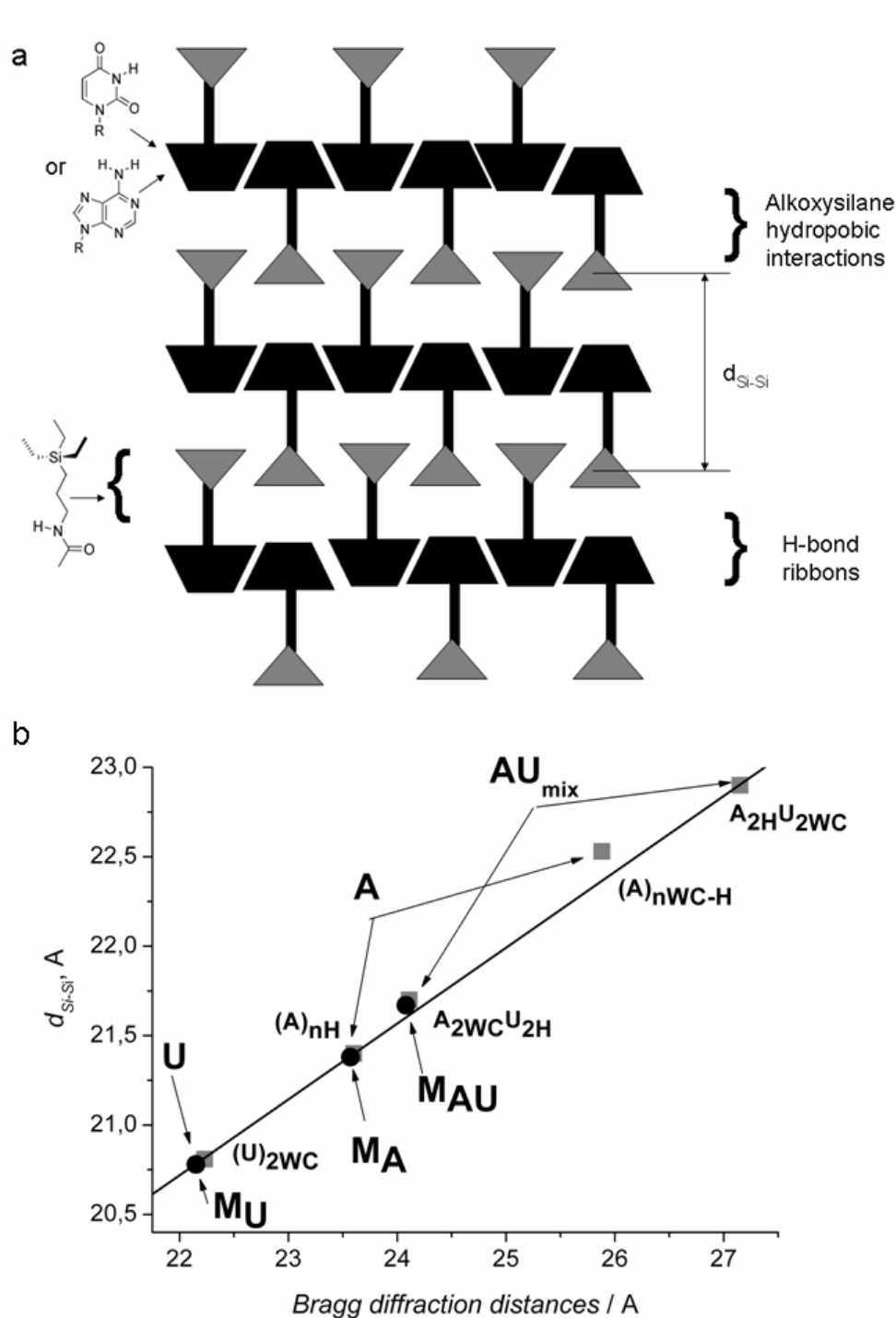
Fig. 7 – Toward a constitutional transcription of base-pairing codes in hybrid materials: a) Postulated model of self-organization of parallel H-bonded nucleobase aggregates and hydrophobic propyltriethoxysilane layers. b) Guide to the eye interplanar $d_{Si\text{-}Si}$ distances calculated from the geometry of minimized structures versus experimental interplanar Bragg diffraction distances. The red squares correspond to the unpolymerized powders of precursors **A**, **U** and their 1:1 mixture **AU**$_{mix}$, while coloured circles correspond to hybrid materials **M**$_A$, **M**$_U$ and **M**$_{A\text{-}U}$.
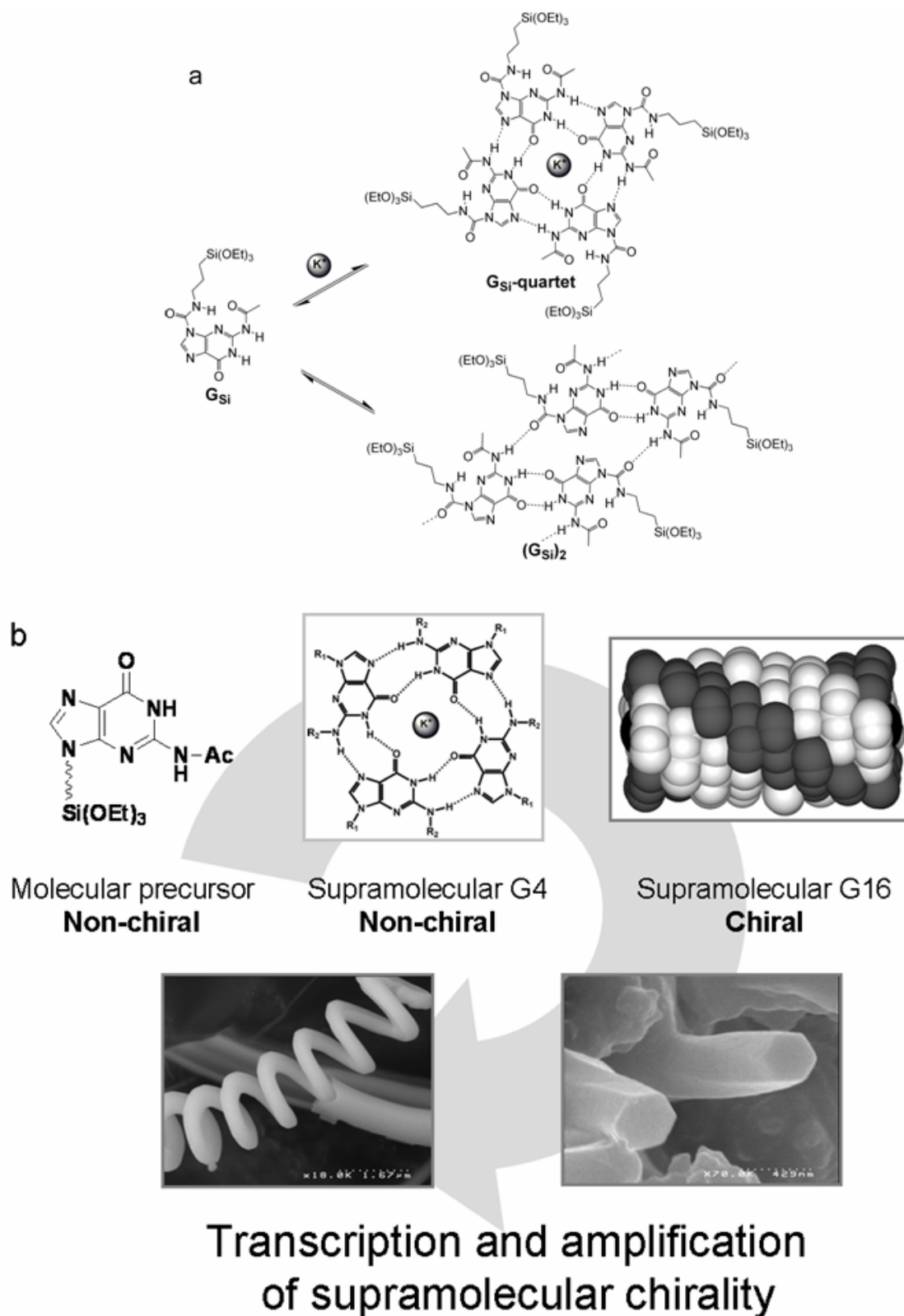
Fig. 8 – (a) The cation-templated hierarchic self-assembly of guanine alkoxysilane gives the **G-quartet** in equilibrium with **G-ribbons,** (b) the chiral **G-quadruplex** transcribed in solid hybrid materials by sol-gel in the presence of templating K$^+$ cation.

We have recently reported a new way to transcribe the supramolecular chirality and functionality of **G-quadruplex** at the nanometric and micrometric scale.[11g,h] **Molecular chirality** may be used as a tool to assemble molecules and macromolecules into supramolecular structures with dissymmetric shapes. The **supramolecular chirality**, which results from both the properties and the way in which the molecular components associate, is dynamic by constitution and therefore examples of large scale transcription of such **virtual chirality** remain rare. Our efforts involved the synthesis and the self-assembly of a guaninesiloxane monomer G_{Si} (Figure 6, 8) in the **G-quartet** and **G-quadruplex** supramolecular architectures, which are fixed in a hybrid organic-inorganic material by using a sol-gel transcription process, followed by a second inorganic transcription in silica, by calcination. The generation of **G-quadruplex hybrid material** can be achieved by mixing G_{Si} derivative with potassium triflate in acetone, followed the sol-gel process performed at room temperature and using benzylamine as catalyst. Then, the hybrid materials were calcined at 400°C in order to transcribe their superstructural features into inorganic silica replica materials. We have observed a long-range amplification of the **G-quadruplex** supramolecular chirality into hybrid organic-inorganic twisted nanorods followed by the transcription into inorganic silica microsprings.[11g,h] We believe that in the first sol-gel step the polycondensation reactions of the inorganic alkoxysilane network take place around tubular twisted superstructure of **G-quadruplex**. By this way, the dynamic **G-quadruplex** is fixed in a covalently bonded siloxane network, and the structural (constitutional) memory of G-quadruplex is transcribed in the hybrid materials. These fixed ("**frozen**") objects are chiral and self-correlate with a hexagonal order to generate anisotropic mesophases interconnected via condensed siloxane bridges. The mixture of these entities contains left and right twisted nanorods, as a result of the non-preferential dissymmetric orientation of the **G-quartets**. They are chiral and no inversion centers have been observed within the same entity.

Amazingly, these materials are at nanometric or micrometric scale topologically analogous to its **G-quadruplex** supramolecular counterpart. After the sol-gel process, the preformed helical silica network has embedded probably enough chiral information to be irreversibly amplified (reinforced) during the calcination process when almost total condensation of Si-OH bonds occurs. By calcinations of the hybrid material, the templating twisted **G-quadruplex** architectures are eliminated and inorganic silica anisotropic microsprings are obtained. They present the same helical topology, without inversion inside the helix. These objects have a different helical pitch, which strongly depends on the self-correlation between hexagonal twisted mesophase domains at the nanometric level.

Our findings showed a new way to transcribe the supramolecular chirality of a dynamic supramolecular architecture; the transfer of the supramolecular chirality of **G-quadruplex** at the nanometric and micrometric scale is reported, thereby creating nanosized hybrid or microsized inorganic superstructures, respectively. Moreover, we obtain **chiral materials** by using a starting **achiral** guaninesiloxane G_{Si} as precursor of **achiral G-quartet** and of **chiral supramolecular G-quadruplex.** Figure 8 represents the first picture of the **dynamic G-quadruplex** constitutionally transcribed at the nanometric level; it unlocks the door to the new materials world paralleling that of biology.

CONCLUSION

The **dynamic metallosupramolecular architectures and hybrid materials** described here are the nice examples of the dynamic constitutional devices adapting their morphology under the pressure of internal and external factors. Complex dynamic and positive feedback between supramolecular partners gives rise to emergent functional entities with a collective behavior. From the conceptual point of view, these systems express a synergistic adaptive behavior: it embodies a constitutional self-reorganization (self-adaptation) of their configuration producing an adaptive response in the presence of internal or external structural factors.

Finally, obtained the results extend the application of **constitutional dynamic chemistry**[2] from materials science to **functional constitutional devices**. This feature offers to materials science perspectives towards self-designed materials that involve modification and control of the intrinsic structural properties of dynamic entities correlated with the dynamic functional. Prospects for the future include the development of these original methodologies towards **adaptive dynamic constitutional materials** and their application to

different processes of interest for the development of a supramolecular approach to nanoscience and nanotechnology toward systems of increasing functional complexity.

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