

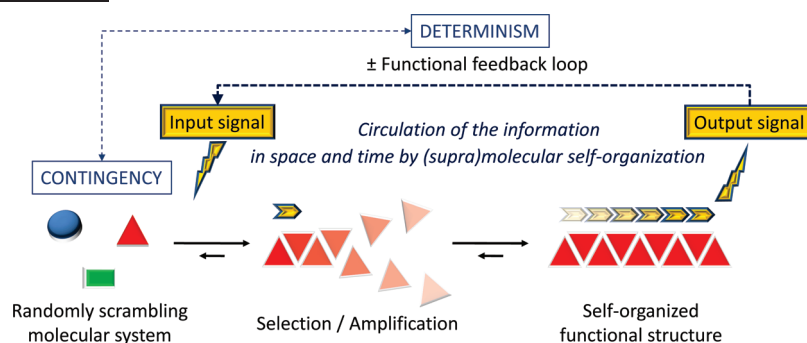
# Toward Self-Constructing Materials: A Systems Chemistry Approach

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## CONSPECTUS



To design the next generation of so-called “smart” materials, researchers will need to develop chemical systems that respond, adapt, and multitask. Because many of these features occur in living systems, we expect that such advanced artificial systems will be inspired by nature. In particular, these new materials should ultimately combine three key properties of life: metabolism, mutation, and self-replication.

In this Account, we discuss our endeavors toward the design of such advanced functional materials. First, we focus on dynamic molecular libraries. These molecular and supramolecular chemical systems are based on mixtures of reversibly interacting molecules that are coupled within networks of thermodynamic equilibria. We will explain how the superimposition of combinatorial networks at different length scales of structural organization can provide valuable hierarchical dynamics for producing complex functional systems. In particular, our experimental results highlight why these libraries are of interest for the design of responsive materials and how their functional properties can be modulated by various chemical and physical stimuli. Then, we introduce examples in which these dynamic combinatorial systems can be coupled to kinetic feedback loops to produce self-replicating pathways that amplify a selected component from the equilibrated libraries. Finally, we discuss the discovery of highly functional self-replicating supramolecular assemblies that can transfer an electric signal in space and time. We show how these wires can be directly incorporated within an electronic nanocircuit by self-organization and functional feedback loops.

Because the network topologies act as complex algorithms to process information, we present these systems in this order to provide context for their potential for extending the current generation of responsive materials. We propose a general description for a potential autonomous (self-constructing) material. Such a system should self-assemble among several possible molecular combinations in response to external information (input) and possibly self-replicate to amplify its structure. Ultimately, its functional response (output) can drive the self-assembly of the system and also serve a mechanism to transfer this initial information. Far from equilibrium, such synergistic processes could give rise to evolving, “information gaining” systems which become increasingly complex because internal self-organization rapidly reduces the potential energy surrounding the system.

## Introduction

The mechanisms of evolution going from divided, to condensed, then self-organized, and *in fine* leading to thinking matter are considered as central questions to be ultimately addressed by science. For instance, statistical physics,<sup>1</sup> information theory,<sup>2</sup> nonlinear dynamics,<sup>3</sup> or systems biology<sup>4</sup>

have elaborated theoretical models and experimental probes to describe the emergence of structures<sup>5</sup> (over scale) and their self-organization properties<sup>6</sup> (over time) which occur in complex systems. Several kinds of complex systems have been intensively studied for their various interests, going from spatial fractals<sup>7</sup> to cellular automata,<sup>8</sup> and from social,<sup>9</sup>

gene,<sup>10</sup> or neural networks<sup>11</sup> to living cells.<sup>12,13</sup> In particular, emergence and self-organization often appear from the collective behavior (integration) of interactions in multicomponent systems, which thus exhibit advanced functionalities that their single components could not produce individually. Furthermore, these new properties are crucial to bridge the gap between inert and living matter:<sup>14</sup> by looking at one of the most advanced complex systems, the living cell, one may characterize it as an evolvable autonomous entity which is able (i) to metabolize, (ii) to undergo mutations in response to its environment, and (iii) to self-replicate.<sup>15</sup>

While systems biology focuses on deconvoluting complexity from already existing superstructures encountered in nature, its molecular counterpart, systems chemistry,<sup>16</sup> aims at building minimal complex systems from their elementary components, in a bottom-up approach. Among the several problematics related to these systems, one can notice the importance of their internal structuring, together with the relationships existing between the presence of environmental factors and the self-organization processes that result when systems are pushed away from equilibrium in gradients of energy.<sup>17</sup> Such a minimal approach toward the fundamental understanding of emerging properties is also of interest to design the future generation of “smart” artificial functional materials which will be able to adapt to their environment. This behavior rests on the system's capability to receive external information (input) and to respond by modulating its internal structure in order to produce new functions (output). Ultimately, this information processing might also result in the transfer of the initially received information along the self-organizing (supra)molecular architecture, through space and time.

Focusing on these core questions, and in an attempt to address them by creating new molecular and supramolecular tools, we have developed a series of minimal chemical systems able to respond to external stimulations by changing their structuring and networking interactions. Some of these systems are described hereafter in order to highlight the internal and external parameters which can lead to selection and amplification processes. We will show that advanced autonomous functional materials can be designed by taking advantage of their networking behavior; in particular, we will discuss why these materials can serve as vectors of information and how they can self-construct for this purpose.

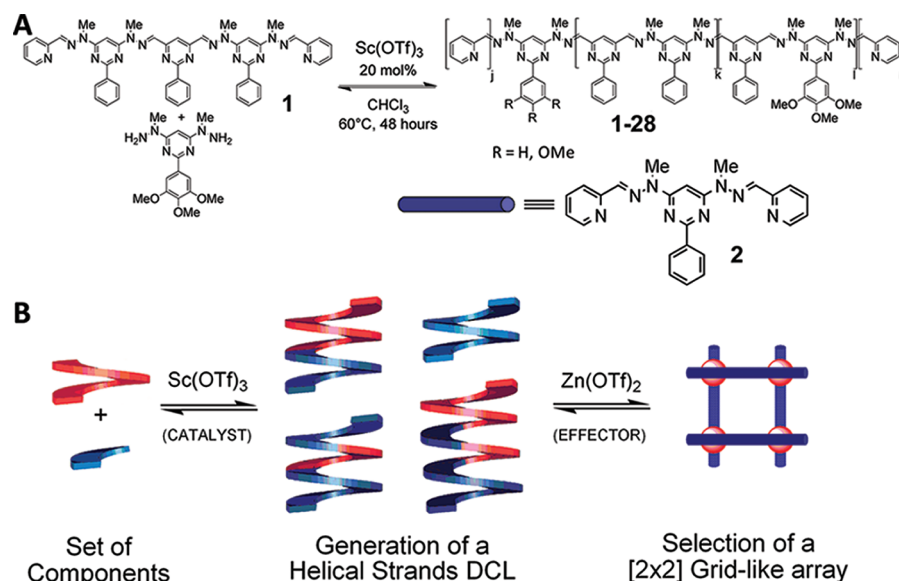
## Diversity Generation and Selection Principles in Dynamic Combinatorial Systems

Dynamic combinatorial libraries (DCLs) represent models for constructing networks of competing reversible chemical

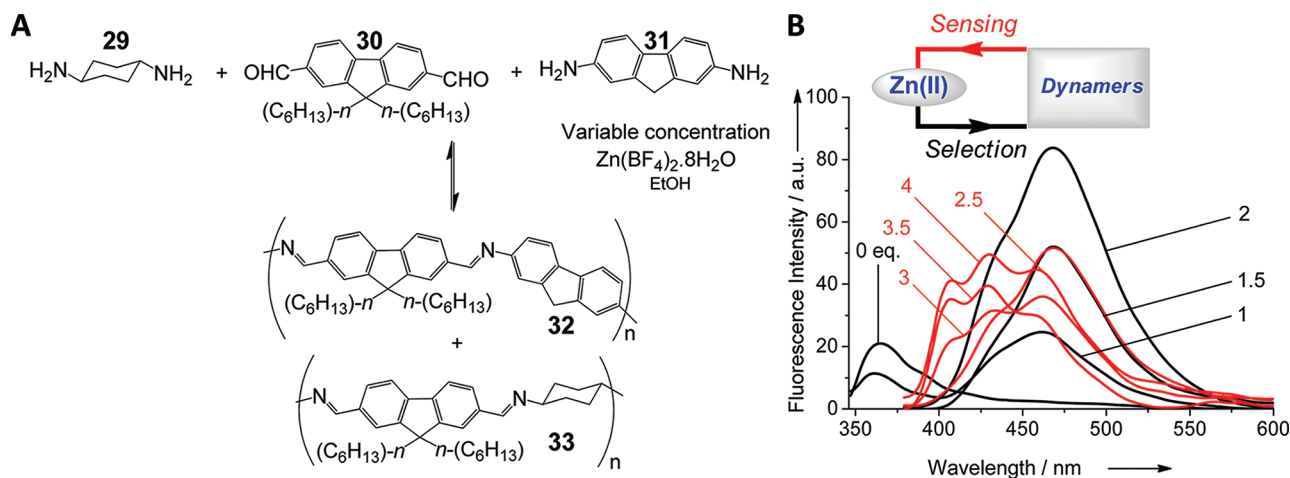
reactions occurring through coupled equilibria.<sup>18,19</sup> The composition of a DCL is thermodynamically driven and, as such, is able to adapt itself to any parameter that, permanently or transiently, modifies its constitution/energy potential surface.<sup>20,21</sup> Thus, by changing internal or external parameters, the involved equilibria can be displaced toward the amplification of given products through an adaptation process that will occur by an *in situ* screening of these species. This approach was extensively studied for the discovery of bioactive products,<sup>22–24</sup> the screening of catalysts,<sup>25,26</sup> or the synthesis of supramolecular receptors.<sup>27–29</sup> To make such libraries operational, several chemical features must be secured, the first of them being the generation of diversity. While weak supramolecular interactions can easily mediate this dynamic due to their kinetic lability, the extension of DCC to covalent bond is interesting to reach new structures but might require the activation of the exchange process using catalysts.

For instance, one example of such a catalyzed exchange was applied to poorly dynamic hydrazone units for the generation of libraries of helical strands.<sup>30–32</sup> In this work, the enforced self-assembly of helical strands by formation of reversible hydrazone-type bonds between pyrimidine-based helicity codons gives access to dynamic libraries of molecular helices. To activate the exchange process and generate diversity, a Sc(OTf)<sub>3</sub> catalysis was first developed to generate isoenergetic libraries,<sup>33</sup> thus avoiding any kind of stabilization of a particular product of the library by the catalyst itself. For instance, Figure 1A shows the chemical structures of a one turn helical strand **1**, being represented here as its linear form for the sake of clarity, and containing four hydrazone groups. The data analysis demonstrated that full recombination between **1** and dihydrazino-pyrimidine takes place under activation by 4% of catalyst. In these conditions, the library of compounds **1–28** was obtained, containing expanded helices of up to 10 hydrazone sites (more than 3 helical turns). Moreover, all the possible cross-combinations with phenyl and/or methoxyphenyl moieties were generated for each size of helical strand, highlighting the efficiency of the reorganization process. Interestingly, the production of product **2** among the members of the library allows the subsequent full reorganization of such libraries; indeed, by adding Zn<sup>II</sup> ions, two-site ligand **2** can self-assemble to yield grid-type complex Zn<sub>4</sub>(**2**)<sub>4</sub> (Figure 1B).

In a broader perspective, the results described above illustrate the ability of constitutional dynamic systems to respond to environmental parameters and to perform effector-driven selection toward the fittest constituent, an essential



**FIGURE 1.** (A) Generation of a library of helices starting from one-turn/4 sites helical compound **1** and dihydrazino-pyrimidine using  $\text{Sc}(\text{OTf})_3$  as catalyst. (B) Schematic representation of the system: (left) Lewis acid-catalyzed generation of dynamic constitutional diversity in helical molecular strands; (right)  $\text{Zn}^{\text{II}}$  recombination toward  $[2 \times 2]$  grid formation. Adapted and reprinted with permission from ref 30. Copyright 2004 John Wiley and Sons.



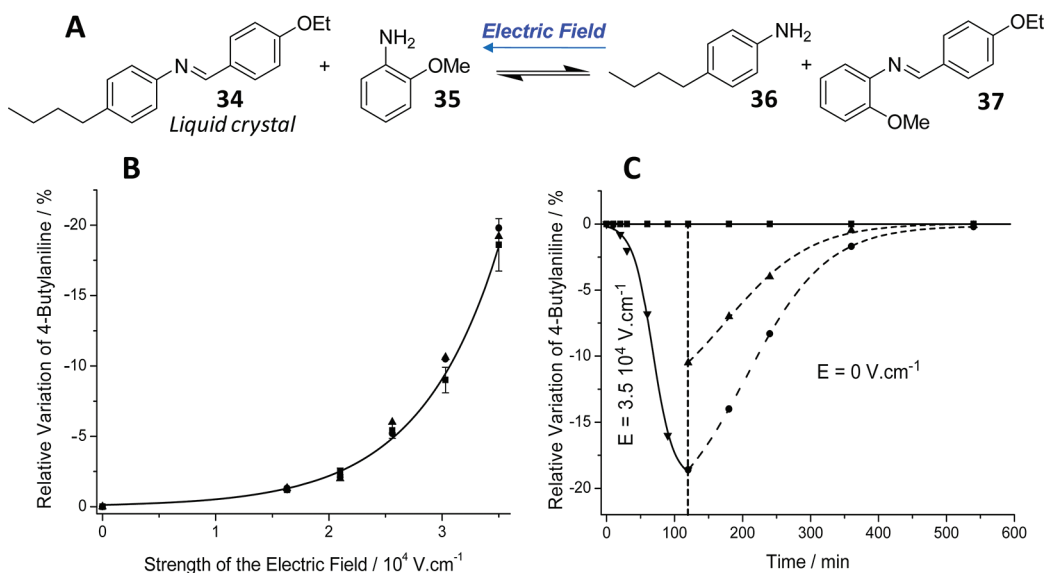
**FIGURE 2.** (A) Combinatorial dynamic library of polymeric iminofluorenes, with  $\text{Zn}^{\text{II}}$  promoted component exchange. (B) Fluorescence titration (0–4 eq  $\text{Zn}^{\text{II}}$ ) illustrating the component exchange process (sensor formation) (black data), and the self-sensing occurring afterward (red data), i.e., beyond 2 equiv of  $\text{Zn}^{\text{II}}$ . Adapted and reprinted with permission from ref 38. Copyright 2004 American Chemical Society.

feature characterizing the adaptive nature of DCC under the pressure of external factors. However, the products of this library do not present a functional property which can be considered as useful for materials science, and a series of works was then developed to implement DCC in this direction, as illustrated hereafter by a series of examples.

## Selection in Functional Dynamic Combinatorial Libraries: Implementations in Materials Science

**Dynamic Combinatorial Fluorescent Polymers.** An example of a material which can adapt its functional behavior

by changing its internal structure was developed using a class of dynamic objects based on reversible polymeric structures called dynamers.<sup>34–37</sup> In this work,  $\text{Zn}^{\text{II}}$  ions were found to promote component exchange within polyimine dynamers, that is, dynamic polymers (**32** and **33**) in which the monomers **29**, **30**, and **31**, are connected by reversible imine bonds (Figure 2A).<sup>38</sup> This recombination process led to a dramatic change in the fluorescence properties of the whole system, with a 100 nm shift of the emission wavelength (Figure 2B, black data). Furthermore, the binding interaction of zinc ions with fluorescent polymers **33** at the imine bond led to marked changes in both emission



**FIGURE 3.** (A) Thermodynamic equilibrium between imines among which **34** displays liquid crystal properties. (B) Effect of the strength of the electric field, at thermodynamic equilibrium, showing the relative amplification of the LC species expressed from a DCL. (C) Kinetics of this relative variation under a field  $E = 3.5 \times 10^4 \text{ V}\cdot\text{cm}^{-1}$  (triangles; plain line curve); kinetics of re-equilibration after stopping the electric field (dots), and for an initial applied field of  $E = 3.03 \times 10^4 \text{ V}\cdot\text{cm}^{-1}$  (triangles, dashed line curve); control experiment without field (squares). The values are given using the relative variation of the free amine entering in the composition of the liquid crystal by imine condensation. Reprinted with permission from ref 41. Copyright 2006 John Wiley and Sons.

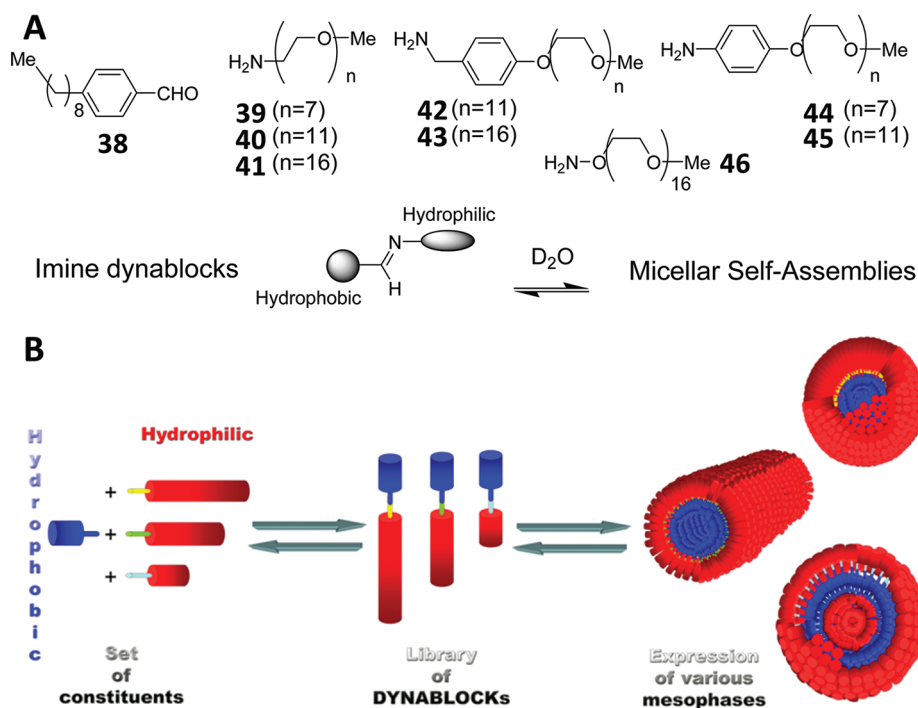
intensity and wavelength after the exchange process itself (Figure 2B, red data). Thus, as a result of the two distinct effects of the metal ions (i.e., polymer selection/enhancement of fluorescence), it was shown that zinc ions induce a constitutional reorganization within the DCL, leading to the selective formation of a polymeric structure whose optical properties are strongly affected by the ions themselves, so that it signals the presence of its own promoter.

Such constitutional reorganization of a system is of special interest for the design of dynamic “smart” materials, allowing the expression/fine-tuning of a given virtual (latent) property and/or producing an adaptative functional response under the pressure of external conditions. Moreover, these results express a synergistic adaptative behavior: the addition of an external effector (e.g., zinc ions) drives a constitutional evolution of the dynamic mixture toward the selection and amplification of that species (compound **32**) producing a signal (here optical), indicating the presence of the effector which has promoted its generation in the first place. It embodies a “dynamic self-sensing” process, that extends the range of self-processes.

Other examples showing the influence of chemical effectors were described for promoting and selecting particular products within libraries of dynamers or of small molecules, the pH being one trigger of particular interest in this respect.<sup>39,40</sup> To go one step further, one may also imagine implementing new physical triggers in order to induce selection.

**Dynamic Combinatorial Liquid Crystals.** In order to extend the range of physical external triggers for inducing selection processes, the possibility was explored of using an electric field to influence the thermodynamic equilibrium in a mixture of constitutionally interrelated compounds.<sup>41,42</sup> To this end, the development of dynamic liquid crystals (LCs) appeared particularly well-suited for two main reasons: (i) the potential existence of various LC phases, such as nematic, smectic, and so forth, depending on the constitution of the mixtures and molecular structure of the components; and (ii) the well-known behavior of LCs to be macroscopically oriented and stabilized in either electric or magnetic fields.<sup>43</sup> It was possible to quantify the disturbances entailed by the variation of an electric field on mixtures of imines and amines, containing an LC type imine with a negative dielectric anisotropy. Two distinct phenomena were observed when an electric field was applied on films sandwiched between indium tin oxide (ITO) plates, involving transitions between isotropic and nematic phases. The first one consists in the expulsion from the LC, upon application of an electric field, of compounds that do not participate in the nematic phase formation due to electrohydrodynamic effects; the second is based on a direct quadratic effect of the electric field on the thermodynamic equilibria in a DCL via coupling of the field to the LC forming entity and its subsequent stabilization/amplification (Figure 3A,B).

Importantly, the amplified constituent was the one coupling the most strongly to the electric field (the liquid crystal),



**FIGURE 4.** (A) Examples of chemical structures based on hydrophobic aldehyde **38** and various hydrophilic amines **39–46** to build amphiphilic Dynablocks. (B) Molecular hydrophobic and hydrophilic constituents competing for their reversible association in Dynablocks. These latter self-assemble due to their amphiphilic properties at the supramolecular level. Consequently, any parameter that can affect one of the thermodynamic equilibria will be coupled to the others, thus linking the responsiveness of these systems at both length scales. Reprinted with permission from ref 46. Copyright 2011 Royal Chemical Society.

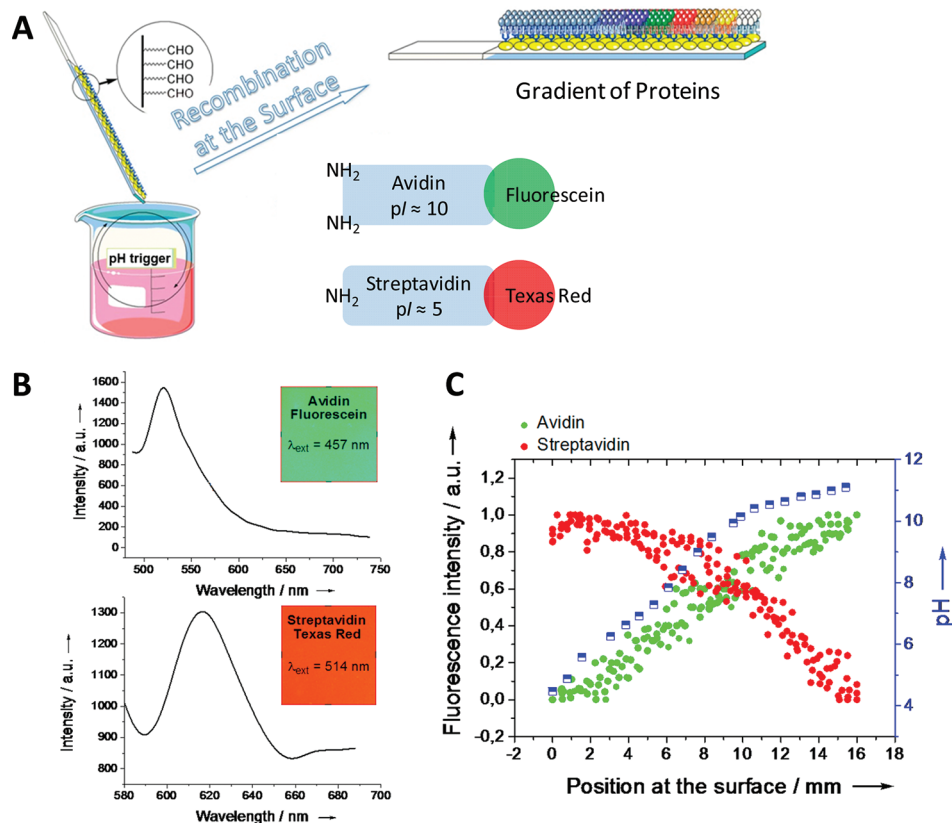
and this amplification can consequently result in a phase transition from liquid to nematic. The processes described here broaden the scope of DCC by demonstrating the influence of a particularly interesting environmental parameter, the electric field, and illustrate the adaptation of dynamic mixtures to physical effectors through the formation of the “fittest” constituent, the one presenting the strongest coupling to the field.

To go further and target more complex structures, that is, more precisely organized at larger scales by long-range interactions, it appears also of importance to implement dynamic reorganization in nanostructured materials.

**Dynamic Combinatorial Nanostructures.** One of the current key objectives in chemistry and materials science is to design new responsive functional systems at the mesoscale.<sup>44</sup> The bottom-up approach from nano- to micrometer scales using programmed self-assembly of molecules represents a key technology toward this direction.<sup>45</sup> In this context, we have discussed the concept and the development of amphiphilic dynamic block copolymers or surfactants (“Dynablocks”) in which hydrophobic and hydrophilic blocks are reversibly linked together. When combined in mixtures, and in suitable solvents, these molecular objects

can lead to changes in their mesophase structuring at the supramolecular level (Figure 4). In particular, we have demonstrated that the chemistry of Dynablocks can be directed by the presence of external triggering parameters, such as pH, with the possibility to reversibly modulate the shapes and sizes of micellar nano-objects.<sup>46,47</sup>

The studies performed on such systems revealed that these objects present several interesting aspects and potential assets for further fundamental and applicative explorations because: (i) they can reach a high level of complexity from a limited number of units by combining hierarchical levels of organization; (ii) they can be analogically modulated by intensive parameters (in particular pH variation); (iii) they have fast and reversible recombination properties; (iv) they present abilities of selection from a minimum of information contained in their building blocks. Overall, this approach is valuable to participate in the design of responsive nano-objects that will vary their structural and associated functional properties from a common set of constituents and as a response to external parameters, and it also presents interest for the development of responsive bioactive materials.<sup>48,49</sup> With similar ideas in mind, other works were developed toward dynamic 2-D nanostructures.



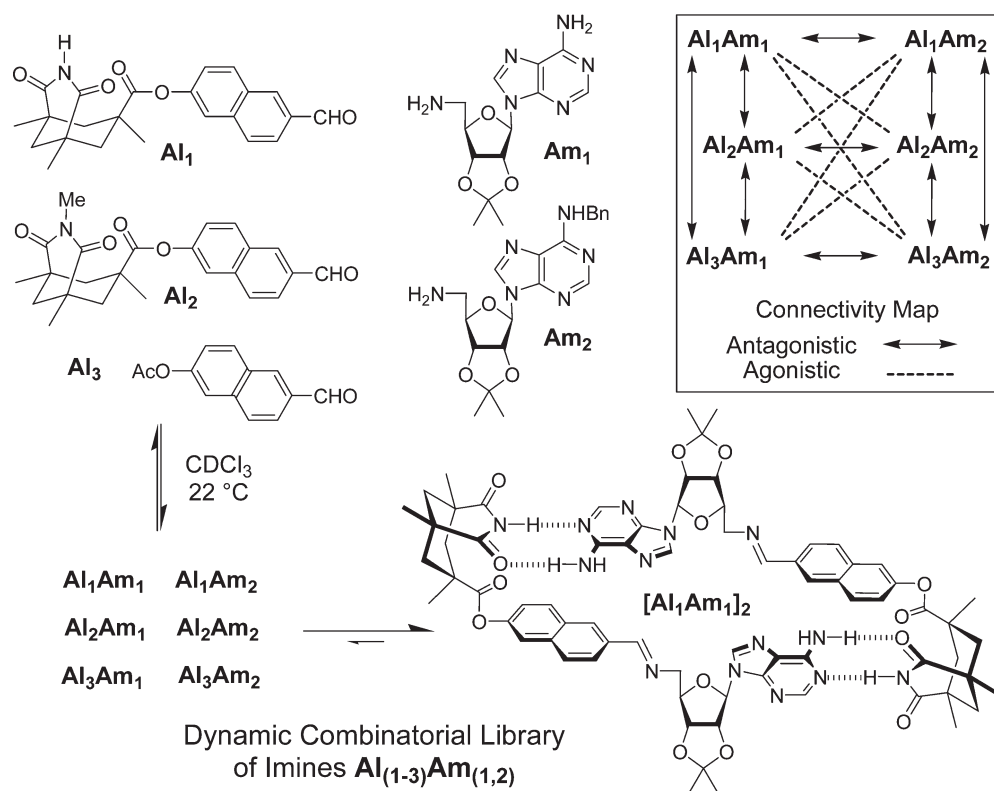
**FIGURE 5.** (A) General principle to create functional surface gradients from dynamic combinatorial self-assembled monolayers and in particular for the differential anchoring of proteins having different isoelectric points ( $pI$ ), due to a different number of arginine and lysine residues, and labeled with different fluorophores. (B) Fluorescence images, and associated spectra, of a quartz aldehyde monolayer associated with an avidin–fluorescein complex and a streptavidin–Texas Red complex. (C) Normalized relative intensity of an avidin–fluorescein (green dots)/streptavidin–Texas Red (red dots) gradient as a function of the pH (blue squares) and as a function of  $\approx 300$  different positions at the surface. Adapted and reprinted with permission from ref 52. Copyright 2009 Nature Publishing Group.

**Dynamic Combinatorial Interfaces.** Surfaces determine how objects interact with their environment and surface chemistry is a research domain of high interest, particularly for the study and design of nanostructures where nearly every atom is interfacial. For example, the spontaneous two-dimensional organization of self-assembled monolayers (SAMs) provides convenient, flexible, and simple molecular systems in the form of thin films which can modify the properties of surfaces.<sup>50,51</sup> SAMs are nano-objects with a number of useful properties that link molecular-level properties to interfacial phenomena such as wetting, adhesion, friction, corrosion resistance, biocompatibility, and so forth. The formation of SAMs is usually based on the chemistry of non-reversible covalent bonds, and dynamic attachments are scarce. Recently, DCC was extended and applied to the chemistry of SAMs, showing its potential as an efficient tool to functionalize surfaces in such a way that their interfacial properties can be controllably varied in space and time.<sup>52</sup> Modulation of pH was also used to tune the fast, selective,

and reversible attachment of functional amines, with different  $pK_a$  values, to an aldehyde-coated surface. In particular, this technique enables the hierarchical construction of mixed gradients comprising either small functional molecules or proteins (Figure 5). The control of the (bio)chemical composition at any point on the surface potentially provides a simple bottom-up method for accessing numerous surface patterns with a broad range of functionalities. Beyond that, it is assumed that this approach is not limited to the formation of gradients, but that it would be readily extended to the design of responsive interfacial nano(bio)objects.

### Amplification by Self-Replication from Dynamic Combinatorial Systems

In the series of examples above, we have described the versatility of systems which change their constitution together with their functional properties to act as tunable materials of various natures. However, the intensity of external stimuli might often not be enough to reorganize



**FIGURE 6.** DCL obtained by mixing the three aldehydes ( $\text{Al}_1$ – $\text{Al}_3$ ) and the two amines ( $\text{Am}_1$ ,  $\text{Am}_2$ ). In this combinatorial set, one imine, namely,  $\text{Al}_1\text{Am}_1$ , can self-assemble through hydrogen bonds and produce homodimer  $[\text{Al}_1\text{Am}_1]_2$ . Reprinted with permission from ref 55. Copyright 2008 American Chemical Society.

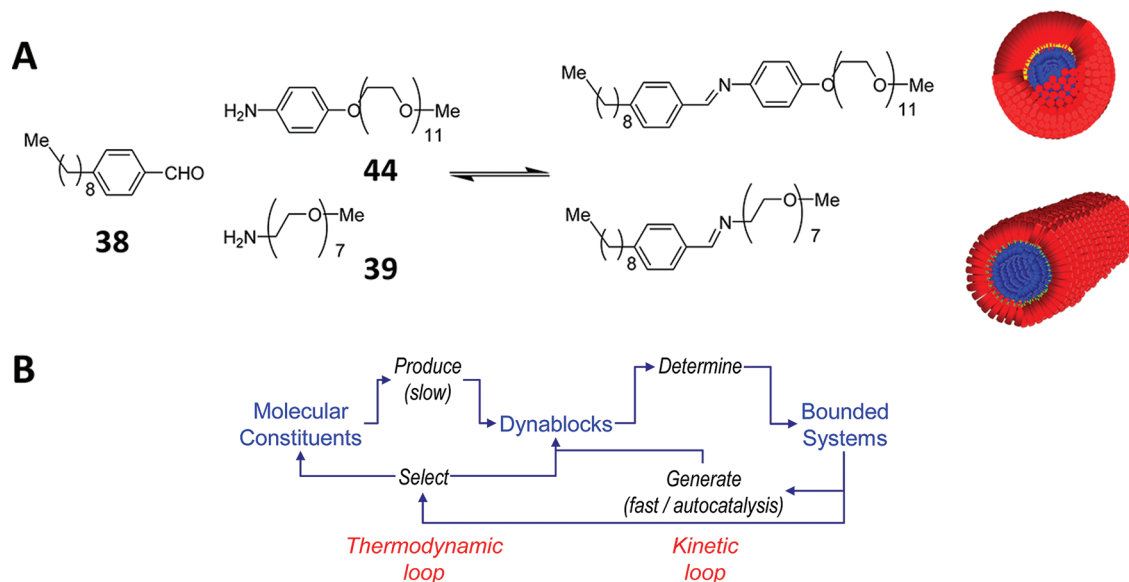
such systems, especially if having a high number of coupled equilibria supporting their network topology, thus being strongly pushed by entropy. For this reason, the implementation of self-replicating loops<sup>53,54</sup> appears of high interest to help the amplification of products (and functions) which could be initially selected by an external stimulus, and then amplified by autocatalysis.

**Dynamic Combinatorial Self-Replication from Small Molecules.** In a first example, and in order to couple a self-replication process to DCC, we have envisioned to design several building blocks capable of (i) reversible covalent associations and (ii) displaying (or not displaying) complementary supramolecular units in order to produce (or not produce) a template with self-recognition properties (Figure 6).<sup>55</sup> The key molecule, inspired by a seminal work of Rebek,<sup>56</sup> was chosen as imine  $\text{Al}_1\text{Am}_1$ , being able to strongly associate with itself into complex  $[\text{Al}_1\text{Am}_1]_2$ , and synthesized by the condensation of aldehyde  $\text{Al}_1$  (derived from a Kemp's imide) and adenosine amine  $\text{Am}_1$ . These units were mixed with other amines and aldehydes, which do not present self-recognition properties, in order to build the DCL presented in Figure 6. It was demonstrated that an important amplification in favor of  $[\text{Al}_1\text{Am}_1]_2$  can be obtained in this system (up to 200%), which

rests on both thermodynamic and kinetic (i.e., self-replicating) features. This example clearly demonstrates that it is possible to self-amplify one product in a DCL, namely, the one that can self-complementarily direct its own formation. Importantly, because of the double reversibility of the system (supramolecular H-bonds and molecular imine condensation), the competition is not only ruled by the differential rates of formation of the components, but also by the possible take-over of the building blocks of the antagonistic competitors, thus leading to the decrease of their absolute concentration. It illustrates the spontaneous screening and selection of the most efficient self-replicator by the destruction of the entities which are not able to replicate themselves.

In order to implement these self-replicating aspects in materials science, it was envisioned to couple them in the previously described Dynablocks approach and to self-replicate large self-assemblies and nanostructures made of surfactants with a selection process.

**Dynamic Combinatorial Self-Replication of Large Self-Assemblies.** The implementation of dynamic combinatorial self-replicating systems made of large supramolecular assemblies was introduced to avoid an important drawback appearing in many systems based on small molecules, and



**FIGURE 7.** (A) Chemical structures and (B) synergistic constitutional relationships observed at two length scales within a model minimal self-replicating DCL. Reprinted with permission from ref 57. Copyright 2009 John Wiley and Sons.

known as product inhibition. The core idea was to take advantage of the growth/division cycles of micellar self-assemblies, which can display a particular case of autocatalysis, namely, *autopoiesis*.<sup>14,57</sup> The minimal criteria defining autopoiesis should verify whether (i) the system has a semipermeable boundary (ii) that is produced within the system and (iii) that encompasses reactions which regenerate the components of the system. By analyzing the behavior of well-defined Dynablocks, it was shown that some of them can self-replicate with an exponential time–concentration profile which rests on an autopoietic behavior, mainly supported by the sequential growth/division process of the micelles (Figure 7). In addition, it was demonstrated that, in competition experiments, the self-replicating nanostructure can increase its population exponentially by taking the molecular constituents of its competitors. Overall, this work describes a general concept for the synergistic relationships which exist at two length scales within a self-replicating DCL.

In a general scheme, the molecular constituents compete at the subnanometer scale for the reversible production of Dynablocks having different length ratios between their hydrophilic and hydrophobic blocks. This ratio mainly determines the formation and the thermodynamic stability of the bounded structures at the tens of nanometers scale. Then, in a first *autocatalytic loop* with a sigmoid concentration–time profile, these self-assemblies are able to generate their own formation by increasing the rate of the Dynablock condensation and they entirely fulfill the required characteristics of a minimal autopoietic process. Moreover, in a

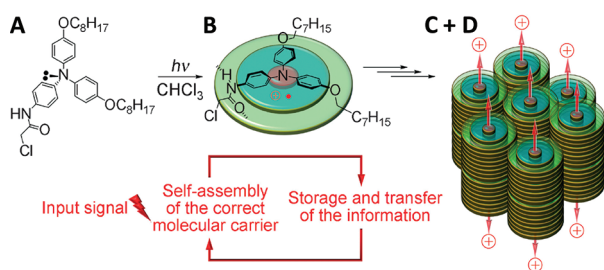
second *thermodynamic loop*, the self-assemblies discriminate between the incorporated Dynablocks and thus favor the preferential synthesis of their own blocks. Such a system, combining cooperative processes at different length scales in networks of equilibria and displaying autocatalysis within DCLs, is of general interest for the understanding of the emergence of collective self-organizing properties.<sup>58</sup>

### On the Synergistic Behavior Coupling a Selection Process to an Emerging Function: An Information Transfer Phenomenon

To go further with self-replicating systems, one may expect to couple a stimulus (input) to an exponential growth of a material displaying a physical functional property (output), and possibly to couple this emerging functional property as a feedback loop reinjected in the system. We hereafter describe a new system of this kind.

**Formation and Amplification of Supramolecular Wires As Smart Interconnects.** Triarylamine-type molecules are considered as very efficient functional units widely used as photoconductors and charge carriers.<sup>59</sup> In particular, they display appreciably high hole-transport mobility and are thus inserted in numerous electro-optical devices. However, despite the profusion of studies performed on triarylamine derivatives, both by academic research and industry, this molecular core was never described as a structuring precursor that would be able to self-assemble in ordered supramolecular architectures, possibly with enhanced physical properties. Recently, it was found that chemically

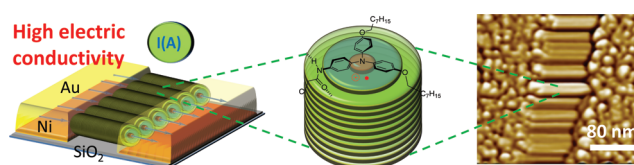




**FIGURE 8.** Hierarchical self-assembly processes that occur upon light irradiation of triarylamine derivatives and produce molecular fibers, which stabilize, store, and transport the holes that were at the origin of their spontaneous formation. Reprinted with permission from ref 60. Copyright 2010 John Wiley and Sons.

tailored derivatives of triarylamine derivatives can self-assemble simply by light exposure (Figure 8A).<sup>60</sup> The structuring process occurs as a result of highly intriguing synergistic phenomena which start with the formation of a triarylammmonium cationic radical upon light stimulation (Figure 8B). This radical can in turn be transferred to other neutral triarylamine derivatives by charge transfer (Figure 8C), thus allowing the supramolecular polymerization<sup>61</sup> of units containing a delocalized cationic radical (Figure 8D). We also assume that, as indicated by EPR spectroscopy, one radical is stabilized within the stacking of about 160 triarylamine units along the induced self-assembled wires. In addition to the charge transfer phenomena and the  $\pi$ - $\pi$  stacking interactions, the structure–property study revealed that at least one hydrogen bond and van der Waals interactions of lateral chains should be combined to produce stable structures. Moreover, it was demonstrated that these molecular wires, which protect holes from quenching, can combine into very strongly packed bundles of larger fibers.

Recently, it was demonstrated by seeding experiments that this process displays a very strong self-replicating behavior, leading to exponential growth of the fibers which can induce their own formation.<sup>62</sup> Thus, from a conceptual point of view, such a system introduces a paradigm for the circulation of information at the supramolecular level that would participate in the construction of “smart” materials. Indeed, the stimulation of this system with light creates an electronic signal which induces the building of the correct self-assembled charge carriers, that is, the supramolecular wires, which in turn are able to stabilize and transfer this first electronic signal over space and time and, in addition, to catalyze their own formation. This represents a minimal example to understand and to design *de novo* stimuli-responsive chemical systems displaying a very fundamental synergistic and dynamic structure/function relationship, i.e. that are able to receive, store, conduct, and exchange physical information by self-organization.



**FIGURE 9.** Spontaneous construction between nanoelectrodes of supramolecular wires, thanks to the simple lighting of a triarylamine solution and to the presence of an electric field (AFM imaging on the right). Adapted and reprinted with permission from ref 64. Copyright 2012 Nature Publishing Group.

To go one step further, we deem it important to show that such a relationship could lead to the construction of a real functional material within a device which would require an electronic transport.<sup>63</sup> Recently, this was achieved by the straightforward interconnection of metallic electrodes by supramolecular organic nanowires, self-assembled from a solution of triarylamine under a combination of light and electric field triggers (Figure 9). Their measured ohmic character relates to outstanding conductivity values, which make these fibers the first supramolecular assemblies presenting a unique metallic character both in the bulk and at the interface with electrodes.<sup>64</sup>

These results illustrate that a systems chemistry approach can be of high potential to develop new functional materials, with enhanced physical properties. Here, the combination of a trigger (light) and of a gradient of energy (the electric field), produces a self-organized architecture which can link spatial coordinates (the electrodes) with the capacity to transfer the conducting information (i.e., the electric charges) through the system. One may for instance draw an analogy with the transfer of information occurring at the cellular level in the brain, which rests on the plasticity of neuronal connexions. This amounts to a self-construction phenomenon, which is able to transfer information by decreasing the potential energy surrounding the system (gain of entropy) through the self-organization of its internal structure (loss of entropy). One may notice that the general conceptual scheme presented in the context of this Account is now relatively close to completion; the remaining step consists only in improving the present conducting system by starting from a random library of competing building blocks.

## Conclusion

For a long time, research related to complex matter has been of central interest in several fields, including mathematics, physics, and biology. The recent advances of analytical tools in chemistry offer novel opportunities to study and further design complex systems ranging from nano- to mesoscales

by using a bottom-up approach. Several works have already discussed the behavior of multicomponent molecular and supramolecular systems which display self-organization properties and produce adapted functional structures by responding to their environment. In particular, these systems can be used to access new responsive materials by achieving the following sequence: (i) diversity generation, (ii) selection, (iii) amplification, and (iv) function. Those have by essence enhanced functional properties compared to their static counterparts, because their network topology holds the capability to modulate their structure/function response according to the presence, or to the variable intensity, of an external trigger. By carrying these ideas further, this Account has discussed the possibility to define a class of self-constructing materials which will result from the synergy existing between the information received by such systems and their subsequent structuring. In some particular cases, the function of the emergent structure will *in fine* serve to transfer the initially received information, both in space and time. These materials, in which a cooperative relationship exists between the surrounding potential energy and the self-organization of their internal structure as information carriers, are highly interesting for the design of evolving systems when pushed far from equilibrium. Thus, a systemic approach of functional materials can yield to self-construction thanks to the faster dissipation of the surrounding gradients of energy.

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#### BIOGRAPHICAL INFORMATION

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The authors declare no competing financial interest.

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