

Self-Sorting Phenomena in Complex Supramolecular Systems

Marina M. Safont-Sempere, Gustavo Fernández, and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg (Germany).

CONTENTS

1. Introduction	5784
2. Self-Sorting: Definition, Types, and Influence of External Variables	5784
2.1. Definition and Types	5784
2.2. External Variables and Concentration of Competitive Species: Influence on Self-Sorting Phenomena	5785
3. Molecular Codes for the Self-Sorting of Complex Mixtures	5789
3.1. Size and Shape	5790
3.2. Complementarity in Hydrogen-Bonded Systems	5793
3.3. Steric Factors	5796
3.4. Coordination Sphere in Metal–Ligand Interactions	5800
3.5. Charge Transfer	5801
4. Chiral Self-Sorting	5805
5. Conclusions	5809
Author Information	5810
Acknowledgment	5810
Biographies	5810
References	5811

1. INTRODUCTION

Nature successfully manages under extremely adverse conditions to accomplish intricate functions responsible for the regulation and control of the vast majority of biological processes that eventually sustain life on our planet.¹ Biological molecules are required to carry out selective functions while often being hindered by surrounding agents which are simultaneously competing to bind the same targets. This high degree of selectivity in nature ultimately depends on the “molecular instructions” encoded in the chemical structure of the interacting species responsible for every single recognition or discrimination event.² The formation of the DNA double helix, for instance, requires the base-pairing (sorting) of complementary nitrogenous bases (adenine–thymine (A–T) and cytosine–guanine (C–G)).^{3,4} These high-fidelity recognition processes are crucial in the storage of genetic information used in the development and functioning of all known living organisms and some viruses. Other sophisticated superstructures such as microtubules,^{5,6} are built upon polymerization of dimers of two different globular proteins (α - and β -globulin), giving rise to cylindrical micrometric arrangements.⁷ The formation of heterodimers composed of two different proteins requires the self-discrimination of equals,

and the simultaneous recognition of complementary units. In the final instance, the small molecules of life (e.g., sugars, amino acids and fatty acids) are able to assemble not only to form such above-mentioned macromolecules, but also to self-sort in one of the most efficient and complex processes known in nature to build the functional basic unit of life: a cell.^{8,9} In a cell, multiple levels of compartmentalization arising from the self-sorting of their molecular components allow the coexistence of different functional architectures acting independently. This exceptional selectivity in nature makes possible the existence of life on our planet.^{10,11}

Unlike the high complexity of natural or biological architectures, the majority of artificial self-assembled systems reported so far have been investigated in isolation. This has been mainly due to the lack of suitable characterization methods and technical or economic constraints, which far exceed the resources of most research institutes. However, the remarkable development of analytical tools is increasingly enabling scientists to pinpoint intractable problems associated to multicomponent mixtures.¹² In this context, *Systems Chemistry* has arisen in recent years as a new discipline that aims to investigate complex mixtures of interacting molecules.^{13–17} These mixtures can give rise to outstanding emergent properties as a result of the interaction of the individual components and cannot be ascribed to any of their components acting in isolation. Although this emerging discipline is still in its infancy, ongoing research advances are enabling current (supramolecular) chemists to unravel the behavior of individual molecules in multicomponent mixtures and to anticipate the reasons that lead artificial molecules to bind or ignore a specific partner in a complex multicomponent environment.

In this review, we will discuss the external variables and intrinsic factors (molecular codes) that influence the recognition or discrimination of supramolecularly interacting chemical species in solution.¹⁸ The comprehension of this “molecular programming” in artificial systems will define the variables that control self-sorting processes, and may ultimately contribute to a better understanding of the self-assembly pathways in natural systems. By restricting ourselves to noncovalent bonds and self-sorting in solution^{19,20} we will not cover self-assembly processes on solid surfaces and self-sorting phenomena based on reversible covalent bonds. However, excellent reviews have recently become available by De Feyter¹⁸ and Otto,^{13,14} which cover these topics.

2. SELF-SORTING: DEFINITION, TYPES, AND INFLUENCE OF EXTERNAL VARIABLES

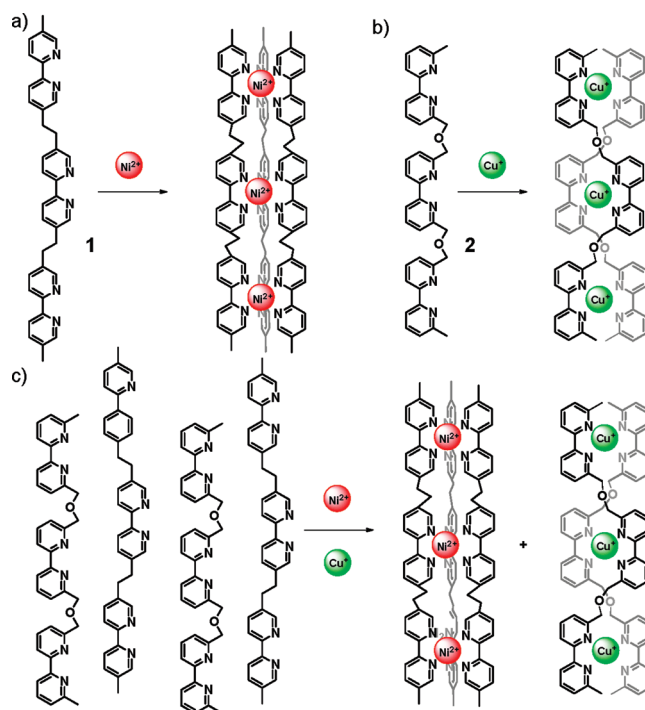
2.1. Definition and Types

The behavior of individual synthetic molecules in complex systems was first investigated in mixtures of different helical

Received: October 25, 2010

Published: August 12, 2011

Scheme 1



metal complexes.¹⁹ Lehn and co-workers studied the coassembly of a mixture of two tris-bipyridine ligands (**1** and **2** in Scheme 1), previously demonstrated to self-assemble independently in the presence of Ni(II) and Cu(I) ions into well-defined triple and double helicates, respectively. When a mixture of 2 equiv of **2**, 3 equiv of **1**, 3 equiv of Cu⁺ and 3 equiv of Ni²⁺ was treated under appropriate conditions, precipitation of only the corresponding double and triple helicates in quantitative yields took place. Fast atom bombardment (FAB) mass spectrometry and ¹H NMR experiments provided evidence supporting the recognition of the tetrahedrally coordinating copper ions by the tritopic ligand **2** and the octahedrally coordinating nickel ions by the ligand **1**, thereby ruling out the formation of crossover, mixed or undesired species. This singular observation was originally termed as *self-recognition*, or recognition of like from unlike and self-from nonself,¹⁹ to explain the preferential binding of like ligand strands on like metal ions (templates) disregarding other species in solution.

In recent years, the more general term *self-sorting* has been evolved to describe such recognition phenomena in multicomponent mixtures based on a suggestion of Isaacs and co-workers^{20,21} and nowadays largely accepted by the scientific community. *Self-sorting* can be defined as high fidelity recognition between molecules (and ions) within complex mixtures.²⁰ If affinity for others is shown we will call this assembly process *self-discrimination* (*social self-sorting*),²² and the affinity for itself will be called *self-recognition* (*narcissistic self-sorting*) (Figure 1).²³

Self-sorting systems can in turn be subdivided into those displaying *thermodynamic* or *kinetic* self-sorting: they have reached a thermodynamic equilibrium, or they can be considered as trapped species under kinetic control. The majority of the self-sorting systems described in literature operate under thermodynamic control. Recently, Schalley and co-workers have further

classified self-sorting systems into *integrative* or *nonintegrative*.²⁴ In *nonintegrative* systems, the elements of the mixture combine to yield more than one final complex (Figure 1, top and bottom left) whereas in *integrative* systems all species present in the mixture are integrated into one global complex (Figure 1, bottom right). Whereas nonintegrative systems can be composed of social or narcissistic ensembles, integrative systems require the socialization of all elements present in the mixture, being a particular case of social self-sorting (Figure 1, bottom right). It is easy to imagine solvent- or temperature-dependent sequences that show a change from nonintegrative to integrative self-sorting. We believe that such hierarchical self-assembly sequences constitute a pathway toward supramolecular architectures and materials with advanced functionalities.

In general, self-sorting events are directed by the same intermolecular forces which govern any molecular recognition process, i.e. hydrogen bonds,^{25–27} metal–ligand interactions,^{28–35} electrostatic interactions,²⁴ π – π -stacking,³⁶ and solvophobic effects,^{37,38} and therefore, the factors that determine these recognition events will compromise the fidelity of the self-sorting processes. In the following section we will investigate how these binding events are compromised upon alteration of external variables or addition of competing species at different concentrations.

2.2. External Variables and Concentration of Competitive Species: Influence on Self-Sorting Phenomena

Similarly to any molecular recognition event or self-assembly process, several external variables (temperature, concentration, solvent, stoichiometry, pH, etc) can affect the outcome of a certain self-sorting process. The presence of water, for instance, prevents the stabilization of hydrogen-bonded assemblies³⁹ but, on the other hand, reinforces the interaction of nonpolar solutes by hydrophobic effect.^{40,41} The effect of different variables on

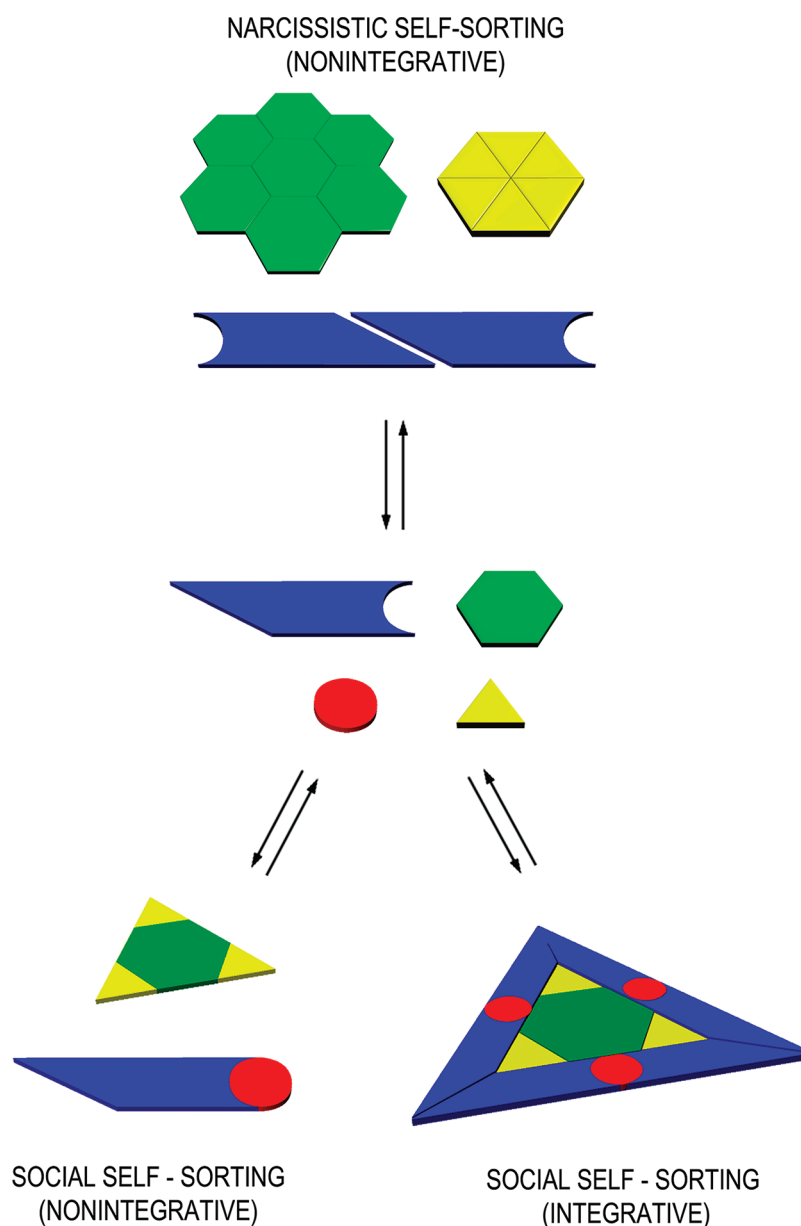


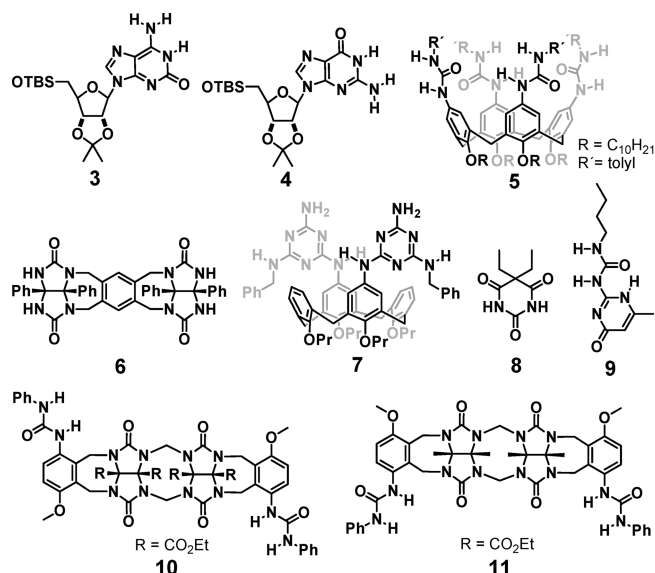
Figure 1. Schematic representation of the different types of self-sorting. Top: *Self-recognition (narcissistic self-sorting)*. Bottom: *Nonintegrative (left) and integrative (right) social self-sorting*.

individual binding events is widely applied to initiate self-assembly processes. However, their influence in complex mixtures of competing species, capable of self-recognizing or discriminating through intermolecular forces remains nearly unexplored. To date, only few authors have purposely investigated how specific equilibria within multicomponent mixtures would respond upon altering some external variables (concentration, temperature, pH, and solvent) or adding competing species. We believe that such studies will disclose important insights into the adaptation of complex mixtures, which will enable chemists to design self-assembled materials whose properties are one level closer to those found in nature.

Isaacs and co-workers pioneeringly studied the impact of different factors in mixtures of synthetic molecules containing hydrogen bonding groups, previously demonstrated to undergo self-assembly processes and give rise to well-defined

supramolecular architectures.²⁰ The authors selected two Davis' ionophores **3** and **4** (capable of self-assembling in the presence of barium picrate into stacked decameric and octameric supramolecular architectures respectively from the corresponding pentameric and tetrameric rosettes), Rebek's calixarene tetraurea **5** and molecular clip **6** (which have the ability to self-assemble into dimeric capsules and tennis-ball-like structures, respectively), Reinhoudt's pyrimidine-based calixarene **7** (capable of self-assembling into rosettes in the presence of barbituric derivative **8**) Meijer's ureidopyrimidinone **9** (which dimerizes via complementary hydrogen bonding) and two molecular clips **10** and **11** (able to form bimolecular tweezers) (Chart 1) and studied the behavior of this mixture in chloroform solution through ¹H NMR. On mixing **3–11** in the presence of barium picrate, the resulting ¹H NMR spectrum is nearly the superposition of the ¹H NMR spectra of the individual supramolecular architectures,

Chart 1



along with small—hardly distinguishable—resonances that might correspond to small amounts of heteromeric crossover species. These results highlight that under these experimental conditions, the mixture of 3–11 and barium picrate clearly undergoes—almost in its entirety—self-recognition.

In these studies, the authors also questioned to what extent some external variables (temperature and concentration) as well as the binding constant and presence of hydrogen-bonding competitors at different concentrations would compromise the self-recognition events.

- Temperature:** At high temperatures (323 K), the resonances of the rosette 7₃–8₆ and ureidopyrimidinone 9₂ assemblies broaden dramatically, whereas the other resonances remain sharp, indicating their high stability. Interestingly, as the temperature is lowered back to 263 K, the majority of the resonances sharpen and new small resonances become noticeable, what the authors attributed to crossover species. Although self-recognition still prevails to a great extent in this system, temperature changes have been demonstrated to lead to an increased amount of crossover species, i.e. larger amounts of social products in mixtures of these pure hydrogen-bonding assemblies (compare Figure 1).
- Equilibrium constants of species subjected to interaction:** The authors performed simulations of a simple two component system comprising two monomers A and B, that can give rise to homodimers (A–A and B–B) and a heterodimer (A–B), whose equilibria are governed by three equilibrium constants (K_{AA} , K_{BB} , and K_{AB}). According to these simulations, when the equilibrium constant of homomeric species is 100-fold or higher than that of heteromeric (K_{AB}), self-recognition products A–A and B–B represent more than 98% of the mixture. When this difference is reduced to only 10-fold, narcissistic self-sorting still prevails to a great extent over social self-sorting.
- Concentration:** While the influence of concentration is already significant for self-assembly processes of individual

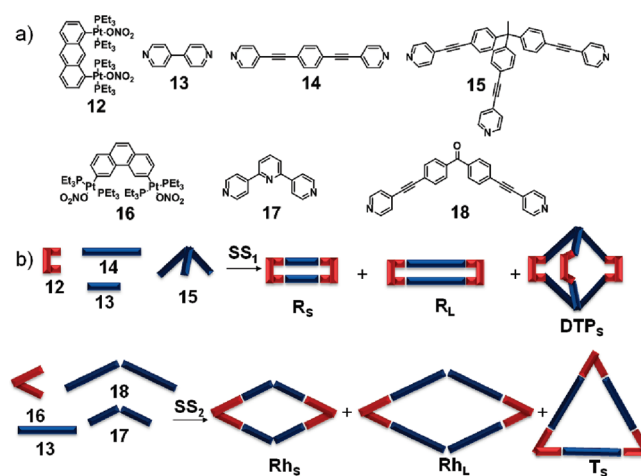


Figure 2. (a) Chemical structure of the building blocks applied by Stang and co-workers in self-sorting experiments. (b) Graphical representation of diverse coordination-driven self-assembled systems: small rectangle (R_S), large rectangle (R_L) and small distorted triangular prism (DTP_S) for SS1, and small rhomboid (Rh_S), large rhomboid (Rh_L), and small triangle (T_S) for SS2.

species, it can be even more pronounced in complex mixtures. Assuming the two component system A and B outlined in the previous section and in the light of simulation experiments, when the concentration of one of the components (A) is remarkably smaller than that of the other (B), self-association of A is less likely than association with B, therefore favoring social self-sorting. However, when the concentration of A approaches that of B, narcissistic self-sorting dominates. These experiments represent a rule-of-thumb for the construction of complex self-sorting systems: *self-recognition is most efficient when all components are present at the same concentration.*

- Concentration of competitive H-bonding species:** Self-sorting can be compromised in the presence of competitors for the hydrogen-bonding sites. When a self-sorted mixture of the corresponding assemblies of 3, 4, 6, 9, 10 and 11 was treated with increasing amounts of 8, the assembly formed by 3 is disrupted, whereas the remaining supramolecular architectures of 4, 6, 9, 10, and 11 barely underwent any appreciable change. These observations highlight that the presence of competitors in high concentration may provoke remarkable changes in some assemblies or, on the other hand, simply indifference. The match or mismatch of the hydrogen-bonding competitors with the members of the self-sorted mixture in this particular example plays a major role in the destabilization of preformed assemblies and the formation of new crossover species.

The external variables that compromise the self-sorting of mixtures of thermodynamically equilibrated H-bonding species, however, may not necessarily apply to self-sorted mixtures involving other, for example, stronger noncovalent interactions. In fact, recent studies have demonstrated that an increase of temperature can provoke quite distinct effects in multicomponent metal coordination-driven self-assembled polygons.⁴² Stang and co-workers investigated the self-sorting ability of nine different metallosupramolecular

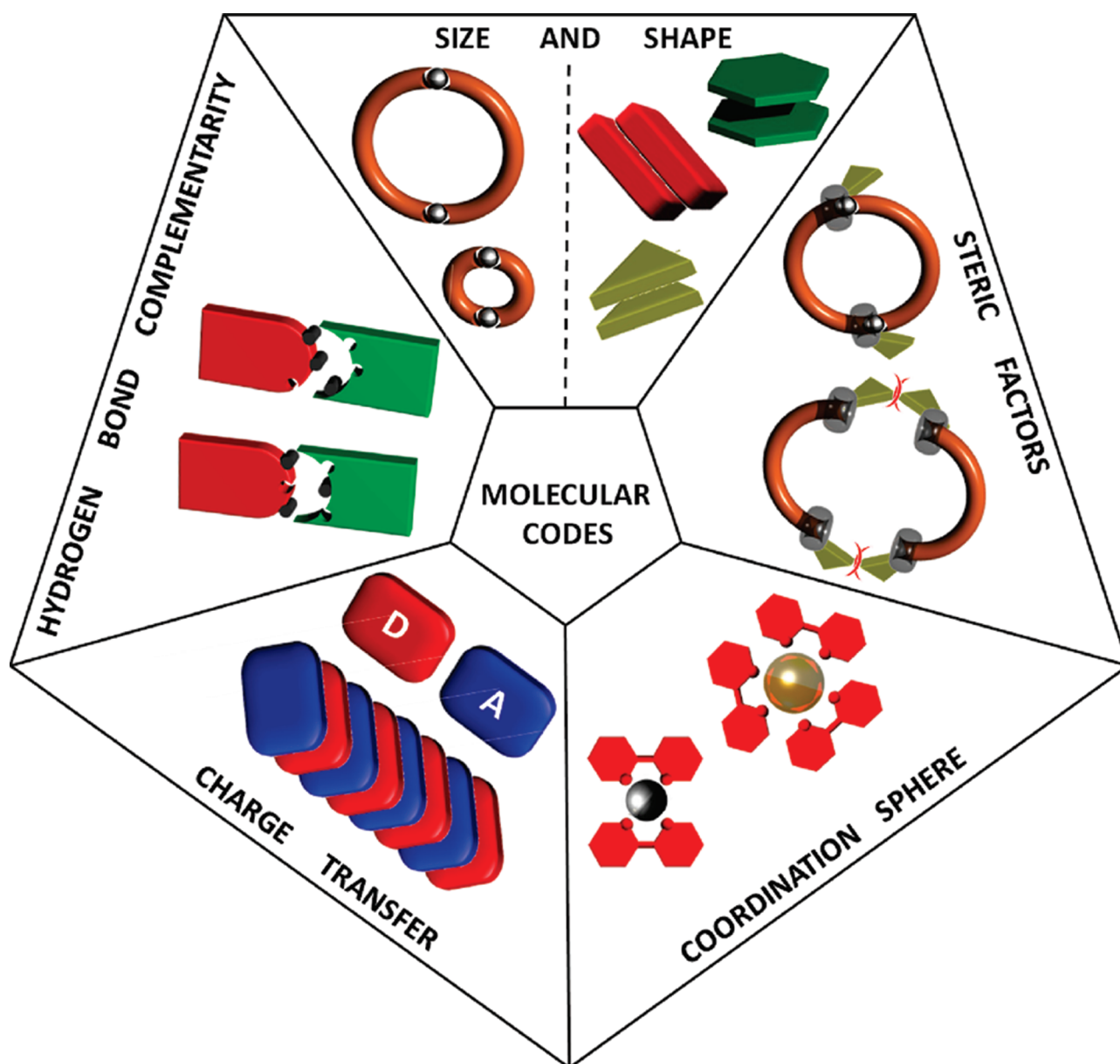


Figure 3. Schematic representation of the different molecular codes considered in this review.

architectures by simultaneous mixing of organoplatinum acceptors (molecular clips **12** and **16** in Figure 2) and different pyridyl donors, well-known to self-assemble in isolation into a wide variety of discrete supramolecular 2D rectangles, triangles and rhomboids and 3D triangular prisms or bipyramids. Each mixture was demonstrated to self-sort into multiple discrete supramolecular polygons, precluding the less stable disordered social assemblies.⁴³

Two different mixtures of compounds **12**–**15** on one hand (SS1) and **13** and **16**–**18** on the other hand (SS2) (Figure 2b) were subjected to temperature and solvent changes and their influence on the self-sorting phenomena was subsequently investigated.

- (a) *Temperature*: At ambient conditions, disordered oligomeric structures are formed as major species by random combinations of the molecular subunits. These results reveal that the self-assembly process occurs extremely

slowly at room temperature and the equilibrium is not reached even after 20 days. However, an increase of temperature to 65–70 °C for 24 h causes a significant increase in the rate of the self-assembly process and the initially disordered species can be dynamically self-corrected to the thermodynamically preferred discrete supramolecular entities.⁴⁴ These findings are in sharp contrast with those observed by Isaacs in H-bonding self-sorted mixtures (Chart 1), where an increase of temperature provoked the destabilization of some of the individual pairs. This notable divergence arises, however, as a simple consequence of the different temperatures required in both systems to reach thermodynamic equilibrium: Isaacs' hydrogen-bonded mixtures are able to reach thermodynamic equilibrium at ambient conditions, whereas the higher binding strength of metallosupramolecular interaction requires a higher

thermal energy to self-correct kinetically trapped species toward the thermodynamically most favored self-sorted architectures.

- (b) *Solvent*: Self-assembly processes are known to be highly sensitive to changes in solvent owing to the different thermodynamic stabilities of intermediate and final species formed in different media.⁴⁵ From among the two self-sorted mixtures investigated in these studies (Figure 2b), only the first one (SS1) formed from clip 12 underwent significant effects upon changing the solvent from *d*₆-acetone/D₂O (1:1) to either CD₂Cl₂ or *d*₆-acetone/D₂O (20:1) whereas the second (SS2) formed from clip 16 showed no appreciable changes. In the particular case of SS1, the initially organized structures R_S, R_L, and DTP_S could be reversibly destructed or regenerated merely by changing the nature of the solvent. The choice of solvent has thus been proven to be critical to the efficiency of coordination-driven self-sorting systems.

In the light of these examples, it is evident that a certain external variable (solvent, temperature, etc) alters not only the stability of different noncovalent interactions but can even modify the composition of self-assembled objects formed by H-bonded or metallosupramolecular interactions within complex mixtures. However, the effect of these variables on complex mixtures of competing species in which several noncovalent interactions participate—as it occurs in nature—remains mostly unexplored.

Isaacs and co-workers investigated the influence of temperature, concentration, stoichiometry and pH in a sophisticated 12-component mixture in aqueous solution composed of different compounds, previously known to generate host–guest complexes through a wider variety of noncovalent forces (metal-coordination, ion-dipole, solvophobic forces, π – π stacking and charge-transfer interactions).²¹ As expected, pH changes cause dissociation or stabilization of some particular assemblies due to changes in protonation states. Interestingly, concentration changes did not appear to influence the recognition events even at micromolar scale. This fact is in contraposition with that observed in H-bonding self-sorting mixtures described above. The relative stoichiometry of some aggregates can also compromise the extent of self-sorting or ultimately generate new assemblies. On the basis of simulation experiments, the authors concluded that *social self-sorting systems may change partners over a relatively narrow concentration range*. This conclusion is in accordance with biological systems, in which self-organization regulates specific reactions, often at very dilute (nM) concentrations while competing with a myriad of other possible reactants without physical barriers.^{46,47}

Temperature variations, as expected, provoke substantial changes in the outcome of the social self-sorted mixture. At high temperatures, the ¹H NMR spectra become highly complex due to the appearance of new sets of resonances, most likely attributed to crossover species. In addition, the system undergoes an irreversible change when the temperature is lowered back to ambient conditions, as a result of crossover interactions between some of the members of the mixture.

In view of these overall studies, it is obvious that some species respond unexpectedly to environmental changes, which on the basis of our current knowledge precludes us from directing specific self-sorting processes in complex mixtures without causing undesired side effects. Current research advances based on a larger variety of self-sorting systems, however, augur well for

the near future. These will be discussed in detail in the next section of this review.

3. MOLECULAR CODES FOR THE SELF-SORTING OF COMPLEX MIXTURES

Disregarding the external factors that can influence the strength of different noncovalent interactions, in this section we will elucidate the encoded information that makes a given molecule in a crowded environment behave the way it does. By *molecular codes* in the field of self-sorting, we refer to the intrinsic information encoded in the molecular structure of a given interacting species that governs the strength of the intermolecular forces of the species with itself and with the rest of the members of the mixture. Molecules will tend to bind their ideal partners by establishing the maximum possible number of intermolecular interactions, which can only take place when the interacting species have been suitably “programmed” with molecular codes.

There are different molecular codes that have been used in the literature by different research groups to efficiently direct self-sorting processes (Figure 3).

- (a) *Geometrical complementarity by size and shape* is unquestionably the molecular code that exhibits a strongest impact on the strength of intermolecular interactions.⁴⁸ Size and shape rule recognition events, as illustrated by the lock-and-key-principle.⁴⁹ Any kind of species able to interact through any kind of noncovalent force must necessarily possess complementary geometric shapes before a subsequent recognition event takes place. In metal-coordination systems, for instance, ligands with different size, shape, or rigidity can self-sort into distinct supramolecular architectures in the presence of a metal ion (Figure 2 and 3). Hydrogen-bonding as well as charge-transfer interactions between two given molecules require in the first instance a geometrical fit of the molecules involved to facilitate the approach of the donor and acceptor groups that ultimately will interact with one another and give rise to noncovalent bond formation.⁵⁰ Van der Waals forces and π – π stacking interactions⁵¹ are maximized as the contact area between the interacting building blocks increases, which indeed depends on their size and shape.⁵² Size and shape codes are therefore a prerequisite to “activate” other molecular codes, which can ultimately drive self-sorting events.
- (b) *Complementarity in hydrogen-bonded systems*: The match between the hydrogen-bonding donor and acceptor groups can decide the outcome of self-sorting events if the size and shape of the interacting species allows their approximation (Figure 3). Obviously, complementary hydrogen-bonding sites that are not geometrically well positioned will not give rise to noncovalent bond formation.
- (c) *Steric effects*: The presence of bulky substituents in some of the building blocks can prevent their interactions with sterically hindered species or eventually facilitate the exclusive selection of unhindered components (Figure 3). This strategy is particularly suitable because a great number of possible structures can be ruled out just by controlling the bulkiness of the substituents of the interacting building blocks. However, the success of

this approach is limited to molecules with a high similarity both in terms of size and shape.

- (d) *Coordination sphere in metal-ligand interactions:* The ability of the metal ions to coordinate into different geometries upon coordination to ligands that can satisfy their coordination sphere is, although thus far scarcely investigated, a powerful tool to drive self-sorting processes. The coordination number and geometry of a metal ion depends fundamentally on its size, charge and electronic configuration and the availability of properly matched ligands. Different metal ions can coordinate alike ligands into diverse geometries (Figure 3), which might become an increasingly relevant molecular code in the pursuit of systems with high complexity.
- (e) *Charge-transfer:* Attractive interactions between species with opposing electron donating and accepting character can also direct self-sorting processes, primarily when their size and shape is very similar. This molecular code is particularly attractive to create social assemblies by organization of the donor and acceptor molecules in an alternating fashion (Figure 3).

The final two molecular codes, coordination sphere in metal-ligand interactions and charge-transfer, are in essence closely related. In the case of the coordination sphere of metal-ligand interactions, the spatial arrangement of the unoccupied orbitals of the metal ion (acceptor) directs the coordination of the occupied orbitals of the ligand (donor) for ligand-to-metal systems (the contrary for metal-to-ligand systems) in a determined manner.⁵³ Similarly in charge-transfer interactions, the correct overlap between the HOMO and LUMO orbitals of the donor and acceptor π -systems participating in the assembly will govern the outcome of the self-sorting process. Although these two molecular codes could be unified into donor-acceptor interactions, we will describe them separately owing to the dissimilarity of the respective supramolecular building blocks.

In the following sections we will explain in more detail the impact of these molecular codes in self-sorting events through different examples collected from the literature.

3.1. Size and Shape

As mentioned above, size and shape are undoubtedly the foremost variables that regulate the outcome of a self-sorting process, as demonstrated by significant number of examples based on hydrogen-bonding, π - π -stacking and metal ion coordination molecular recognition events. Regarding metal-coordination-based self-sorting systems and shortly after the pioneering example described by Lehn,¹⁹ Raymond and co-workers studied the self-sorting behavior of a mixture of three rigid bis(bidentate) catecholamide ligands²⁸ (**19–21**) demonstrated in isolation to self-assemble into triple helicates of varying size in the presence of trivalent metal ions.²⁸ The three ligands **19–21** were designed to increase the metal-metal distance systematically in the dinuclear helicates to probe the effect that size has on the ability of the helicates to form by self-assembly. Remarkably, when mixtures of any two or three of the ligands were reacted with Ga(III), only complexes containing one type of ligand were formed and no trace of mixed-ligand species could be observed in solution with ¹H NMR or electrospray ionization (ESI) mass spectrometry (Figure 4). Along with Lehn's example, this experiment revealed that self-recognition can be successfully

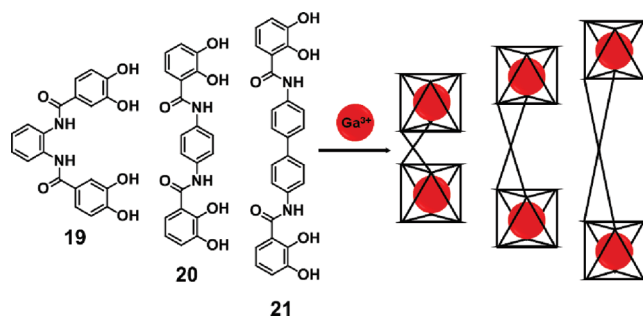
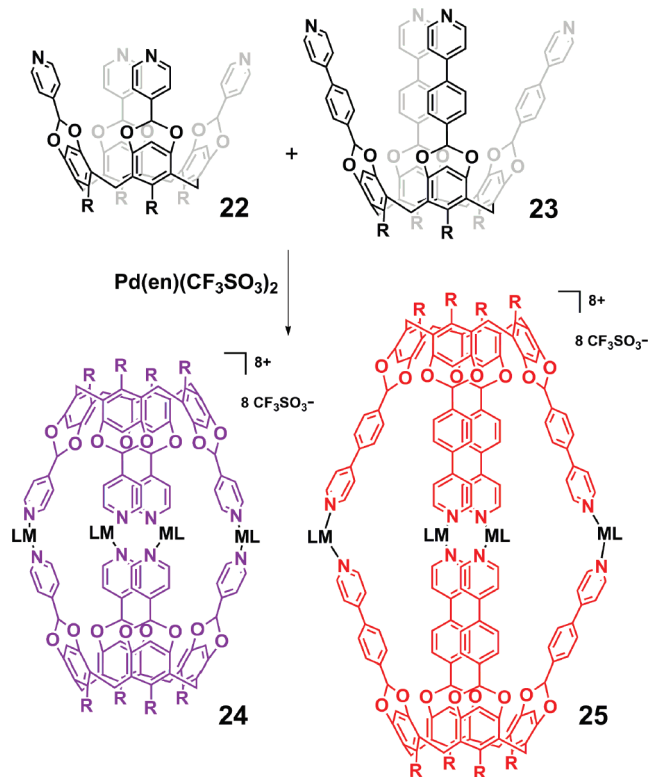


Figure 4. Chemical structure of ligands **19–21** and schematic representation of their self-recognition into triple helices upon treatment with gallium (III) acetylacetonate.

Scheme 2. Self-Recognition of Cavitands **22** and **23** ($R = \text{CH}_2\text{CH}_2\text{Ph}$) into Homocages **24** and **25** upon Addition of $\text{Pd}(\text{en})(\text{CF}_3\text{SO}_3)_2$ ($\text{en} = \text{ethylenediamine}$)



achieved by controlling a geometrical variable, the distance between two metal coordination sites.

Stang and co-workers have extensively made use of rigid pyridyl-based donors and organoplatinum acceptors for the construction of a wide variety of coordination-driven 2D polygons and 3D cages (see Figure 2).^{44,54–58} This approach is based mainly on the size and shape that are encoded within the individual ligand building blocks, highlighting that structural information can efficiently drive the self-sorting processes, which has also been demonstrated to be very useful in the formation of cages.^{59,60} In this regard, Dalcanale and co-workers succeeded in the exclusive formation of self-recognizing nanoscale cavitand-based coordination cages (Scheme 2).⁵⁹

These authors investigated the cage self-assembly of a series of pyridyl-based cavitands.

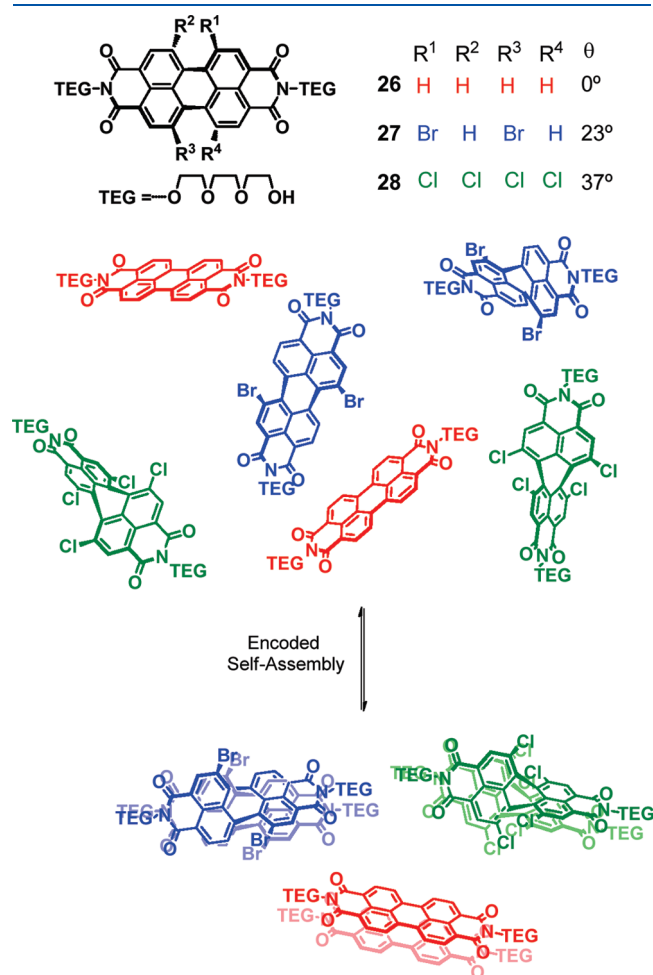


Figure 5. Self-recognition of perylene bisimides 26–28 via π – π -stacking governed by the contortion of the π -surface.

On treatment with Pd(II) or Pt(II) complexes, the cavitands self-assemble into dimeric capsules of varying depth, depending on the length of the pyridyl anchoring units. Interestingly, a competition experiment in which two cavitands of different length (22 and 23) were mixed with a stoichiometric amount of metal precursor was performed to verify whether a self-discrimination process takes place in this system or whether, as one might expect, a more likely self-recognition process is operative. ^1H NMR experiments of mixtures of 22, 23, and Pd(ethylenediamine)(CF₃SO₃)₂ in acetone-*d*₆ showed the exclusive formation of signals belonging to homocages 24 and 25 (Scheme 2). The geometrical mismatch between the biting angles of two cavitant ligands disfavors heterocage formation during the self-assembly process. On the basis of these observations we can conclude that self-recognition is most efficient when the individual pairs are structurally most different from one another.

Aside from metal complexes which are ultimately based on metal–ligand point interactions, π – π -stacking interactions between aromatic scaffolds are also governed by the geometry of the interacting surfaces involved.^{40,41} However, the surface area of intermolecular contact is in this case remarkably large, so dispersion forces and desolvation are particularly important.⁶¹ Thus, a strong influence of the size and shape of the available surface area on the outcome of a self-sorting event is again anticipated for compounds bearing several aromatic building blocks.

Li and co-workers have recently examined the self-sorting behavior of a mixture containing three bay-substituted perylene bisimide dyes 26–28 (Figure 5) that are characterized by a different twist angle between the two naphthalimide subunits.³⁶ It is established that bulky bay substituents twist the perylene unit dihedrally out of the plane with angles from 0 to 37°,^{62–64} thereby influencing the available contact surface area for π – π -stacking. Molecules with different twist angles were demonstrated through ^1H NMR and UV–vis spectroscopy in chloroform to preferentially self-recognize into segregated nanostructures, even in the presence of other building blocks, thus revealing their unique molecular encryption (Figure 5).

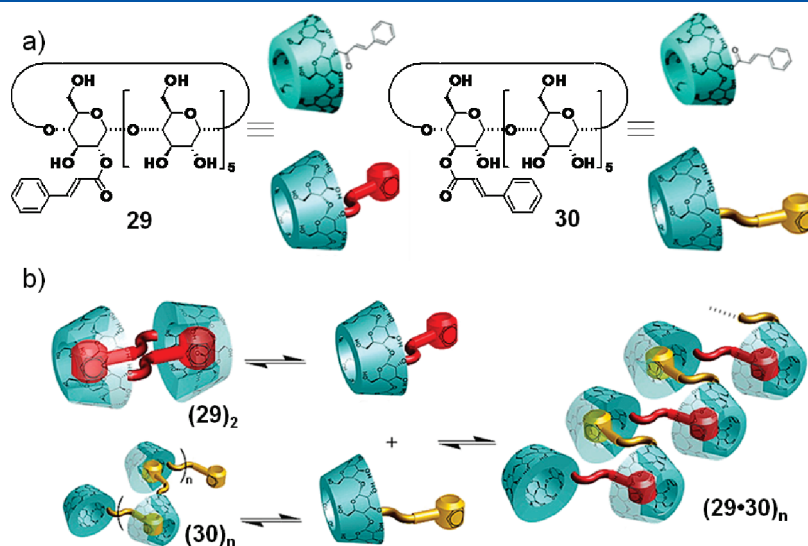


Figure 6. (a) Chemical structures and cartoon representation of cyclodextrins 29 and 30. (b) Self-assembly of isolated and mixed cyclodextrins 29 and 30. Reproduced with permission from ref 76. Copyright 2009 American Chemical Society.

The great majority of the examples described in literature involving narcissistic or social self-sorting systems are investigated in organic solvents. This fact is in sharp contrast with biological systems, which operate in aqueous media. Unlike conventional organic solvents, water molecules are arranged into a peculiar infinite network of hydrogen bonds with a localized structure,⁶⁵ which accounts for their extraordinary physical properties and also for the *hydrophobic effect*: water

molecules are predisposed to form a cage around very nonpolar solutes to minimize solvent–solute interactions.⁴¹ Along with the molecular codes, this premise will thus condition to a great extent the outcome of a self-sorting process in aqueous media.

Cucurbit[*n*]urils (CB[*n*])^{66–68} and cyclodextrins^{69–71} are undoubtedly among the most deeply investigated building blocks within complex mixtures in aqueous media because of their ability to form stable host–guest complexes in water. Harada and co-workers have devoted extensive studies to the investigation of cyclodextrin-based supramolecular architectures.^{72–76} Recently, these authors have synthesized two isomers of cinammoyl cyclodextrins **29** and **30** and investigated their self-assembly separately in aqueous solutions (Figure 6).⁷⁶ Cyclodextrin **29** was found to form a double threaded dimer (**29**)₂, as demonstrated by single crystal X-ray analysis and supported by pulse field gradient (PFG) NMR experiments. In contrast, cyclodextrin **30** formed extended supramolecular polymers (**30**)_n above a concentration of 32 mM. Interestingly, two-dimensional (2D)-ROESY spectra of the mixture of both isomers did not show a correlation between the same species. Rather, correlation peaks between cyclodextrins **29** and **30** were observed, which account for the formation of an alternating supramolecular polymer (**29**·**30**)_n (Figure 6b) and not a self- or random supramolecular complex.

Although it is evident that solvophobic forces contribute to a great extent to this behavior, the difference in the substitution position on a glucopyranose unit—the shape—is far from being an innocent effect in the stabilization of these architectures.

With regards to other systems investigated in water, CB[*n*] derivatives constitute prime components for the preparation of complex self-sorting systems primarily due to their high affinity and selectivity for a wide variety of inclusion guests.⁷⁷ CB[*n*]s are pumpkin-shaped macrocycles featuring a hydrophobic cavity and two identical hydrophilic carbonyl-containing portals (Figure 7).^{78–80} The hydrophobic cavity can be effectively exploited to host hydrophobic guests, whereas the hydrophilic portals benefit from interactions with positively charged groups through ion-dipole forces and hydrogen bonding.⁷⁸ Although the

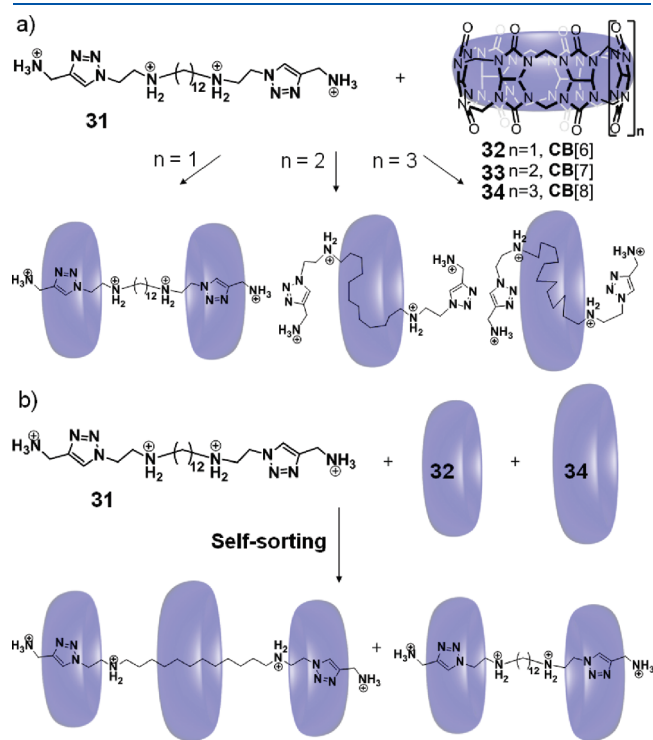


Figure 7. (a) Chemical structure and self-assembly of axle **31** in the presence of CB[*n*]s **32**–**34**. (b) Self-sorting of a mixture of axle **31** and CB[*n*]s **32** and **34**.

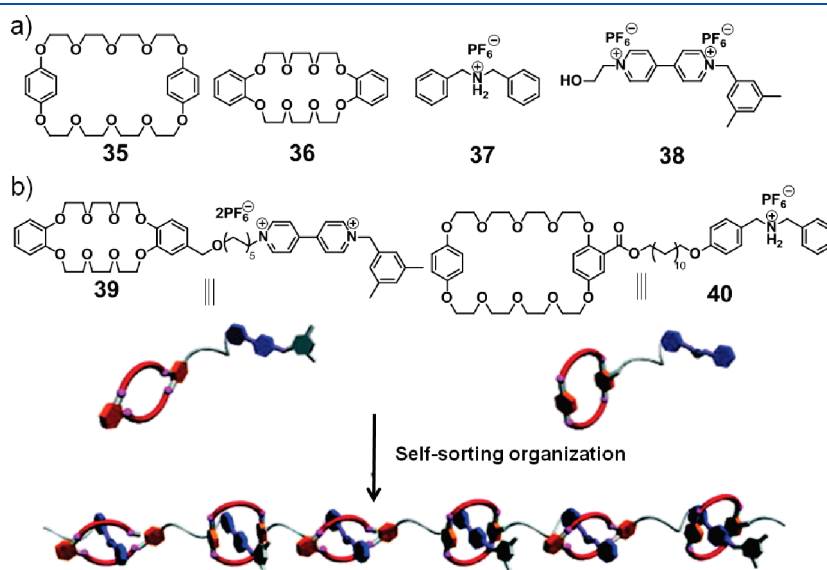


Figure 8. (a) Chemical structure of precursors **35**–**38**. (b) Chemical structure and cartoon representation of heteroditopic **39** and **40** and their self-sorting into alternating supramolecular polymers via integrative self-discrimination. Reproduced with permission from ref 85. Copyright 2008 American Chemical Society.

hydrophobic effect is a decisive factor in the interaction of CB[n]s with guests, the affinities are ultimately determined by the size of the hydrophobic pocket.

Isaacs and co-workers studied the binding ability of three members of the CB[n] family (CB[6], CB[7], and CB[8]) toward a set of up to 24 different guests with different chemical nature.⁷⁷ ¹H NMR competition experiments were used to measure the values of K_{rel} for CB[6], CB[7], and CB[8] toward a variety of guests referenced to an absolute K_a determined by UV–vis studies. Remarkably, the authors observed a high level of selectivity and affinity of each member of the family and also high levels of selectivity exhibited by different members of the family for a common guest, which anticipates their utility in the investigation of more complex self-sorting systems. Several authors have subsequently proven the validity of CB[n]s as ideal building blocks for the preparation of functional biomimetic systems.^{81–83} Interestingly, these studies reveal that upon careful optimization of experimental conditions, CB[n]s undergo dynamic behavior that can be thermodynamically or kinetically controlled.

Recently, Tuncel and co-workers have investigated the self-sorting ability of CB[n]-based pseudorotaxanes in aqueous media.⁸⁴ In a first step, the affinity of an axle **31** (Figure 7) equipped with two recognition sites, a central hydrophobic dodecyl chain and two diammonium triazoles, toward CB[6] (**32**), CB[7] (**33**), and CB[8] (**34**) was investigated independently through ¹H NMR titrations. Driven by size selectivity and reinforced by additional ion-dipole interactions, CB[6] prefers to bind the diaminotriazole sites, as triazole has an appropriate size to fill the cavity of CB[6]. In contrast and driven by solvophobic forces, CB[8] and CB[7] encapsulate the dodecyl protons but not the triazole units, since in this way the nonpolar spacer maximizes the interactions with the hydrophobic cavity, thereby finding refuge from the solvent (Figure 7a). In the next step, the authors examined what would occur when both CB[6] and CB[8] are available to bind with the axle (Figure 7b). ¹H NMR experiments revealed that the coexistence of both species does not influence each other's ability to complex with the axle, thus enabling an integrative self-sorting process (compare Figure 2). These findings imply that CB[8] remains associated with the dodecyl spacer whereas CB[6] prefers to bind the ammonium triazoles, the analogous situation to than observed in isolation. After a certain time the reaction reaches an equilibrium resulting in two species: hetero[4]pseudorotaxane minor and [3]pseudorotaxane major species (Figure 7b). These results are likely because of the blocking effect of the peripheral CB[6] units that prevents CB[8] from being threaded on to the dodecyl spacer.

In addition to CB[n]s, successfully demonstrated to self-sort into various pseudorotaxanes in aqueous media, other authors have made use of this strategy to construct rotaxane-like supramolecular polymers in organic solvents. Huang and co-workers synthesized two AB-type heteroditopic monomers **39** and **40** and investigated their coassembly into supramolecular copolymers.⁸⁵ Monomer **39** comprises a dibenzo-24-crown-8 (**36**) unit attached to a paraquat derivative (**38**), whereas monomer **40** features a bis(*p*-phenylene)-34-crown-10 (**35**) connected to a dibenzylammonium salt (**37**) (Figure 8). It is well-known that crown ethers **35** and **36** can effectively form 1:1 complexes with paraquat derivatives and dibenzylammonium salts, respectively.^{86,87} Self-sorting experiments carried out on precursors **35**–**38** demonstrated that the complexation of crown ether **35** with paraquat derivatives is much stronger than the complexation with dibenzylammonium salts, while the

complexation of **36** with dibenzylammonium salts is stronger than that with paraquat derivatives. These control experiments anticipate that monomers **39** and **40** arrange into alternating supramolecular copolymers (Figure 8b). A thorough collection of experiments (concentration-dependent ¹H NMR, cyclic voltammetry (CV), viscosity, dynamic light scattering (DLS) and scanning electron microscopy (SEM)) demonstrated the formation of long high-molecular weight assemblies of alternating supramolecular copolymers. This remarkably high degree of selectivity is clearly driven by the different size of the crown ether moieties, and the complementarity of ion-dipole interactions between the macrocycles and the positively charged recognition elements. Recently, this strategy has been exploited to construct main-chain polyrotaxanes with supramolecular polymer backbones.⁸⁸

3.2. Complementarity in Hydrogen-Bonded Systems

Complementarity plays a particularly important role in the stabilization of hydrogen-bonded assemblies,^{89,90} to the point that it facilitates the approximation of the functional groups involved.⁵⁰ The pairing of nitrogenous bases (A-T and C-G) in the DNA double helix is undoubtedly one of the most obvious examples of complementary systems in nature.⁹¹ Although appropriate geometrical correspondence of the interacting groups is always a prerequisite, the match or mismatch between the pattern of hydrogen donors and acceptors ultimately decides the outcome of a recognition event, since in this way only the “right” pairs are allowed to form. In the stabilization of the DNA double helix, interactions among pyrimidines (C, T) are unfavored because the molecules are too far apart whereas purine–purine (A, G) pairings are too close, therefore leading to electrostatic repulsions. In the only other possible pairings (G-T and A-C) the pattern of hydrogen donors and acceptors do not correspond, which makes A-T and C-G the only remaining possibility in which base-pairing can take place, stabilized both in terms of hydrogen bond complementarity and geometrical fit. The importance of hydrogen-bonding complementarity in nature thus anticipates its significant role in the stabilization of artificial self-sorting systems as well.

Reinhoudt, Timmerman and co-workers investigated the self-sorting of hydrogen-bonding-based supramolecular systems already in 1999.²⁵ Following their seminal work in which they studied the formation of a (**41**)₃·(**42**)₆ box-like double rosette stabilized by 36 hydrogen bonds upon co-assembly of calixarene-based bismelamine derivative **41** and barbiturate **42**,⁹² they wondered whether the introduction of an additional bismelamine unit would influence their behavior in the presence of barbiturate units (Figure 9). In a similar manner to bismelamine derivatives **41a**–**b**, tetramelamines **43a**–**b** were demonstrated by ¹H NMR to self-assemble into tetra(rosettes), although with a remarkably lower stability than bismelamine rosettes. When tetra(rosette) assembly (**43a**)₃·(**42**)₁₂ was mixed with bismelamines **41a** or **41b**, the stability order was reversed, and assembly (**41**)₃·(**42**)₆ was observed to form at the expense of (**43a**)₃·(**42**)₁₂. The reduced stability of (**43a**)₃·(**42**)₁₂ was attributed to the inward curvature of the two rosette planes that prevent the complete filling of the space between the two double rosettes. Finally, the self-sorting degree in mixtures of bis- and tetramelamines in the presence of **42** was also examined. Mixtures of **41a** and **43a** or **43b** in a 2:1 ratio with a slight excess of **42** exclusively revealed the formation of homomeric assemblies (**41**)₃·(**42**)₆

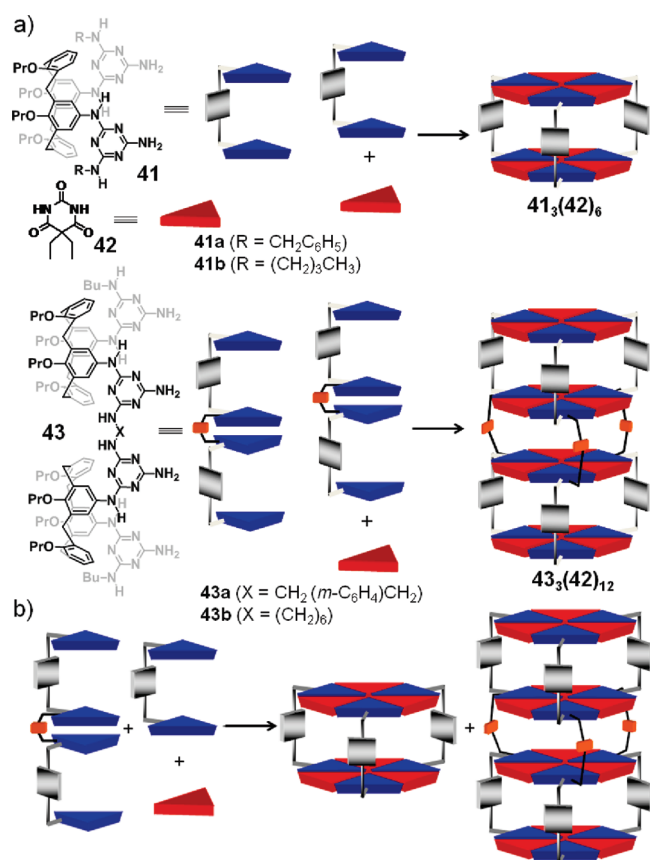


Figure 9. (a) Chemical structure of derivatives 41–43 and their schematic representation. (b) Self-recognition process in a mixture of 41–43.

and (43)₃·(42)₁₂ and no trace of heteroassemblies was detected (Figure 9b). However, when equal amounts of 43a and 43b were mixed with 42, heteromeric assemblies were observed. These results are a clear consequence of the interplay of various molecular codes, namely, molecular shape and flexibility of the bis- or tetramelamine building blocks and hydrogen-bonding complementarity.

The role of hydrogen bond complementarity has also been widely explored in the field of supramolecular polymers.^{93–97} Meijer, Sijbesma and co-workers reported the formation of supramolecular copolymers based on mixtures of 2-ureido-4[1H]-pyrimidinone **44** (Upy) and 2,7-diamido-1,8-naphthyridine **45** (Napy) building blocks (Figure 10).⁹⁸ Upy units were previously shown to yield self-complementary supramolecular polymers with high degrees of polymerization in bulk as well as in solution with dimerization constants (K_{dim}) up to $6 \times 10^7 \text{ M}^{-1}$ in CHCl_3 .^{99–102} In an extension of this work, Li and co-workers have demonstrated that quadruple hydrogen bonds between the 6[1H] tautomeric form of **44** and Napy gives rise to complexes with binding constant of $K_a \approx 5 \times 10^6 \text{ M}^{-1}$ (Figure 10a).¹⁰³ Despite of the lower value of this binding constant compared to the former, Upy dimers are disrupted in the presence of one equivalent of Napy in CDCl_3 . This behavior can be rationalized by the fact that the hydrogen bonding pattern of **45** is not self-complementary. Accordingly, saturation of all hydrogen-bond donor and acceptor sites is only achieved in the heteroassembled stack. On the basis of these findings, a collection of Upy and Napy-based bifunctional monomers (**46**, **47**) were synthesized with the aim to study their self-assembly into supramolecular copolymers.⁹⁸ In all cases, mixtures of linear polymers

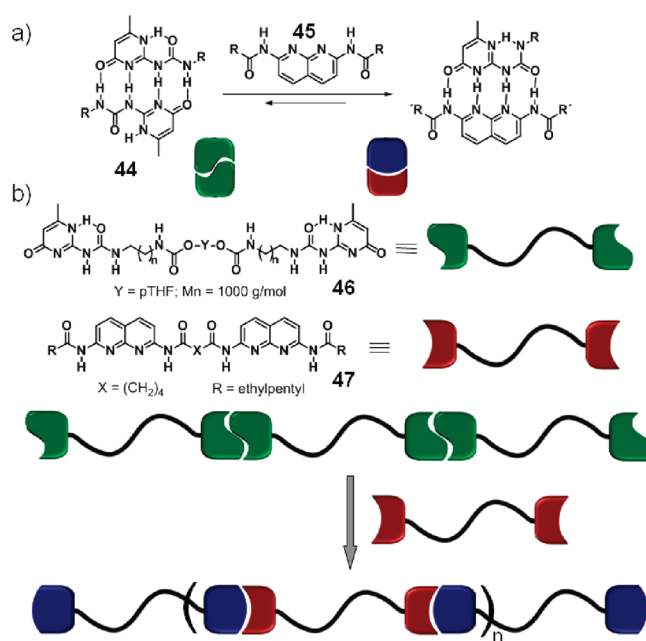


Figure 10. (a) Chemical structures of precursors **44** (Upy) and **45** (Napy) and their self-assembly via hydrogen-bonding. (b) Chemical structures of oligomeric **46** and **47** and cartoon representation of the self-discrimination process in a mixture of both.

along with their cyclic homologues were observed, as indicated by ^1H NMR and viscosity experiments. Interestingly, upon titration of bifunctional monomer **46** with **47**, almost insignificant amounts of cyclic products were observed. Instead, **47** was incorporated in the supramolecular polymer chain of **46** until an alternating copolymer is obtained at a 1:1 ratio of monomers (Figure 10b). If the ratio of monomer **47** exceeds that of 1:1, the excess molecules of **47** act as end-cappers and the chain length of the polymer is reduced. The selectivity of the copolymerization process was also examined to be concentration-dependent by ^1H NMR dilution and fluorescence spectroscopy experiments of Upy and Napy monomers. The combined techniques revealed a value of minimum concentration ($5 \times 10^{-5} \text{ M}$) above which the formation of heterodimers, that is, self-discrimination, is favored. Shortly afterward, Zimmerman and Park showed another beautiful example for the formation of alternating supramolecular multiblock copolymers based on a Napy bifunctional monomer in combination with the butylurea of guanosine.¹⁰⁴ The concentration and the ratio of the blocks in the mixture were demonstrated to strongly influence the degree of polymerization.

The concept of self-sorting has also been applied in the field of conventional polymer science. Here, self-assembly of macromolecular building blocks provides access to hierarchical functional materials that combine a wide range of applications and may respond to external conditions.^{105,106} Further elaboration toward complex self-sorting mixtures will give rise to a large variety of functionalized polymers with distinct well-defined architectures.^{105,107} Nature utilizes these principles to create vast libraries of biological materials in a simultaneous multistep self-assembly process that is reversible, selective, self-healing and spontaneous.¹⁰⁸ Typical examples are the biopolymers DNA and RNA, in which the self-sorting of base pairs along a polymeric backbone with very few mistakes is essential for the replication and translation of genetic material. In contrast to low molecular weight organic

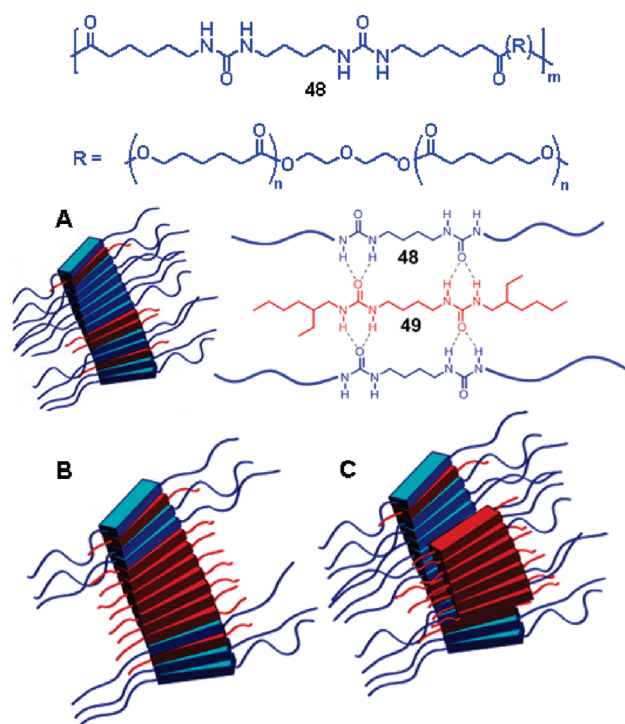


Figure 11. Top: Molecular structure of the thermoplastic polymer **48** and molecular filler **49** and cartoon representation of their co-assembly up to 28.6 mol % of filler **49** (A). Bottom: Schematic representation for two possible interpretations (B and C) above 28.6 mol % of filler. Reproduced with permission from ref 114. Copyright 2006 American Chemical Society.

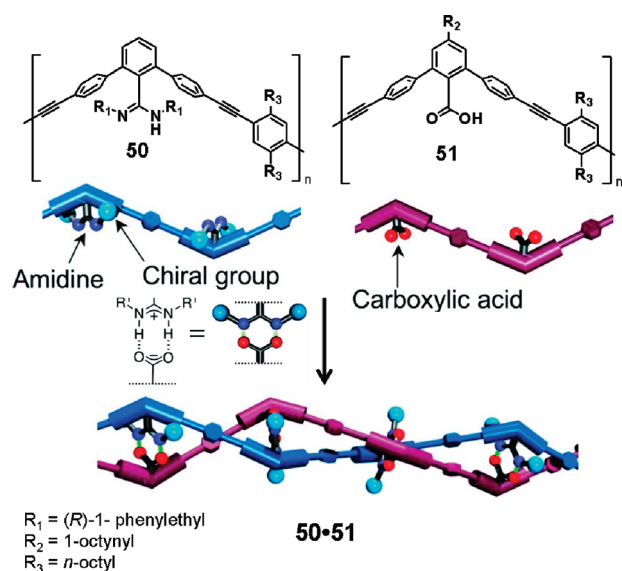


Figure 12. Chemical structure of chiral amidine **50** and achiral carboxylic acid **51** polymers and cartoon representation of their social self-sorting into a double-stranded helical polymer **50·51**. Reproduced with permission from ref 120. Copyright 2008 American Chemical Society.

molecules, the self-sorting phenomena in polymeric and complex systems have been relatively less explored.⁹⁷

In recent years, thermoplastic elastomers (TPEs) assembled through bis-urea hydrogen bonding groups have been subject of

increasing investigations primarily due to their strength, high specificity and excellent mechanical properties.^{109–113} Meijer and co-workers have investigated the intercalation of small molecules (the so-called molecular fillers) featuring urea functionalities in the bis(ureido)butylene stacks of a poly(ϵ -caprolactone)-based polymer.¹¹⁴ These authors demonstrated that a well-defined thermoplastic elastomer **48** is efficiently capable of incorporating in its hard segments molecular filler **49** through hydrogen bonding, as depicted in Figure 11. Interestingly, upon addition of increasing amounts of molecular filler **49** to the assembly formed by the polymer **48**, the Young's modulus increased up to 29 MPa at 28.6 mol %, which is more than twice the value (12 MPa) of the pristine polymer **48**. These results were rationalized in terms of an intimate mixing (social self-sorting) between the fillers **49** and the hard segments of the polymer **48**. Surprisingly, the yield stress, tensile strength, and strain at break were not influenced with increasing amounts of filler up to 28.6 mol %. However, when more than 28.6 mol % of filler **49** was added, a drop in the Young's modulus, as well as a decreasing trend for both tensile strength and elongation at break, was observed. Furthermore, differential scanning calorimetry (DSC) experiments and AFM images showed the presence of crystallites of only the filler as a second hard phase with a separate melting transition. The authors suggested two different explanations to interpret these findings: either large domains of filler are present within the polymer backbone with enough size to be detectable by DSC or a phase separation (self-discrimination) of the fillers from the polymer hard segments takes place when the ratio of filler exceeds 28.6 mol % (Figure 11C). More recently, Sijbesma and co-workers utilized the same strategy by mixing pyrene-based fluorescent probes with segmented polytetrahydrofuran (pTHF) block copolymers both equipped with urea functionalities.¹¹⁵ Interestingly and in line with Meijer's results, only those pyrene-based molecules with "matching" bis-urea moieties are randomly dispersed in the hard blocks of pTHFs. On the other hand, when the bis-urea groups of the pyrene and polymer probes possess a different alkyl spacer length between the urea groups a phase separation between both components takes place.

As a related motif to bis-urea hydrogen bonding groups, amidinium-carboxylate ion pair has extensively been exploited by Yashima and co-workers for the construction of double-stranded helical polymers.^{116–119} In a particularly illustrative example, the authors synthesized a double-stranded helical polymer consisting of complementary homopolymers of chiral amidines **50** and achiral carboxylic acids **51** with *m*-terphenyl backbones (Figure 12).¹²⁰ Upon mixing in THF, the self-complementary homopolymers self-discriminate into a preferred-handed double helix through interstrand amidinium-carboxylate salt bridges, as supported by circular dichroism, UV-vis and IR experiments. The mixture of **50** and **51** in chloroform, however, forms an imperfect double helix featuring a randomly hybridized cross-linked structure. The double-stranded helical structure can be again recovered upon treatment with a strong acid followed by neutralization with an amine, thereby accounting for the reversible nature of the process. Again, complementary hydrogen bonding groups between molecules possessing identical geometry is an efficient strategy to drive self-sorting processes.

Rebek and co-workers, as well as Atwood and co-workers, have devoted extensive studies toward the investigation of hydrogen-bonded self-assembled capsules.^{121,122} These are formed exclusively when, and only when suitable guests are

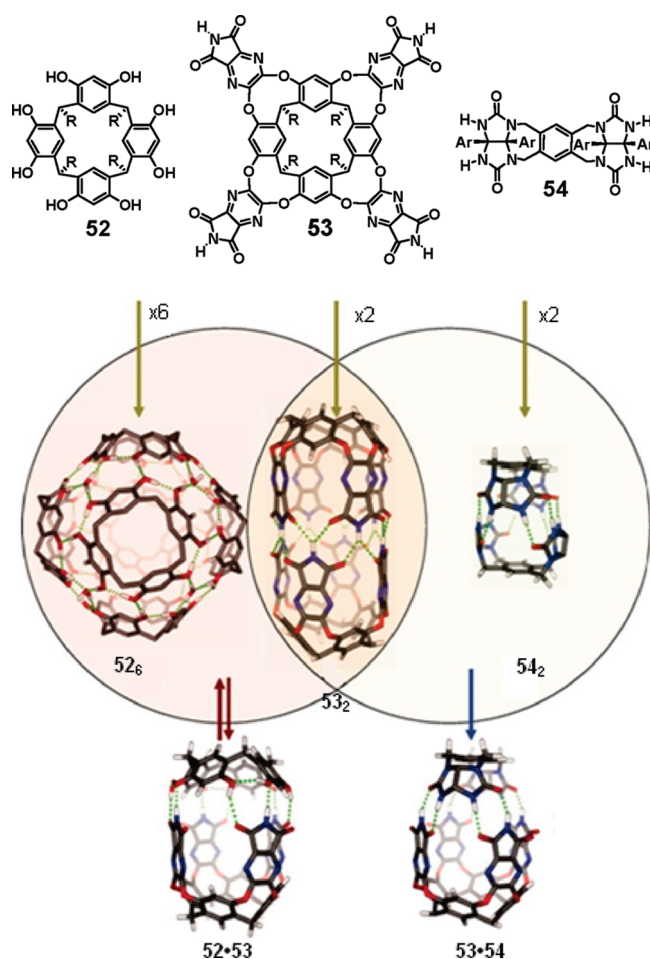


Figure 13. Chemical structures of derivatives **52**–**54** and energy-minimized structures of hexameric capsule **52**₆, cylindrical capsule **53**₂, hybrid capsule **52**·**53**, “tennis ball” **54**₂, and hybrid capsule **53**·**54**. Peripheral alkyl and aryl groups ($R = C_{11}H_{23}$, $Ar = pC_6H_4-N(Bu)_2$) in the calculated structures have been removed for clarity. Reproduced with permission from ref 129. Copyright 2009 National Academy of Sciences.

present to fill the space inside. Thus, capsule formation is biased by a combination of geometry, hydrogen-bonding complementarity and the choice of a proper guest. For instance, six molecules of resorcinarene **52** (Figure 13) self-assemble into a hexameric capsule stabilized by 60 hydrogen bonds in the presence of eight molecules of water,¹²² or with wet solvents,^{123,124} such as $CHCl_3$ or benzene, or in the presence of large quaternary ammonium ions.^{125,126} On the other hand, resorcinarene congener cavitand **53** self-assembles into a dimeric capsule through a seam of eight hydrogen bonds encapsulating three molecules of $CHCl_3$. Alternatively, on mixing the homomeric capsules **52**₆ and **53**₂ a hybrid structure **52**·**53** that coexists with the homomeric capsules forms (Figure 13).¹²⁷ These results are attributed to the fact that both capsules share resorcinarene modules with comparable dimensions, symmetries, and hydrogen-bonding patterns. Accordingly, their codes are too similar to afford self-recognition. To explore the possibility to obtain high-fidelity social self-sorting capsule systems, the authors questioned whether the “tennis-ball” capsule **54**₂,¹²⁸ previously known to dimerize in the presence of small guests such as methane, could give rise to hybrid capsules in the presence of cavitand **53**.¹²⁹ At first glance,

this assumption appears unlikely, given the different sizes, symmetries and hydrogen-bonding patterns of **53**₂ and **54**₂. However, molecular modeling studies suggested that a slight torsion of the building blocks **53** and **54** can efficiently pair most of the hydrogen bond donor and acceptors, leaving only four imide oxygens unsatisfied. To their surprise, ¹H NMR experiments proved the immediate and exclusive formation of a hybrid assembly **53**·**54** in $CDCl_3$, whereas no sign of homomeric capsules was observed. This social capsule was also demonstrated to form in the presence of solvent molecules other than $CHCl_3$, such as tetrachloroethane, *p*-xylene and ethane to name a few. Although this high selectivity depends to a great extent on the hydrogen-bonding complementarity between the interacting capsules, the nature and size of the guest is also of importance. The template effect of guest molecules was also recognized to have a vital importance in the self-sorting behavior of metal-coordination-based cages.¹³⁰

3.3. Steric Factors

Steric effects arise as a consequence of the spatial arrangement and bulkiness of atoms or substituents within a molecule. Accordingly, they are in essence geometrical codes related to shape. However, due to the increasing attention devoted by several research groups to the decisive effect of steric codes in self-sorting phenomena, we will regard them separately in an independent section. Their contribution, however, will only play a determinant role when the interacting building blocks are structurally similar in terms of geometry and/or hydrogen-bonding pattern.

In 2002, a decisive contribution of steric codes in self-sorting events was investigated by Zimmerman and co-workers in mixtures of hydrogen-bonded cyclic assemblies.²⁷ This work was based on earlier studies of the same group on hexameric self-assemblies of monomers **56** composed of complementary ADD and DDA hydrogen-bonding arrays in chloroform or even in more polar 15% aq. THF mixtures.¹³¹ To elucidate self-sorting effects these authors examined the influence of the attachment of dendrons of different size (**55**, **56**) on the self-assembly (Figure 14).²⁷ ¹H NMR, size exclusion chromatography (SEC), and DLS experiments demonstrated the formation of cyclic hexameric aggregates (**55**)₆ and (**56**)₆ from the individual precursors in **55** and **56**, respectively. Next, the authors questioned whether self-sorting in mixtures of third-(**55**) and first-(**56**) generation monomers would take place or, on the other hand, crossover species would form (Figure 14b). Statistically, a mixture of up to 11 distinct hexameric aggregates is probable to form. Interestingly, the broadness of the SEC signal at intermediate mixing times suggests that many, if not all, of these possible aggregates coexist. However, after longer periods of time a progressive sharpening of the SEC peak takes place, suggesting that the initial mixture of aggregates convert to a discrete structure, different from (**56**)₆ and (**55**)₆. Given the low stability of the complex (**55**)₆, mainly because of steric constraints, the authors hypothesized that the destabilizing steric interactions between the peripheral dendrons can be minimized if the fully mixed and alternating (**55**·**56**)₃ is formed. This hexamer would be particularly stabilized in terms of geometry, symmetry, and hydrogen-bonding complementarity and, ultimately, biased by steric effects (Figure 14b).

More recently, the combination of steric and electronic codes has been applied for the self-sorting of metallosupramolecular squares or prisms by the groups of Fujita and Stang.^{132,133} For

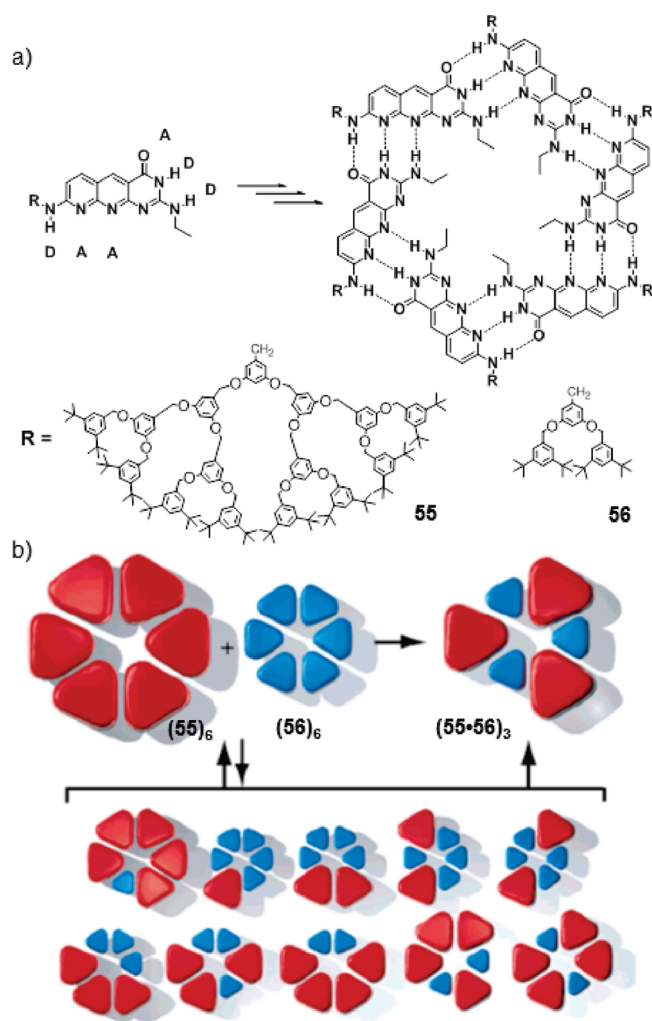


Figure 14. (a) Chemical structures of third and first generation dendrons **55** and **56**, respectively and cyclic assemblies formed thereof. (b) Possible mixed aggregates formed from mixing of (55)₆ and (56)₆. Reproduced with permission from ref 27. Copyright 2002 American Chemical Society.

instance, Stang and co-workers¹³³ synthesized a set of unsymmetrical bis(4-pyridyl)acetylene ligands (**57**–**60**) and investigated their self-sorting behavior in the presence of Pt(II) building blocks. All ligands are unsymmetrical, featuring one sterically hindered pyridyl ring connected to one or more substituents (depicted as navy blue hexagons in Figure 15) and one uncrowded pyridyl group (depicted in green). In the absence of any biasing interactions, there are four different isomers that may be formed upon self-assembly with a 90° Pt(II) acceptor unit (depicted as a golden sphere): isomer **A**, in which all unsymmetrical donors are oriented in an alternating fashion leading to identical coordination spheres at each Pt center (*C*₄ symmetry), isomer **D**, in which every acceptor is coordinated by two of the same pyridyl moieties leading to two distinct sets of Pt corners (*D*₂ symmetry) and the less symmetrical isomers **B** and **C** that contain three different types of Pt corners (symmetry *C*_s and *C*₂, respectively) (Figure 15). Whereas ligands **57** and **59** may, in theory, form four isomeric [4 + 4] assemblies when combined with acceptor **60**, an even more complex set of isomeric cycles is possible for **58** depending on the relative orientations of the α-Cl

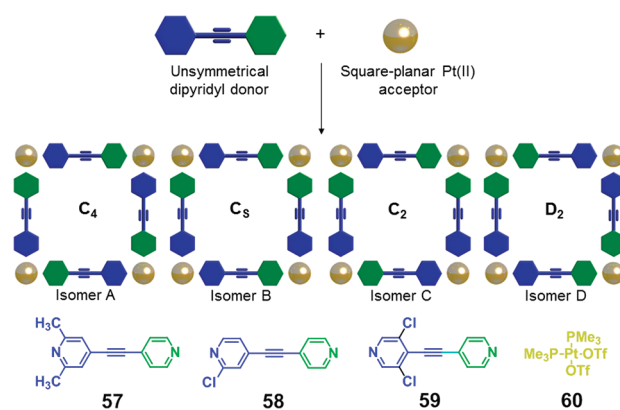


Figure 15. Chemical structure and schematic representation of the different metallasupramolecular squares that may form upon self-sorting of ligands **57**–**59** and Pt(II) acceptor **60**.

atoms within each square (A–D). Interestingly, upon mixing **57** and **60** in a 1:1 ratio, only one of the possible squares (isomer **A**) is formed, as demonstrated by ¹H and ³¹P NMR in CD₃NO₂. This high degree of self-sorting appears to arise as a result of interligand α-Me/α-Me steric interactions that prohibit the coordination of two of the bulky dimethyl pyridyl moieties to the same Pt(II) center or electronic effects associated to different electron-donating abilities. However, the efficiency of the self-sorting process diminishes drastically when the sterically bulky methyl groups are replaced by one (**58**) or two (**59**) Cl atoms in the presence of stoichiometric amounts of **60**. This has been mainly attributed to the decrease of the steric bulk of Cl atoms and the more similar electron-donating character of Cl-substituted and unsubstituted pyridyl moieties. These conclusions were supported by molecular modeling, which showed that the two chlorine atoms are too remote from the Pt–N coordination site to have any significant steric influence. These overall results highlight that unsymmetrical ditopic ligands can effectively direct self-sorting by steric and electronic effects, ruling out –due to identical size and shape– any geometrical bias.

A number of groups have recently made use of steric codes to direct the efficient self-sorting in mixtures of tetraurea calix-[4]arenes^{134–136} which are known to form dimeric capsules.^{137,138} In a recent particularly appealing example, Böhmer and Schalley and co-workers studied the self-sorting behavior in a complex mixture comprising of up to eleven structurally related building blocks (Figure 16).¹³⁵ All calixarenes (**61**–**71**) are substituted by four urea groups on their wide rim and fixed in the cone conformation by four pentyl ether groups (Figure 16). They thus possess analogous size, shape and hydrogen-bonding patterns, thereby precluding any geometrical or complementarity bias. Their only difference concerns the nature –small or bulky– of the peripheral substituents attached to the urea groups. Whereas calixarenes **61**–**66** are known to dimerize through a seam of 16 hydrogen bonds,^{137,138} dimerization is obstructed when adjacent urea residues are covalently connected¹³⁹ through one or more loops, as is the case of calixarenes **67**–**71**. Nevertheless **67**–**71** still have a strong tendency to dimerize if a suitable partner (for instance “open chain” calixarenes **61**–**66**)^{140,141} equipped with nonbulky groups is available, whose urea substituents are small enough to penetrate the loops.¹³⁴ If, on the contrary, the substituents are too bulky, dimerization does not occur. Statistically, the 11-component mixture can combine to form 66 different dimers.

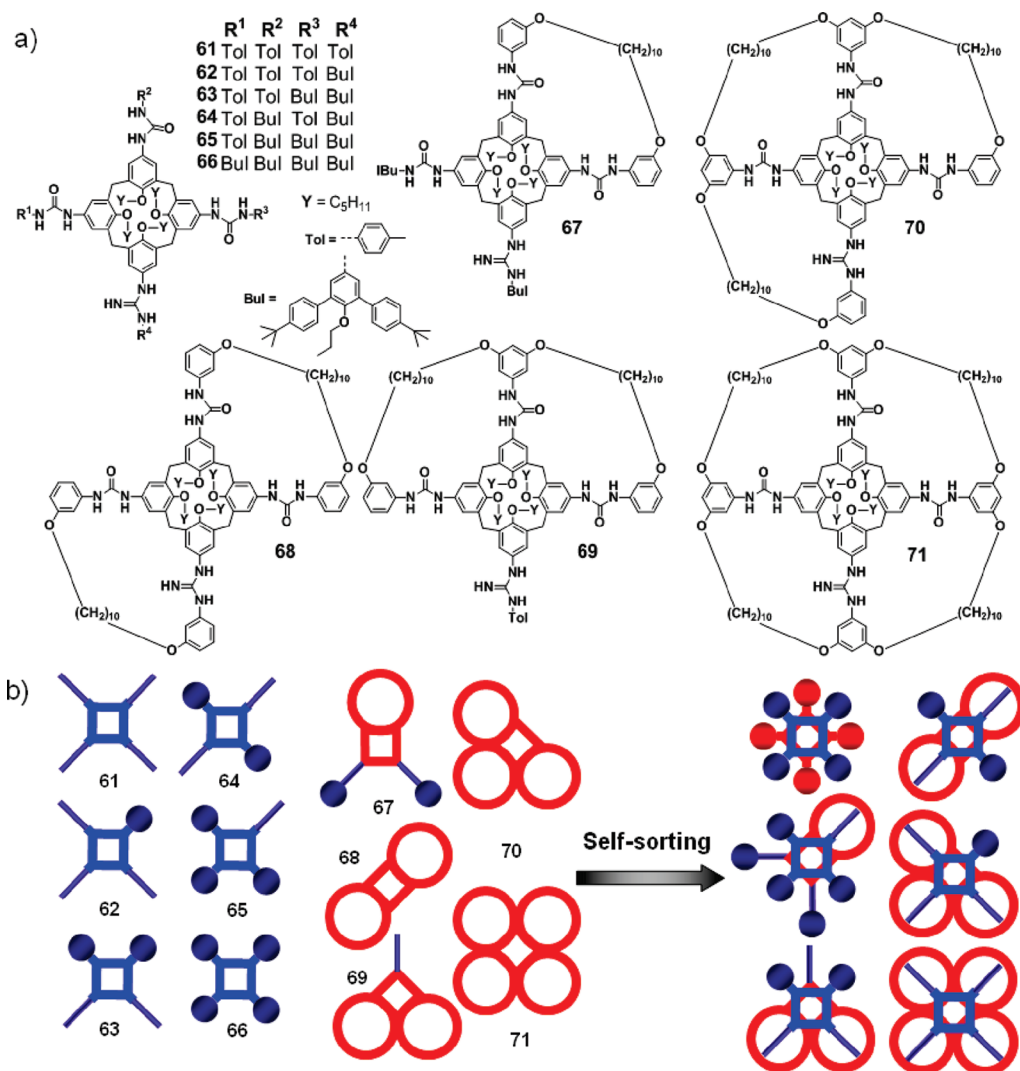


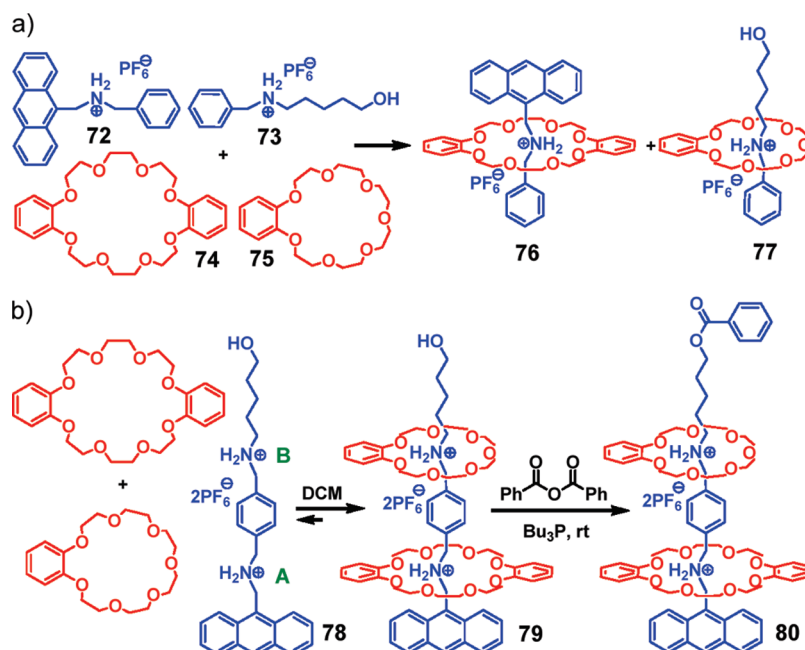
Figure 16. (a) Chemical structures of calixarenes 61–71. (b) Cartoon representation of the self-sorting process in the mixture of eleven tetra-urea calix[4]arene derivatives 61–71 into their six allowed assemblies.

However, taking into account the above-mentioned premises and by controlling the stoichiometry, an equimolar mixture of 61–71 should self-sort into only six different dimers: 61·71, 62·70, 63·69, 64·68, 65·67, and 66·66. ¹H NMR experiments in CDCl₃ were initially performed on a slightly less complex mixture comprising calixarenes 61, 64, 68, 71, and 66 to evaluate the self-sorting processes. As anticipated, only the pairs 61·71, 64·68, and 66·66 were detected by NMR, in agreement with the rationales explained above. Unfortunately, more complex 10 or 11-component mixtures could not be properly analyzed by ¹H NMR. The authors therefore made use of electrospray ionization Fourier transform ion cyclotron (ESI-FTICR) mass spectrometry to analyze the mixtures. Initial control experiments performed on every independent pair demonstrated that the expected dimers 61·71, 62·70, 63·69, 64·68, 65·67, and 66·66 are by far the most abundant species. However, the spectrum of the mixture of all eleven monomers also showed the appearance of unexpected peaks. The authors attributed this observation to the liberation of monomers because of the low concentration regime in which these MS experiments were performed. By increasing the concentration of hindered compounds 67–71 in a 20% excess with respect to

61–66, the equilibria could be successfully shifted back toward the exclusive formation of the expected capsules, thereby demonstrating that small external influence may significantly alter the behavior of a mixture.

On the basis of pseudorotaxane structures from Huang,¹⁴² as well as those from Stoddart and Williams^{143,144} (see Scheme 3), a series of most illustrative examples on the utilization of sterical codes in self-sorting systems was introduced by Schalley and co-workers. Secondary dialkylammonium ions are able to thread through the cavity of benzo-21-crown-7 (C7) 75, leading to pseudorotaxanes.¹⁴² Phenyl groups can effectively suffice as stoppers in these systems to trap 75 on the axle. In contrast, dibenzo-24-crown-8 (C8) 74 units can form pseudorotaxanes with secondary dibenzylammonium ions, revealing that phenyl groups are not bulky enough to act as efficient stoppers for this larger macrocycle.^{143,144} These premises were subsequently exploited to achieve efficient four component self-sorting systems composed of two crown ether units (C8 (74) and C7 (75)) and two ammonium salts (72 and 73).²⁴ Crown ether 75 is too hindered to slip onto axle 72 because of the presence of sterically demanding benzyl and anthracenyl stoppers on both sides,

Scheme 3



whereas sterically less demanding axle 73 fits too loosely in the larger cavity of crown ether 74 (Scheme 3a). As anticipated by these prerequisites, the ESI mass spectrum of an equimolar mixture of all four compounds in dichloromethane revealed the presence of only two peaks corresponding to the complexes 76 and 77 which was further confirmed by ^1H NMR experiments. This type of self-sorting was termed as *nonintegrative*, because it leads to a smaller than possible set of discrete complexes from subunits each equipped with just one binding site (Scheme 3a; for definition see also Figure 1).

These investigations were later extended into *integrative* self-sorting systems, in which more than two different subunits are bound in two or more recognition events with positional control.^{24,145} To this end, a divalent ammonium receptor axle 78 equipped with two binding sites A and B was synthesized, and its self-sorting in the presence of crown ethers C7 75 and C8 74 was investigated. ^1H NMR studies revealed that on mixing, crown ether 75 binds exclusively at site B of 78. In contrast, the addition of 1 equivalent of 74 provoked changes for the protons corresponding to both A and B sites, but the changes in A were more obvious, indicating that crown ether 74 prefers to bind A once the mixture has reached the equilibrium. Accordingly, in the presence of both crown ethers 74 and 75, 79 is the major component.

Finally, this complex was subjected to an esterification reaction with benzoic anhydride to yield a “stopper cascade”. In this rotaxane, the upper and middle phenyl ring of the axle prevent the slipping of the C7 75 ring, whereas C8 74 can still slip over the central phenyl group but not over C7 75, so that it is also trapped (Scheme 3b). Recently, the same authors have expanded this concept for the design of highly sophisticated rotaxane-based self-sorting systems comprising multiply threaded complexes.^{145,146} ESI-FTICR mass spectrometry was demonstrated to be a very useful tool to monitor the self-assembly intermediates, wrongly assembled structures as well as the final thermodynamic products of the self-sorted mixtures.

The examples described so far reveal that steric codes can significantly alter the self-sorting equilibria in either metallosupramolecular or hydrogen bonding-based assemblies. Their influence in systems assembled by means of other noncovalent forces remains, however, almost unexplored. In one distinct example, Würthner and co-workers studied hydrogen-bonding and π - π -stacking driven self-assembly, co-assembly and gelation ability of a series of perylene bisimide dyes functionalized with benzamide groups at the imide position and peripherally connected to different alkyl substituents (Figure 17).¹⁴⁷ Solvent and temperature dependent UV-vis and circular dichroism (CD) experiments demonstrated that perylene bisimide derivatives equipped with linear side chains (e.g., 81) formed H-type aggregates (hypsochromically displaced major absorption band) giving rise to red gels,¹⁴⁸ whereas by introducing sterically demanding branched alkyl chains (e.g., 82) the formation of J-type aggregates (bathochromically displaced major absorption band) yielding green gels was observed (Figure 17a).¹⁴⁹ This difference in self-assembly behavior was subsequently exploited to investigate the coassembly of mixtures of perylene bisimides equipped with linear and branched chains. UV-vis and CD spectroscopy studies performed on 80:20 mixtures of methylcyclohexane (MCH)/tetrahydrofuran (THF) revealed that, when dye 82 was mixed with dye 81 at low 82/81 ratio, an exclusive formation of red H-type aggregates containing both chromophores was observed. However, the incorporation of the more bulky derivative 82 in these H-type π -stacks is limited to an amount below 50% (Figure 17). This ratio implies that 82 is incorporated in the mixed assembly with 81 in an alternate fashion, in which unfavorable steric constraints among two adjacent face-to-face π -stacked 82 are prevented. When the amount of 82 approaches 50% the system separates into H-type and J-type π -stacks and ultimately leads to a narcissistic self-sorting in which 81 and 82 form their respective independent assemblies. The latter situation is particularly

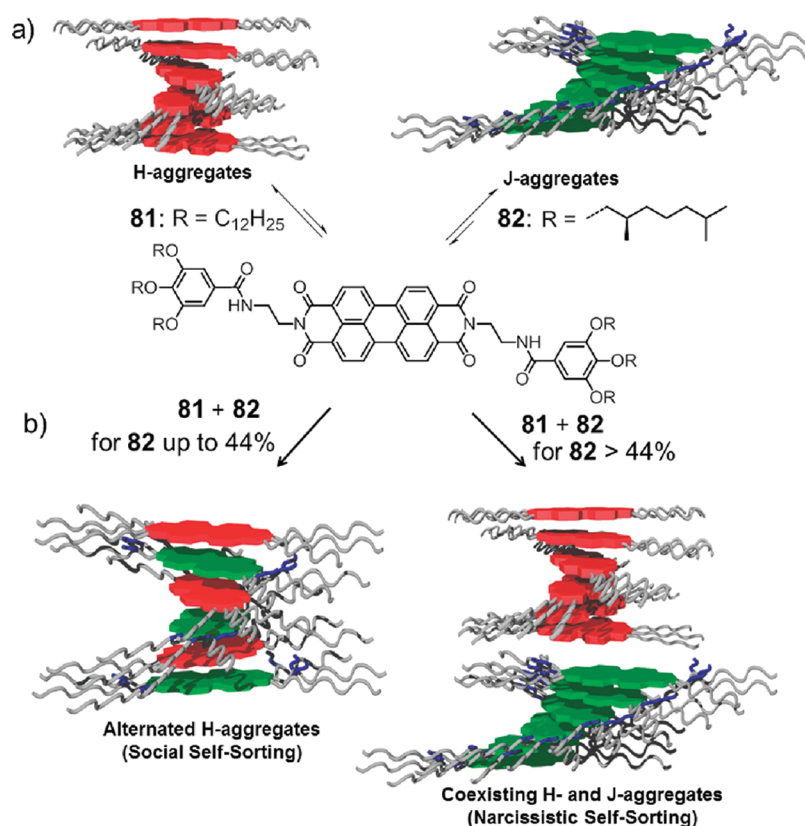


Figure 17. (a) Chemical structures and independent self-assembly pathways for perylene bisimides **81** and **82**. (b) Self-sorting processes in mixtures of perylene bisimides **81** and **82** depending on the relative concentration of the components in the mixture.

avored at high ratios of **82** due to the energetic penalty associated with the packing of **81** into slipped J-aggregate stacks and the steric problems encountered upon incorporation of larger amounts of **82** into more compact H-type π -stacks (Figure 17b).

Recently, another example for the self-sorting capability of extended supramolecular networks was reported by Moffat and Smith.¹⁵⁰ These authors demonstrated a significant steric influence on the self-sorting ability of three different hydrogen-bonded organogelators. Two organogelators possess amide groups anchored to long alkyl surface groups, whereas the remaining gelator features carbamate groups and lacks any additional chain. The joint effect of hydrogen bond complementarity and steric factors was proposed to control the self-sorting process, since only organogelators equipped with analogous hydrogen-bonding functionalities and steric restraints were demonstrated to socialize. Mixtures of the most structurally different gelators led, on the other hand, to complete self-recognition.

3.4. Coordination Sphere in Metal–Ligand Interactions

As illustrated in previous sections, metal–ligand interactions are most useful for the construction of supramolecular architectures. We have elucidated in section 3.1 that the size, shape and predefined geometry of organic ligands can serve as an efficient molecular code to direct self-sorting phenomena when combined with a metal center that is typically of ionic nature and occasionally a neutral metal species (see for instance Figure 4 and Scheme 2). The high selectivity in these recognition processes is primarily of geometrical basis—for both illustrated systems all possible narcissistic or social assemblies involve the same

metal–ligand point interactions—which rules out any intrinsic influence of the metal center on the self-sorting behavior. The situation, however, becomes far more complex if two or more different metal ions are available to bind with one or more ligands. Under these conditions, a wide variety of combinations of metal complexes with numerous geometries is in theory possible to form. This diversity of complexes will largely depend on the *coordination sphere* in metal ligand interactions,⁵³ which can be defined as the number of ligands and their geometrical arrangement around the metal ion. Three main factors govern the coordination sphere in a complex: (a) the size, charge, hardness, and polarizability of the metal ion,^{151,152} (b) the identity (and sterics) of the ligands, and (c) the electronic interactions between the ligands and the central metal ion.⁵³ Ligands will follow the principle of “maximal site occupancy”^{89,153,154} by realizing metal coordination at the maximum number of available sites, which is ultimately imprinted by the interactions between s and p molecular orbitals of the ligands and the d orbitals of the metal ions. Transition metals with vacant d-orbitals are known for their quite specific coordination modes which obviously constitute most appealing molecular codes to direct self-sorting phenomena.^{19,30,153} In general, ions of larger radii give rise to high coordination numbers, especially when the metal ion possesses a small number of valence electrons because that would mean that the metal ion can accept more electrons from Lewis bases, like for instance in $[Mo(CN)_8]^{4-}$. Small metal ions, on the other hand, lead to low coordination numbers particularly if the ions are rich in electrons, so that they are less able to accept electrons from Lewis base ligands, for example, $[PtCl_4]^{2-}$.

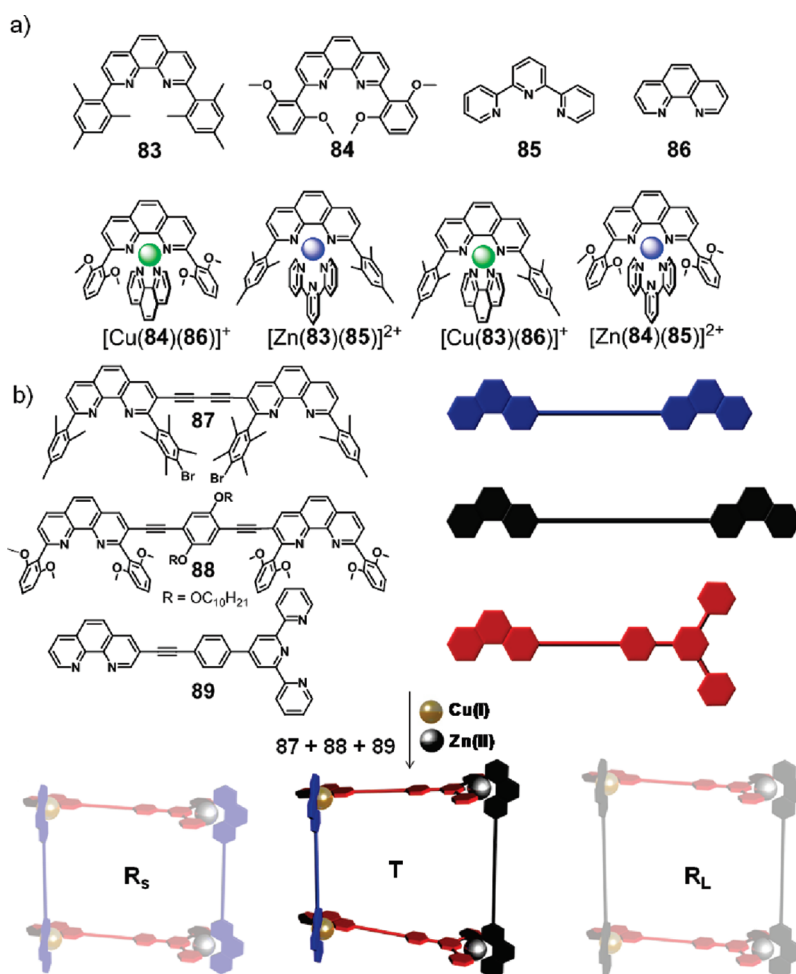


Figure 18. (a) Molecular structure of ligands 83–86 and their respective nonintegrative self-sorting. (b) Chemical structure of polyfunctional ligands 87–89 and their integrative self-sorting in the presence of Cu^+ and Zn^{2+} . Reproduced with permission from ref 159. Copyright 2009 American Chemical Society.

This high geometrical versatility when different metal ions and ligands are combined should place metal ion-coordination among the most relevant codes applicable for driving self-sorting processes in supramolecular systems. Indeed, in the field of dynamic combinatorial libraries, the coordination geometry of the metal ion^{155,156} and steric constraints¹⁵⁷ have been applied to drive the outcome of reversible chemical reactions. However, the influence of such metal ion-based coordination codes in mixtures of different metal ions and ligands has been to date practically unexplored, which prevents us from drawing a realistic conclusion about their quantitative true relevance to the field.

In their seminal work Lehn and co-workers¹⁹ took advantage of the tetrahedral coordination of Cu(I) ions and octahedral coordination of Ni(II) ions to accomplish self-recognition in mixtures of bipyridine-based ligands, yielding double and triple helicates respectively (see Scheme 1). This example highlights that the ability of the metal ions to coordinate into different geometries (along with the geometry of the ligands) can direct the self-recognition process. Nevertheless, since this early investigation little attention has been devoted to the study of systems comprising more than one metal ion in the presence of different ligands.

In an exciting example, Schmittel and co-workers have revealed a self-sorting process in mixtures of four different terpyridine or phenanthroline-based ligands (83–86) and two

different metal ions (Zn(II) and Cu(I)).^{158–160} Out of 20 possible combinations, the self-sorting library ended up with only two metal complexes: $[\text{Cu}(\mathbf{84})(\mathbf{86})]^+$ and $[\text{Zn}(\mathbf{83})(\mathbf{85})]^{2+}$ or $[\text{Cu}(\mathbf{83})(\mathbf{86})]^+$ and $[\text{Zn}(\mathbf{84})(\mathbf{85})]^{2+}$ depending on the relative stoichiometry chosen, as demonstrated by ^1H NMR, ESI-MS and differential pulse voltammetry (DPV). This high degree of self-sorting has been attributed to geometrical, steric and electronic factors and, more importantly, to the extra stabilization gained from maximum site occupancy, that is, the difference in coordination number associated to Zn(II) and Cu(I) . In a subsequent step these highly selective small building blocks were implemented into three polyfunctional ligands 87–89 whose integrative self-sorting in the presence of Cu(I) and Zn(II) led exclusively to the formation of a hitherto unknown supramolecular structure, a trapezoidal (T) metal–ligand assembly, whereas no trace of the other possible large (R_L) or small (R_S) rectangles could be observed (Figure 18). Recently, these authors have exploited their elegant concept for the fabrication of a five and eight-component supramolecular triangle from structurally similar building blocks.^{161,162}

3.5. Charge Transfer

Electroactive molecular materials^{163,164} have gained great attention in recent years for the fabrication of optoelectronic devices,

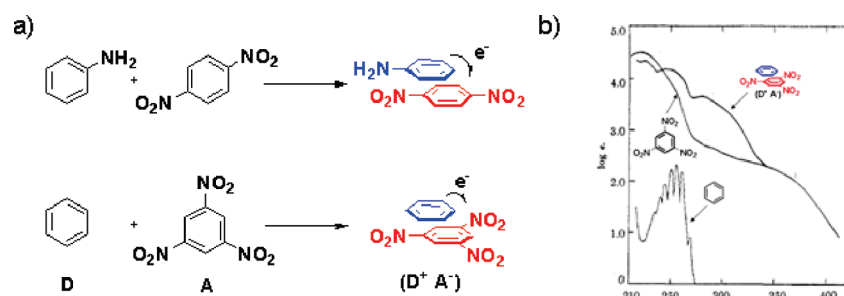


Figure 19. (a) Formation of charge-transfer complexes in mixtures of aniline/1,4-dinitrobenzene (top) and benzene/1,3,5-trinitrobenzene (bottom). (b) Absorption spectra of benzene, 1,3,5-trinitrobenzene and benzene/1,3,5-trinitrobenzene molecular complex recorded in *n*-heptane. Reproduced with permission from ref 177. Copyright 1952 American Chemical Society.

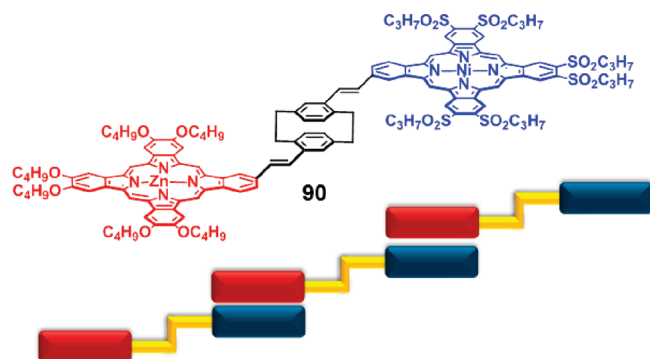


Figure 20. Chemical structure of phthalocyanine **90** and schematic representation of the self-discrimination process within supramolecular aggregates.

such as organic field effect transistors^{165–169} or photovoltaic devices.^{170–173} An adequate control of the nanometer-scale morphology between electroactive molecules in such systems is a prerequisite for good performance.^{174,175} In the particular case of bulk heterojunction (BHJ) solar cells, electron-donor and acceptor molecules must segregate into chemically homogeneous domains with typical sizes of the order of the exciton diffusion length (10–20 nm). This arrangement requires a good balance between phase separation into nanometric domains (narcissistic self-sorting) and the interaction between donor and acceptor molecules of different domains (social self-sorting) to ensure an efficient charge transfer process at the interface.

A charge transfer (CT) complex (or donor–acceptor complex) is formed when two or more molecules or different parts of a large molecule associate, so that a fraction of electronic charge is donated from D (donor) to A (acceptor) with weak covalent bond formation between the molecular entities.⁴⁰ In the valence bond model this attraction can be related to the mixing of the neutral state (AB) with a charge-separated state (A^+B^-). Charge transfer complexes manifest by the appearance of a weak electronic transition in the long-wavelength region of the absorption spectrum. These optical transitions are often referred to as *charge-transfer bands* (CT bands). Typical examples are mixtures of electron rich aromatic amines, i.e. aniline, and electron poor dinitrobenzenes (Figure 19a).^{176,177} The UV–vis spectra of aniline or dinitrobenzenes alone in chloroform solutions are characterized by the absence of any absorption in the visible region. Mixtures of aniline and either 1,3- or 1,4-dinitrobenzene, however, give rise to colored solutions as a result of the emergence

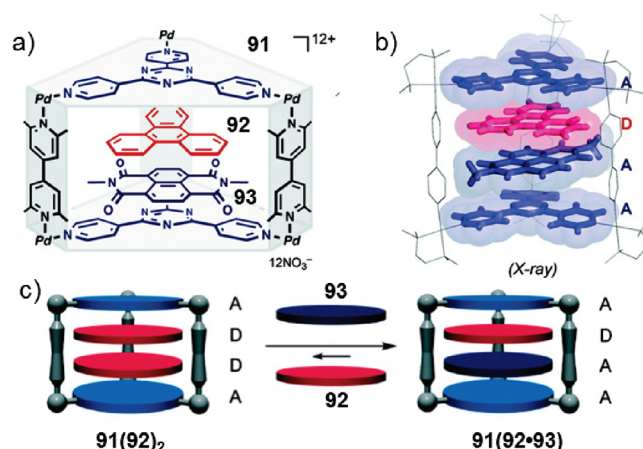


Figure 21. (a) Chemical structure of cage **91**, and guests **92** and **93**. (b) Structure of the resulting self-assembly of inclusion complex $91 \cdot (92 \cdot 93)$ in single crystals. (c) Guest exchange between complexes $91 \cdot (92)_2$ and $91 \cdot (92 \cdot 93)$. Reproduced with permission from ref 188. Copyright 2010 American Chemical Society.

of a new charge-transfer band centered at ~ 480 nm.¹⁷⁶ The presence of an intermolecular charge-transfer transition at ~ 300 nm indicates the formation of a molecular complex between benzene and 1,3,5-trinitrobenzene (Figure 19b).¹⁷⁷ The low value of binding constant in this system (4.1 M^{-1} in *n*-heptane) clearly reflects that charge-transfer interactions make a very small contribution to the stability of the ground state of π -stacked molecular complexes.^{40,178} In contrast, by simply replacing the nitro groups of 1,3,5-trinitrobenzene by alkylamide substituents, the resulting discotic triamides are able to self-assemble into one-dimensional rod-like associates of several micrometers by hydrogen-bonding and π -stacking, affording binding constants of $\sim 5 \times 10^8 \text{ M}^{-1}$ in heptane.^{179–181}

These findings highlight that charge-transfer interactions have a remarkably smaller weight in comparison with similar systems assembled by stronger noncovalent interactions such as hydrogen bonds, which allows us to hypothesize that charge-transfer contributions should have only a modest influence on the outcome of a self-sorting mixture. Nevertheless, when the structural similarities and the type and number of participating noncovalent forces among the interacting molecules reach a maximum, geometrical complementarity is obviously less relevant and molecular codes that apparently have a small weight, such as charge transfer interactions, become important to the point that

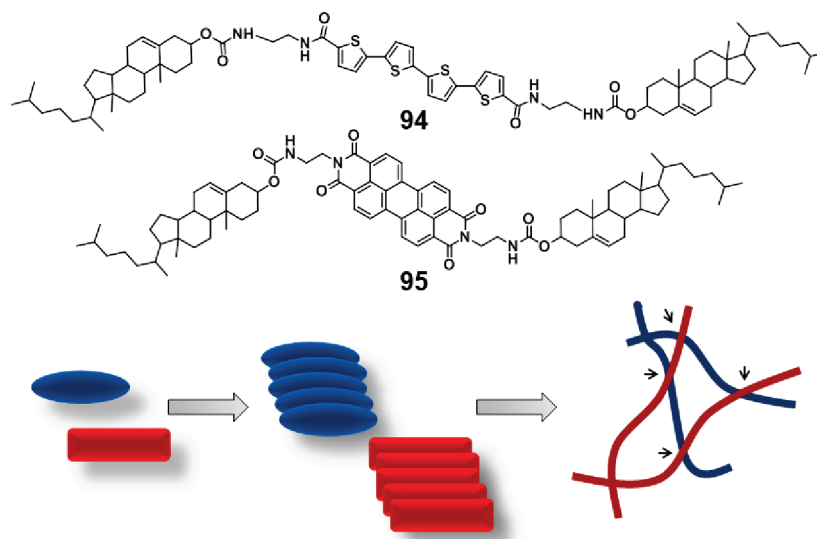


Figure 22. Chemical structures of **94** and **95** and representation of their “orthogonal” self-assembly into independent fibers of electron rich oligothiophene and electron poor perylene bisimide stacks with only few *p-n*-heterojunction nodes (black arrows).

they can bias the molecular recognition events. This strategy has been successfully applied in several examples of π -conjugated self-sorting systems published in the literature.^{182–184}

Torres and co-workers reported a convincing example in which similar geometry of the involved molecules in the self-sorting process allows electronic charge transfer interactions to be the chief driving force for the social self-sorting event.¹⁸⁴ They reported a dimeric system composed of two phthalocyanines covalently connected by a [2,2]paracyclophane unit (**90**). Each of these covalently linked phthalocyanines possesses a different electronic character because of the presence of electron donating alkoxy or electron withdrawing alkylsulfonyl substituents. The presence of a charge-transfer (CT) band in UV–vis absorption spectra in CHCl_3 demonstrated that the molecules self-sort in a self-discriminating manner driven by their complementary electronic character (Figure 20).

In another example, Fujita and co-workers masterfully captured the simultaneous influence of geometrical as well as charge transfer codes for an efficient self-sorting process in coordination cages.^{185–188} They recently reported the interaction of cage **91**, formed by two large organic panels with electron acceptor properties and D_{3h} geometry, three rod-like pillars, and six metal hinges, with naphthalenediimide acceptor **93** and three different donors (triphenylene (**92**), perylene, and pyrene).¹⁸⁸ As shown by a series of experiments, if the number of stacked guest molecules *n* in the cavity (this can be controlled simply by adjusting the length of the organic pillar sets) is odd, alternating donor–acceptor (D–A) arrays, for example, A–D–A–D–A, are favored, leading to self-discrimination driven by the electronic nature of the molecules.¹⁸⁵ On the other hand, when *n* is even, such preferred alternating D–A arrays are excluded (Figure 21), which makes the prediction of the preferred stacked structure less trivial. A–A interactions were apparently better tolerated than D–D interactions, which turned cage **91** into a good candidate for exchange studies. The formation of the A–D–D–A complex **91**·(**92**)₂ was achieved by treatment of cage **91** with pure donor **92**. Next, ¹H NMR studies demonstrated that after addition of acceptor **93** to the former assembly **91**·(**92**)₂, substitution of one donor unit **92** by one acceptor **93** unit takes

place, whereas A–A–A–A stacking **91**·(**93**)₂, was not obtained. Moreover, cold spray ionization mass spectrometry (CSI-MS), ¹H NMR spectroscopy and X-ray diffraction experiments clearly supported the formation of the A–D–A–A inclusion complex **91**·(**92**·**93**) from a 1:1 mixture of donor **92** and acceptor **93** (Figure 21c). These results suggest that charge-transfer contributions are relevant for the final arrangement of the guests inside the cage.

The importance of the donor geometry could be made evident by the calculated energy barriers for the exchange process between different donors (triphenylene (**92**), perylene, and pyrene) and acceptor **93** from temperature-dependent ¹H NMR data. Here, the highest energy barrier was observed for the exchange of the donor triphenylene (*C*₃ symmetry), which is geometrically most related to the cage panel unit. Since dispersion and charge transfer interactions both depend on the area of the π – π contact surface this is a very reasonable result.

The success in the socialization of different molecules possessing opposite electronic nature, is therefore, strongly dependent on a good geometrical complementarity. When, on the other hand, the structural fit is reduced, the weak charge transfer forces between the interacting molecules can not overcome the penalty associated to the loss of dispersion interactions that are in general larger between identical molecules owing to identical size of the contact surface. As a consequence, the equilibrium will shift from self-discrimination toward self-recognition.^{189,190} In this regard, an example from Shinkai and co-workers is quite illustrative as it describes the self-sorting of electron rich quaterthiophene **94** and electron poor perylene bisimide **95** organogelators.¹⁸⁹ UV–vis, CD and SEM studies revealed an independent formation of oligothiophene and perylene bisimide nanofibers from a 1:1 mixture of both molecules, respectively, which are in contact only in some nodes (Figure 22).

Two main reasons have been identified by the authors why self-recognition dominates the self-assembly of these molecules: (i) the formation of four hydrogen bonds is possible between two quaterthiophene **94** molecules, whereas only two are formed between two perylene bisimides **95**, and (ii) a much larger overlap of the π -surfaces can occur if equal molecules are stacked, that is, similar geometry of the molecules favors π -stacking in a

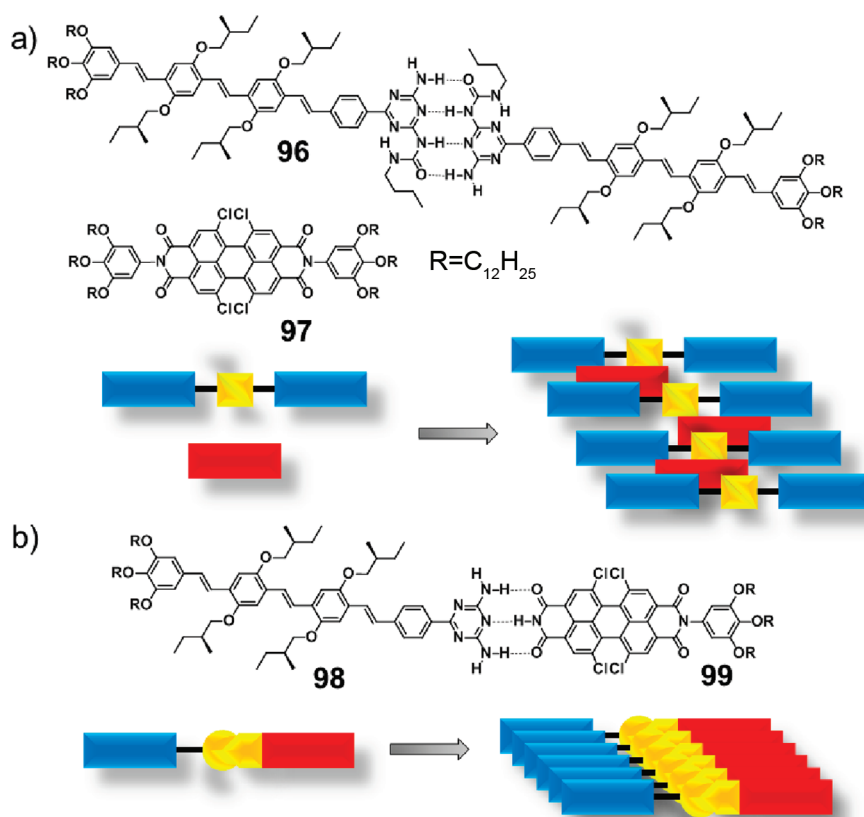


Figure 23. (a) Chemical structure of studied OPV **96** and perylene bisimide **97** and cartoon representation of the social coassembly process. (b) Chemical structure of modified OPV **98** and perylene bisimide **99** and schematic representation of their self-assembly into p- and n-type stacks.

self-recognition manner. These two joint effects account for the higher binding constant of **94** ($>10^5 \text{ M}^{-1}$ in CHCl_3) compared to that of **95** ($1.3 \times 10^3 \text{ M}^{-1}$ in CHCl_3). Such substantial difference (>100 -fold) between the association constants of both components suggests—as discussed by Isaacs and co-workers²⁰—an efficient self-sorting process if no additional interactions come into play. Obviously, charge transfer interactions between oligothiophenes and perylene bisimides are too weak to bias the system toward self-discrimination. Based on the same rationale, hydrogen-bond-directed formation of nanofibers of perylene bisimide **82** (Figure 17) was achieved in a matrix of electron-rich semiconducting polymers to give bulk heterojunction solar cells.¹⁹¹

On the basis of these observations one might anticipate that only members of a mixture featuring nearly identical geometry and suitable complementarity of additional noncovalent forces would allow electronic charge-transfer effects to determine the outcome of the self-sorting process. For more complex aggregate systems, however, this is not necessarily the case which can be illustrated by a series of studies on the co-assembly of oligophenylenevinyls (OPVs) and perylene bisimides.^{192–195} Thus, an example for an integrative co-assembly of structurally rather dissimilar molecules is given by the OPVs **96** and the electron poor perylene bisimides **97** (Figure 23).^{192,194} OPV derivative **96** features, besides a relatively large aromatic π – π -surface, a self-complementary ureidopyrimidinone (Upy) unit on one side and long alkyl chains on the opposite side to increase solubility in nonpolar media. The joint contribution of π – π -stacking, quadruple hydrogen-bonding, and additional peripheral van der Waals contacts between alkyl chains leads to the formation of H-type

helical π -stacks upon self-assembly in heptane. Perylene bisimide **97**, on the other hand, self-assembles in nonpolar solvents via π – π interactions and van der Waals forces among peripheral alkyl chains into slipped stacks.¹⁹⁶ Mixing **96** and **97** in a 1:1 ratio in hexane, however, results in the appearance of a weak charge transfer (CT) band in UV–vis studies, which points to the formation of a mixed assembly of **96** and **97** (Figure 23a).¹⁹⁴ Obviously, the opposite electronic character of **96** and **97** governs the co-assembly including self-discrimination features that are favored by the attractive charge transfer interaction between OPV donors and perylene bisimide acceptors. This effect appears to be particularly pronounced for chlorinated perylene bisimides due to their strong electron acceptor character.¹⁹⁷

Further investigations addressed the question whether the opposite self-sorting behavior could take place in mixtures of structurally different OPV **98** and perylene bisimide **99**, which are designed to form a hydrogen-bonded complex with each other (Figure 23b). UV–vis studies in heptane revealed the appearance of a red-shifted perylene bisimide band. However, this band was a slipped π -stack of cofacially aggregated dyes **98** and **99**.¹⁹⁴ In this mixture hydrogen-bonding and geometrical factors are clearly the most relevant codes that govern the desired narcissistic self-sorting of these functional dyes into supramolecular p-n-heterojunction π -stacks.^{193,195}

To summarize, charge transfer interactions between donor and acceptor π -systems in solution are very weak, and only play an important role when other premises have been fulfilled. It is also noteworthy to point out that charge transfer complexes are not always easy to detect as the charge transfer bands are often hidden beneath other absorption bands due to their low intensity.

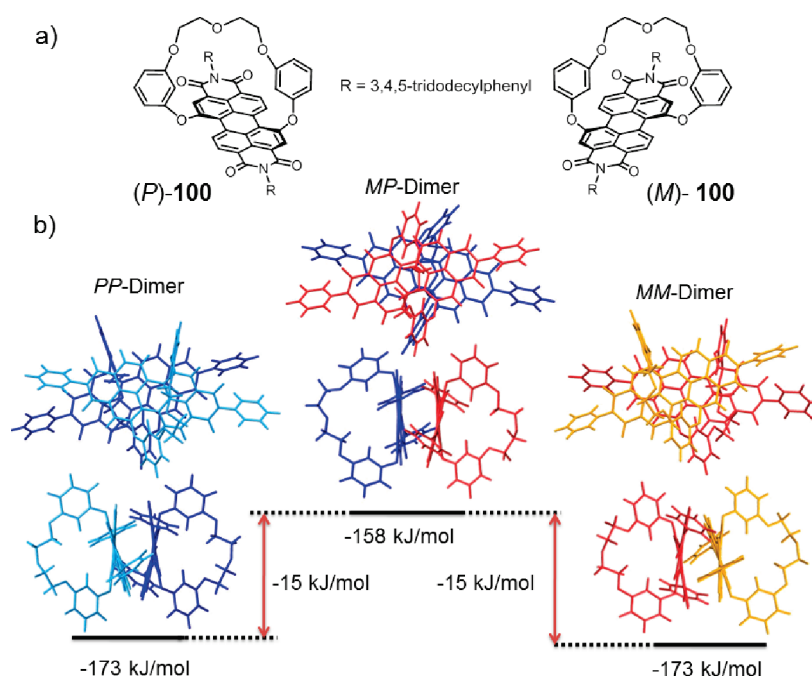


Figure 24. (a) Structures of atropo-enantiomeric (*P*)-**100** and (*M*)-**100**. (b) Structure optimization calculations performed at RI-BLYP-D/TZV(P)-level of homo and heterochiral dimers.

4. CHIRAL SELF-SORTING

In the previous sections, we have discussed the molecular codes that can independently or jointly direct efficient self-sorting processes in artificial systems. Although it must be underlined that the molecular codes directing chiral self-sorting are not distinct from those discussed above for “general” self-sorting, due to the relevant implications of chiral recognition in natural systems we will draw special attention to chiral self-sorting systems and, as such, will regard them separately.

Chiral recognition,^{198–200} that is, the ability of a chiral molecule to differentiate between two enantiomers, is of great significance both in biological processes and organic synthesis as demonstrated in asymmetric catalysis^{201–203} or enantioselective recognition by enzymes and protein receptor sites.^{204,205} Nevertheless, the origin of homochirality of important natural building blocks (e.g., L-amino acids and D-sugars and the biopolymers derived thereof) still remains a fundamental question despite the great efforts invested in the last decades to elucidate this matter.^{206–211} A better understanding of chiral recognition is thus a key for a more rational catalyst design for asymmetric synthesis, new materials with intriguing chiral properties and may contribute to a better understanding of the origin of homochirality in biological molecules.

In accordance with the definition of self-sorting, chiral recognition between enantiomeric pairs can lead to self-recognition or self-discrimination, depending on whether an enantiomer preferentially recognizes itself or its mirror image, to generate homo- or heterochiral self-assemblies respectively. However, an important consideration has to be taken into account regarding chiral systems, that is, pairs of enantiomers, in contrast to the previously described self-sorting systems, to which we will refer as “general”: in chiral self-sorting the physical properties of the interacting monomers (enantiomers) are, except for their interaction with polarized light, equal and

hence, they exhibit identical spectroscopic features. These can only be differentiated when both enantiomers interact with themselves or their mirror images to afford homo- or heterochiral aggregates, which in turn possess diastereomeric nature and thus display different spectroscopic properties. This constraint makes the analysis of chiral self-sorting mixtures more challenging in comparison with “general” self-sorting systems. Consequently, the control of the molecular codes directing chiral self-sorting is a demanding task.

As discussed previously in the section on “general” self-sorting, size and shape are undoubtedly the most relevant molecular codes that make a particular pair of molecules recognize (or discriminate) each other. In chiral self-sorting systems this molecular code has a lower weight, as pairs of enantiomers possess identical size and shape and differ only in the relative spatial orientation derived from their opposite chirality (i.e., mirror-image shape). This suggests that geometrical factors will not exhibit such an overwhelming preponderance as occurred in conventional self-sorting systems. Although in the past the greatest attention has been devoted to the study of chiral self-sorting upon crystallization,^{34,212,213} we will focus exclusively on those investigations carried out in solution to ensure that derived molecular codes are of thermodynamic origin.

Extended twisted π -surfaces appear to be most suitable targets for such investigations because they combine sufficiently large van der Waals contact areas, as required for self-assembly in dilute solution, and pronounced chirality. Our group has very recently reported such an example for chiral self-sorting of atropo-enantiomeric core-twisted perylene bisimides (*P*) and (*M*)-**100**.^{214,215} We have synthesized the chiral 1,7-disubstituted macrocyclic perylene bisimide **100**, and resolved their atropo-enantiomers (*P*)-**100** and (*M*)-**100** (Figure 24) by high-performance liquid chromatography (HPLC) using a chiral stationary phase. The bridging unit on one π -face of **100** ensures, on one hand, a clean dimerization process by interaction of free π -faces

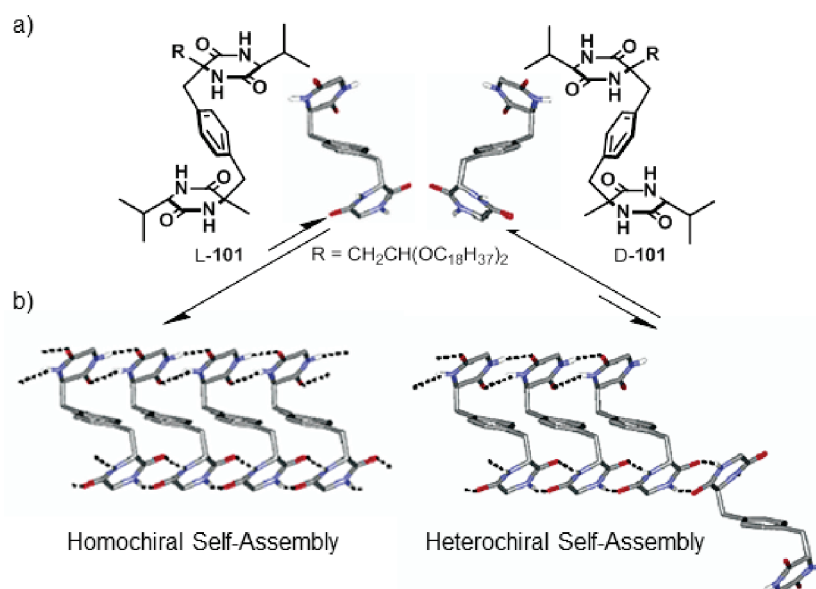


Figure 25. Chemical structure of “S” shaped xylene-bridged bis(cyclic dipeptide) **101** and schematic representation of its supramolecular polymerization in a self-recognition process. Reproduced with permission from ref 221. Copyright 2002 American Chemical Society.

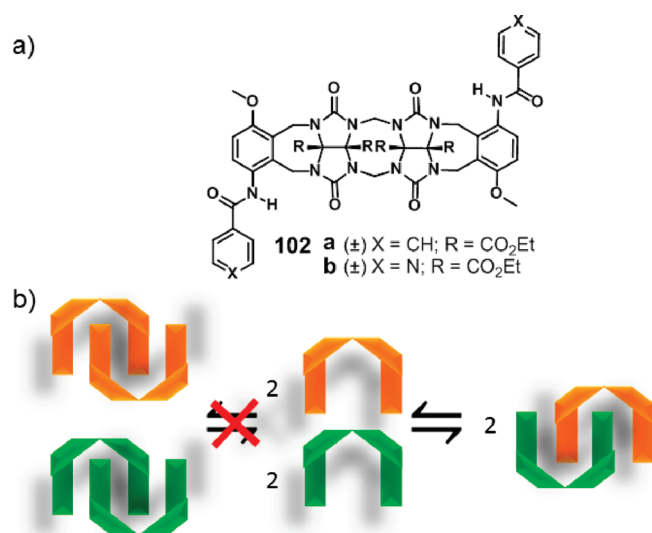


Figure 26. (a) Chemical structure of chiral clips **102a,b**. (b) Cartoon of their self-sorting process.

(in contrast to the common self-assembly of perylene bisimides into extended columnar aggregates)¹⁹⁶ and, on the other hand, prevents the interconversion between *M* and *P* enantiomers.⁶³

UV–vis and CD studies along with ¹H NMR were performed to examine the behavior in solution of (*rac*)-**100**, (*P*)-**100** and (*M*)-**100**. By means of concentration-dependent UV–vis studies the binding constants of the (*rac*)-**100** and (*P*)-**100** (= (*M*)-**100**) in *n*-hexane at 331 K were derived. Further quantitative analysis²¹⁶ of these binding constants revealed the preference for the formation of homochiral ($K_D = 2800 \text{ M}^{-1}$) over heterochiral dimers ($K_D = 400 \text{ M}^{-1}$). The difference of these binding constants is sufficient for self-sorting of racemic mixtures leading to 93% homochiral and 7% heterochiral dimers in the thermodynamically equilibrated state.²¹⁴ These findings are

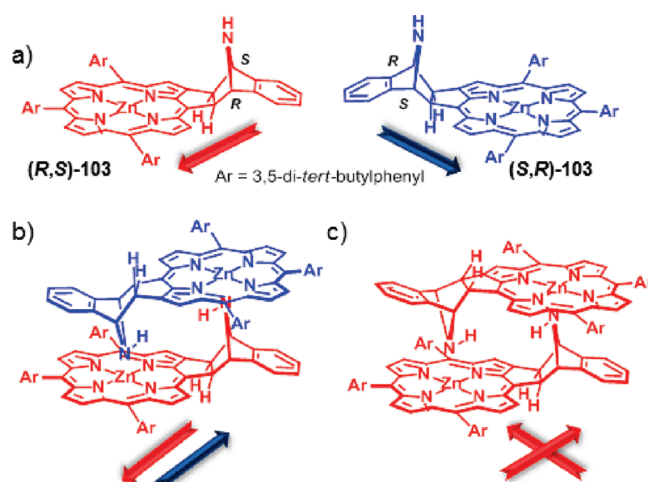


Figure 27. (a) Structures of enantiomeric (*R,S*)-**103** and (*S,R*)-**103**. Schematic representation of (b) hetero- and (c) homochiral dimer aggregates derived thereof. The arrows represent an approximation of the orientation of the dipole moments.

rationalized by a greater π – π overlap in homochiral than in heterochiral dimers²¹⁷ and could be confirmed by force field energy minimized models of hetero vs homochiral assemblies (Figure 24b).²¹⁵ Homologous molecules with longer bridges showed a lower degree of self-recognition but higher binding constants, which was rationalized in terms of an induced-fit planarization process upon π – π stacking.²¹⁵ Other authors have shown that in helicenes²¹⁸ and propeller-like molecules bearing aromatic rings²¹⁹ the formation of homochiral assemblies is also favored over heterochiral ones due to the better overlap of the π -surfaces, leading to a highly efficient self-recognition process.

Although self-recognition between closely packed contorted chiral π -surfaces appears most interesting from the crystal engineering point of view²²⁰ the above example illustrates its

limitations, that is, only a modest bias between self-recognition and self-discrimination. Accordingly, most of the published examples on chiral self-sorting take advantage from stronger intermolecular forces, such as recognition by multiple hydrogen bonds or metallosupramolecular intermolecular forces. In this regard, Aida and co-workers synthesized a racemic “S” shaped xylene-bridged bis(cyclic dipeptide) **101** which possesses L and D chirality.²²¹ The “S” shape of their molecules could be proven by the single crystal X-ray analysis of a derivative of molecule **101**. By means of SEC they could determine that these molecules form a supramolecular polymer capable of self-associating with a high degree of enantioselectivity (self-recognition).

The reason for the exclusive formation of homochiral assemblies is the shape complementarity derived from the “S” shaped molecules. In the case of homochiral supramolecular polymerization, participation of the two diketopiperazine units in the

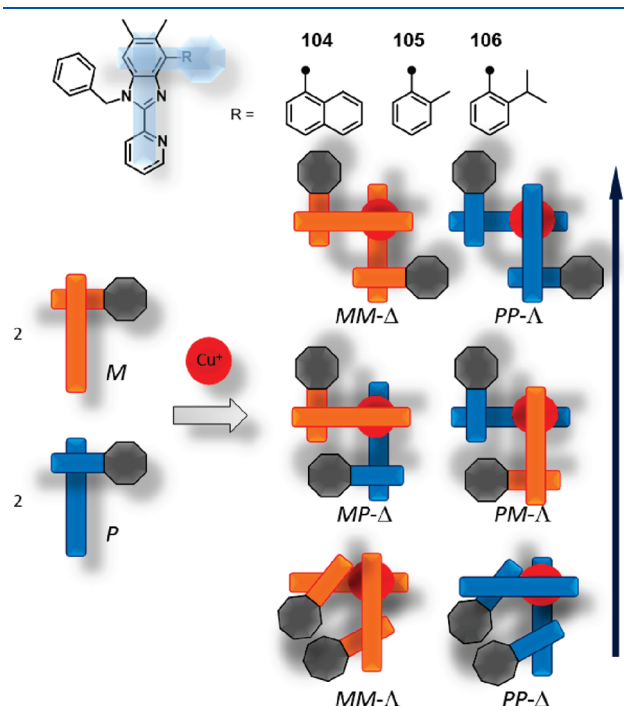


Figure 28. Chemical structure of ligands **104**–**106** and schematic representation of the possible isomers formed upon complexation of ligands **104**–**106** with Cu^+ .

formation of four simultaneous hydrogen bonds via complementary H-bonding takes place (Figure 25b, left). This is not possible for a heterochiral assembly, in which only one diketopiperazine is allowed to participate in the hydrogen-bonding formation because of the possible mismatch of the hydrogen donor–acceptor arrays (Figure 25b, right).

Isaacs and co-workers investigated the self-recognition behavior in a series of chiral molecular clips assembled by the accumulation of different intermolecular forces.^{12,222} They described the synthesis and characterization of “C” shaped methylene-bridged glycoluril dimers bearing H-bonding groups attached at their aromatic rings (**102a,b**), which enables self-assembly via hydrogen-bonding in combination with π – π -stacking (Figure 26). ^1H NMR in CDCl_3 and X-ray analysis of the crystalline structure obtained for **102b** revealed that these aggregates display high levels of chiral discrimination giving rise to heterochiral dimers.

The preference in the formation of heterochiral over homochiral dimers was attributed to the possibility of simultaneous formation of π – π -interactions and two hydrogen bonds, whereas the hypothetical homochiral dimer can only be stabilized by π – π -interactions and one hydrogen bond. Accordingly, the spatial orientation of the H-bonding groups controls the self-sorting process by favoring aggregates with the highest accumulation of intermolecular contacts.

Osuka, Shinokubo, and co-workers reported the synthesis of a racemic porphyrin **103** and the resolution of its enantiomers by chiral HPLC (Figure 27a).²²³ The binding constant of the pure enantiomers and the racemate for the formation of homo- and heterochiral dimers could be determined by concentration-dependent fluorescence spectra in CHCl_3 as $K_{\text{homo}} = 1.2 \times 10^7 \text{ M}^{-1}$ and $K_{\text{rac}} = 1.8 \times 10^8 \text{ M}^{-1}$, respectively. Using these binding constants given by the authors the heterodimerization binding constant can be calculated as $K_{\text{D(hetero)}} = 7 \times 10^8 \text{ M}^{-1}$.^{214,216} Accordingly, a racemic mixture contains 3% homo versus 97% heterochiral dimers, that is, chiral self-discrimination takes place.

Additional proof was provided by ^1H NMR spectra for solutions of the pure enantiomers and the racemic mixture, which revealed the presence of different assemblies. Single-crystal X-ray analyses of the homochiral dimers obtained from the solution of the pure enantiomers and that of the heterochiral dimers obtained from the racemic mixture provided structural details to rationalize the preference for the formation of heterochiral dimer aggregates. Whereas in the heterodimer

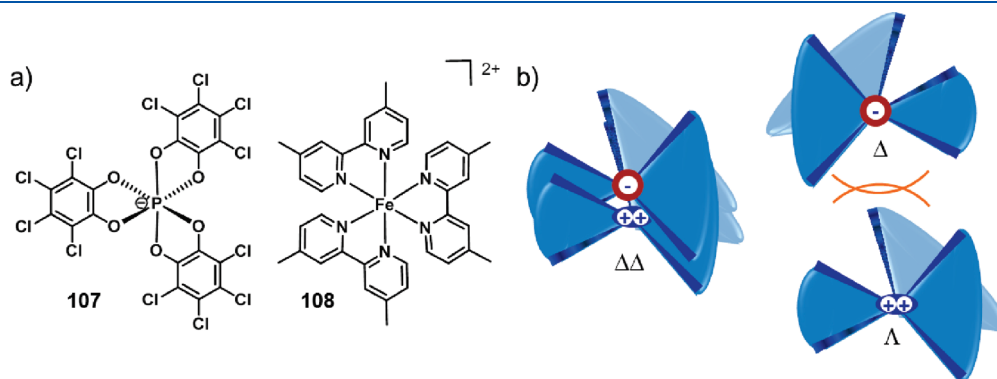


Figure 29. (a) Chemical structures of enantiopure TRISPHAT anion **107** and racemic $[\text{Fe}(\text{4,4'}\text{-Me}_2\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) **108**. (b) Schematic representation of the formed homochiral assemblies (left) and the unfavorable heterochiral assembly.

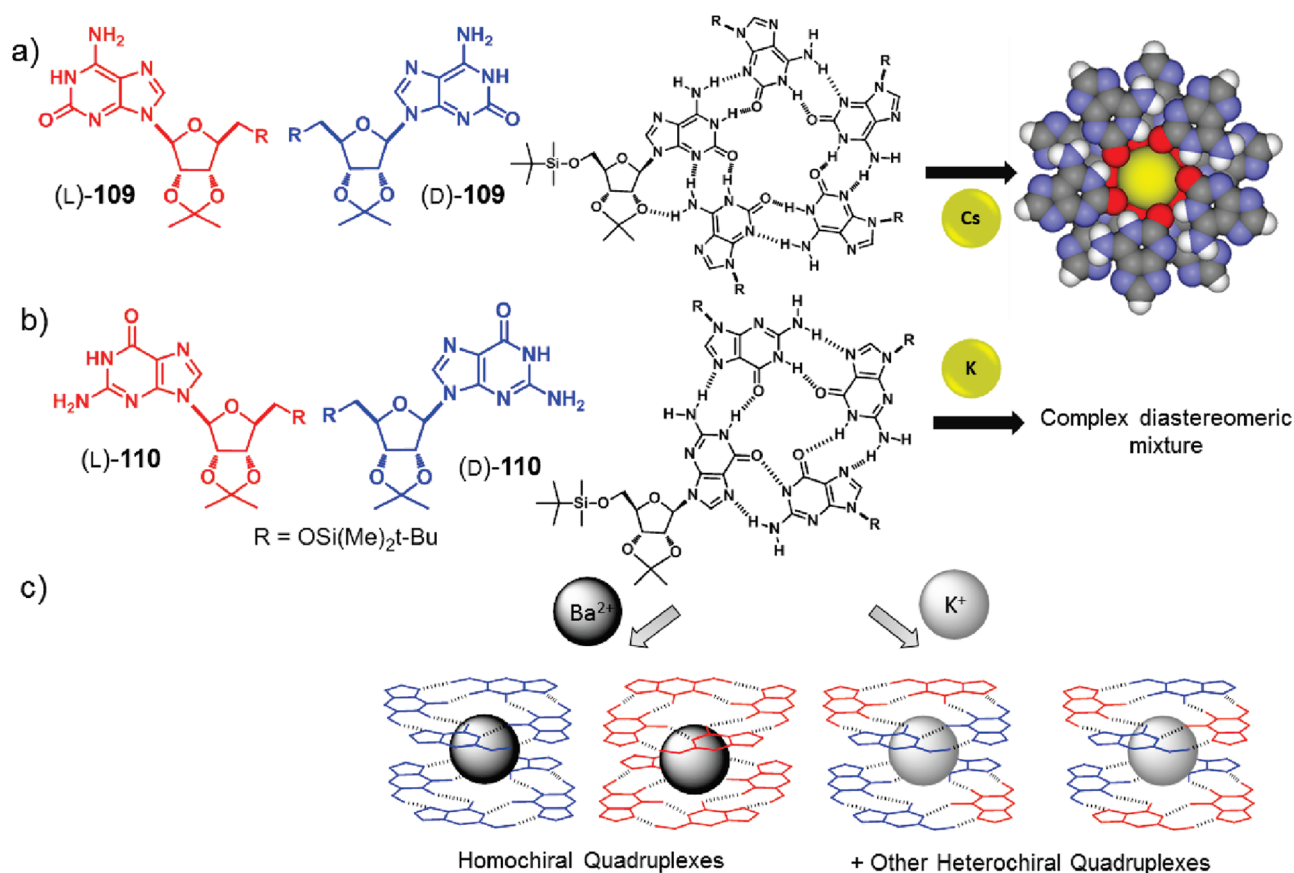


Figure 30. Chemical structures of iso-guanosine derivatives **109** and hydrogen-bonded quintuplet (a) and guanosine derivative **110** and corresponding hydrogen-bonded quadruplex (b) and chiral self-sorting processes in the presence of alkali ions (a,b). (c) Homochiral and heterochiral quadruplexes formed by **110** in the presence of Ba²⁺ and K⁺.

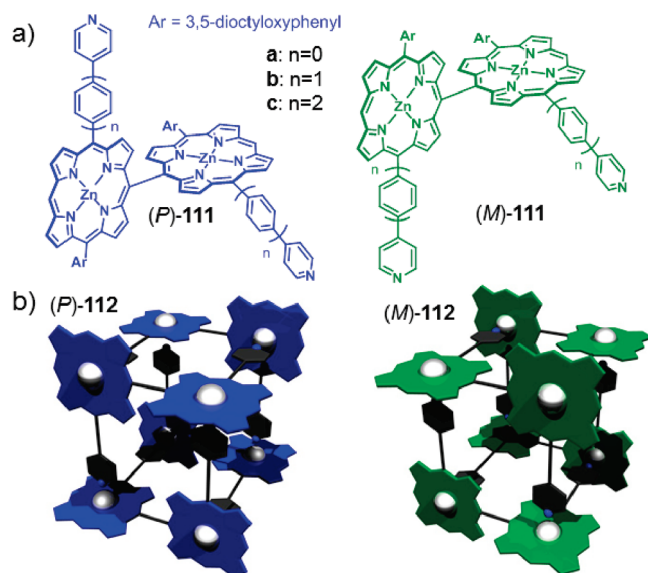


Figure 31. (a) Chemical structures of chiral porphyrins **111a–c**. (b) Homochiral boxes **112a–c** derived thereof.

the porphyrins are arranged in a centrosymmetric fashion, homochiral dimers require the screwing of the porphyrin planes to realize both metal–ligand contacts. As pointed out by the

authors the former assembly is electrostatically favored owing to the cancellation of the dipole moments (Figure 27b, c). Additionally, minor structural differences observed between the crystal structures of the hetero- and homochiral dimers, small variations in the intermolecular distances and relative position of the structures, distortion of the molecules in the case of the homochiral dimer to enable the Zn–N coordinative bond, may influence the self-sorting process.

In addition to geometry and complementarity of intermolecular forces, steric factors have been demonstrated to be rather useful molecular codes to achieve high-fidelity chiral self-sorting.^{224–227} Verlhac and co-workers reported a family of atropisomeric bidentate ligands with a dissymmetric benzimidazole-pyridine binding site (**104–106**).²²⁸ Naphthyl (**104**), tolyl (**105**) and cumyl (**106**) substituents were introduced to study the steric impact on the fidelity of chiral self-sorting after copper complexation. When two equivalents of **106** were treated with one equivalent of [Cu(MeCN)₄]⁺ in CD₂Cl₂, a single symmetric C₂ metal species could be observed through ¹H NMR in 95% yield, which corresponds to the homochiral assembly pair *MMΔ*/*PPΔ* (Figure 28). Minor traces (5%) of more sterically hindered *MPΔ*/*PMΔ* were also found, whereas no sign of the most sterically hindered isomers *MMΔ*/*PPΔ* was observed. ¹H NMR experiments revealed that the decrease in the bulkiness of the substituents in **104** (naphthyl) and **105** (tolyl) leads to larger amounts of *MPΔ*/*PMΔ* and even traces of *MMΔ*/*PPΔ* species, although in all cases the major species remained the homochiral

MMΔ/PPΔ assemblies. Figure 28 illustrates the key structural features responsible for the metal ion-directed self-recognition process. It is evident that in the homochiral complexes *MMΔ/PPΔ* the bulky substituents are pointing in opposite directions. The bulkiness of the substituents will determine to what extent the more sterically demanding heterochiral complexes *MPΔ/PMΔ* are formed, while the most hindered homochiral *MMΔ/PPΔ* species in which both substituents are pointing in the same direction are impeded. It can be realized from this study how the adequate selection of substituents with different steric requirements can lead to highly efficient chiral self-sorting.

Bozec, Maury, Lacour, and co-workers took advantage of the electrostatic nature of ionic metal–ligand complexes to induce chiral self-sorting in diastereomeric cation–anion propeller pairs.^{229–233} When enantiopure counterions are combined with chiral ions, two different diastereomeric ion pairs which possess different chemical and physical properties and, consequently, interaction energies can be formed. As a consequence, high levels of asymmetric recognition between chiral cations and anions can be achieved.^{229–233} The authors rationalize the high fidelity recognition to an optimization of the electrostatic interactions between cation and anion propellers, as demonstrated for the TRISPHAT anion **107** and the [Fe(4,4'-Me₂bpy)₃]²⁺ (bpy = 2,2'-bipyridine) cation **108**.²²⁹ As sketched in Figure 29, the anion/cation distance can be reduced much more in the homochiral association than in the heterochiral to stabilize the ionic pair.

The use of cation templates has been successfully exploited by Davis and co-workers to program chiral self-sorting.^{234,235} First, they probed the self-assembly of chiral iso-guanosine units (*D,L*)-**109** and guanosine (*D,L*)-**110** in the presence of K⁺ and Cs⁺, respectively (Figure 30a,b).²³⁴ ¹H NMR in CD₃CN and single crystal X-ray diffraction experiments, both in the presence of templating cations, evidenced the formation of a defined decameric complex (assembled by Cs⁺-templated stacking of two pentameric hydrogen-bonded cycles for **109**), and an octameric complex (assembled by K⁺-templated stacking of two tetrameric hydrogen-bonded cycles for **110**) for the enantiopure starting materials (Figure 30a,b). While in assemblies of **109** sugar-base hydrogen bonds can be formed, this is not possible for **110**. This makes **109** an excellent candidate for chiral self-recognition. Indeed, a racemic mixture of guanosine **110** in the presence of K⁺ showed more than ten separate signals in the ¹H NMR spectra, unlike the simple set of signals observed for the pure enantiomers, pointing to the formation of a diastereomeric mixture of the racemate.

In contrast, the racemic mixture of iso-guanosine **109** in the presence of Cs⁺ showed only one major set of signals. These signals were different to those corresponding to the enantiomeric decamers, indicating the predominance of a new species. After X-ray analysis of the supramolecular structure of (*D,L*)-**109** in the crystalline state it was confirmed that (*D,L*)-**109** undergoes chiral self-sorting in the presence of Cs⁺ giving rise to a meso-decamer by stacking of a (*D*)-**109** pentamer and (*L*)-**109** pentamer. Similar experiments for iso-guanosine (*D,L*)-**109** with differently sized alkali cations (Li⁺, Na⁺, K⁺, or Rb⁺) did not provide convincing evidence for such a self-sorting. Thus, the size of the templating cation plays a major role. In further work, the authors showed that not only can the size of the cation direct self-sorting, but the charge is also important.²³⁵ ¹H NMR in CD₂Cl₂ and X-ray studies revealed that guanosine **110** self-assembles into homochiral quadruplex stacks in the presence of Ba²⁺, whereas a mixture of heterochiral quadruplex

stacks was obtained in the presence of K⁺ (Figure 30c). Since the size of Ba²⁺ and K⁺ is very similar, the cation's charge has been recognized as the driving force directing self-sorting. The unfavorable entropy associated to the self-recognition of eight enantiomers can be overcome by enthalpic stabilization derived from cation-dipole interactions, G-quartet hydrogen bonds and G-quadruplex-picrate (counteranion) interactions through the divalent cation.

A final, particularly elegant example of a self-sorting process was reported by Osuka, Kim and co-workers,^{236–239} based on meso–meso linked-pyridine-appended zinc(II) porphyrins **111a–c** possessing axial chirality leading to noninterconvertible *P* and *M* enantiomers.²³⁶ In noncoordinating solvents such as CH₂Cl₂, dimeric porphyrins **111a–c** self-assemble into three-dimensional porphyrin boxes **112a–c** (Figure 31), as evidenced by ¹H NMR studies and X-ray diffraction of their crystalline structures. These porphyrin boxes form from racemic solutions with extraordinarily large binding constants through simultaneous eight-point metallosupramolecular coordination. Boxes formed from **111a–c** could be demonstrated to be chiral by CD spectroscopy after resolution of their enantiomers using chiral HPLC. As expected after chiral resolution, mirror image CD spectra were obtained. The formation of these chiral boxes was attributed to a rather specific self-recognition process of the dimeric porphyrins, which can only form such boxes from identical, that is, single enantiomer, building blocks. Otherwise, upon co-assembly of both enantiomers polymeric structures would form. This last example is most illustrative for a predefined self-assembly pathway that has been properly encoded in the molecular building blocks to direct a sequence of self-recognition processes. The interplay between enthalpic and entropic contributions obviously directs a high fidelity self-sorting process under the given experimental conditions.

5. CONCLUSIONS

In this review, we have collected the first decade of research on artificial molecules that were shown to exhibit high levels of selectivity in the molecular recognition or discrimination of surrounding species within complex mixtures. We have discussed the *molecular codes* (size and shape, complementarity in hydrogen-bonded systems, sterics, coordination sphere of metal ions and charge-transfer) that lead synthetic molecules in a crowded environment to bind only or at least preferentially to their ideal partners. We have shown that the geometrical parameters *size* and *shape* play the most prominent role among these molecular codes. As a general rule, size and shape complementarity between the elements of a mixture is a prerequisite before other molecular codes can come into play and eventually direct self-sorting processes. The species that can potentially bind any specific member of a mixture must first approach the target and ultimately establish a noncovalent contact. This can only happen when both elements are geometrically complementary. Accordingly, *complementarity in hydrogen-bonded systems* requires an appropriate geometrical correspondence between the interacting arrays for the match or mismatch between the pattern of hydrogen donors and acceptors to take place. This molecular code is most strikingly demonstrated in double-stranded DNA and has been successfully exploited to direct social or narcissistic self-sorting in mixtures of hydrogen-bonded assemblies.

In metallosupramolecular systems, the geometry and rigidity of the ligands as well as the *coordination sphere in metal–ligand*

interactions determine to a great extent the outcome of a self-sorting mixture. Different ligands can coordinate into varying geometries, which has already been exploited to construct fascinating supramolecular architectures of remarkable size and shape. Several research groups have also elucidated *steric* and *charge-transfer effects* to direct high-fidelity self-assembly processes within complex mixtures. However, their weight is quantitatively smaller in comparison with the above-mentioned codes and can only provide sufficient bias when the interacting building blocks are structurally most similar in terms of size and shape, hydrogen-bonding pattern or coordination ability.

Because of the importance of chiral recognition in nature, we have dedicated an independent section to chiral self-sorting systems. The high similarity of the molecules involved in chiral self-sorting—pairs of enantiomers have equal size and shape, differing only in their mirror image spatial orientation—makes their investigation particularly demanding. The examples collected in this review include those showing self-discrimination and those showing self-recognition, however, mostly with rather modest bias.

It is not only intrinsic molecular codes which are important in the fidelity of self-sorting events. Self-sorting processes depend to a great extent on the external variables (solvent, temperature, concentration, pH, etc) that can influence differently the equilibrium and/or the stability of independent recognition processes involving different noncovalent interactions. For instance, in a very recent article Schenning, Meijer, and co-workers have reported a very intriguing example for a dilution-induced self-assembly of porphyrin aggregates as a consequence of coupled equilibria.²⁴⁰ This given example demonstrates that we are to date still far from deriving a general rule that can predict how a complex mixture involving different noncovalent forces would behave upon variation of a given external variable.

However, the achievements to date in the field of supramolecular chemistry allow us to be optimistic in the years to come. We currently know how to make use of the principles of self-assembly to create supramolecular architectures of remarkable complexity with well-defined size and shape by proper design of their small constitutive building blocks. Highly organized structures such as vesicular assemblies, which are in essence small membrane-enclosed containers that can transport substances, are nowadays already routinely constructed by different research groups upon self-assembly of artificial amphiphilic molecules and used for catalytic or transporting purposes.²⁴¹ The construction of superstructures that can resemble nature's creations require, therefore, advances in this direction, and self-sorting is undoubtedly one of the indispensable means. Recently, synthetic amphiphilic molecules have been successfully programmed to self-sort, so that distinct types of molecules self-assemble into different domains or compartments in aqueous media.^{242,243} Compartmentalization is one of the prerequisites for the emergence of life. The cell membrane, for instance, protects the inner components from an adverse environment²⁴⁴ and multicompartmentalization is essential for the achievement of simultaneous functions in isolated environments within cellular organisms. The marriage between self-assembly and self-sorting will certainly open up groundbreaking possibilities for the creation of sophisticated synchronous multifunctional systems. We could envision, in a not too distant future, the construction of artificial systems that can resemble the intricacy of a cell. Whether or not this approach is a chimera, still remains to be seen. But one issue is clear: self-sorting is one of the means toward this goal.

AUTHOR INFORMATION

Corresponding Author

*Fax: +49/931/31-84756. Tel: 49/931/31-85340. E-mail: wuerthner@chemie.uni-wuerzburg.de.

ACKNOWLEDGMENT

We sincerely acknowledge Ana Reviejo and Dr. Ralf Schmidt for their support in graphic design. G. F. thanks the Alexander von Humboldt Foundation for a Postdoctoral Fellowship.

BIOGRAPHIES



Marina M. Safont-Sempere studied chemistry at the University of Zaragoza (2001–2006), where she received her diploma degree in 2006 awarded with the “Casañal Poza” prize. In February 2006, she joined the group of Professor Frank Würthner at the University of Würzburg, where she completed her diploma thesis enjoying an Erasmus fellowship. She finished her PhD thesis under the supervision of Professor Frank Würthner in February 2011. Since March 2011 she is a researcher chemist at Sion Power in Tucson, AZ. Her main research interests concern the synthesis, optical properties, and self-sorting of chiral functional dyes in solution and condensed state.



Gustavo Fernández received his Ph.D. from the Universidad Complutense de Madrid (Spain) in 2009 under the supervision of Professors Nazario Martín and Luis Sánchez for work on donor–acceptor covalent and supramolecular systems based on [60]fullerene. His Thesis has been recognized with the European

Young Chemist Award 2008 and more recently with the Honorable Mention Award associated with the IUPAC Prize for Young Chemists 2010. Between February 2009 and December 2010, he enjoyed an Alexander von Humboldt postdoctoral research fellowship in the group of Professor Frank Würthner working on supramolecular aggregates based on (bis)merocyanine dyes. He has recently built up his independent junior research group at the University of Würzburg in the framework of the Sofja Kovalevskaja programme granted from the Humboldt foundation and funded by the German Federal Ministry of Education and Research. His main research interests concern the study and characterization of supramolecular architectures based on dye aggregates, self-assembly in aqueous media and the investigation of supramolecular multicomponent systems based on π -conjugated scaffolds.



Frank Würthner is professor at the University of Würzburg, where he has served as head of the Institute of Organic Chemistry, dean of the Chemistry and Pharmacy Department, and coordinator of the Wilhelm Conrad Röntgen Research Center for Complex Material Systems. He received his education in Chemistry at the University of Stuttgart (Germany) and received the doctoral degree in 1993 for work on donor–acceptor substituted oligothiophenes. Afterwards he was a Feodor Lynen fellow of the Alexander von Humboldt foundation at the Massachusetts Institute of Technology and a research chemist at BASF Central Research in Ludwigshafen (Germany). From 1997 to 2002, he headed a junior research group at the University of Ulm where he received the *Venia Legendi* for Organic Chemistry in 2001. In 2002, he was honored with the Arnold-Sommerfeld award of the Bavarian Academy of Sciences and became full professor at the University of Würzburg. His main research interests are the synthesis and characterization of complex supramolecular architectures based on functional dyes, the investigation of light-induced processes in dye-based nanosystems, and the application of dye aggregates in organic electronics, photonics, and photovoltaics.

REFERENCES

- (1) Campbell, N. A.; Reece, J. B.; Taylor, M. R.; Simon, E. J.; Dickey, J. L. *Biology: Concepts and Connections*, 6th ed.; CA: Benjamin/Cummings Publishing Company, San Francisco, CA, 2008.
- (2) Oshovsky, G. V.; Reinhoudt, D. N.; Verboom, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 2366.
- (3) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737.
- (4) Lehninger, A. L.; Nelson, D. L.; Cox, M. M. *Lehninger Principles of Biochemistry*, 5th ed.; W. H. Freeman and Company: New York, 2008.
- (5) Amos, L. A.; Baker, T. S. *Nature* **1979**, *279*, 607.
- (6) Desai, A.; Mitchison, T. J. *Annu. Rev. Cell Dev. Biol.* **1997**, *13*, 83.
- (7) Weisenberg, R. C. *Science* **1972**, *177*, 1104.
- (8) Alberts, B.; Johnson, A.; Lewis, J.; Raff, M.; Roberts, K.; Walter, P. *Molecular Biology of the Cell*, 4th ed.; Garland Science: New York, 2002.
- (9) Lodish, H.; Berk, A.; Matsudaira, P.; Kaiser, C. A.; Krieger, M.; Scott, M. P.; Zipurksy, S. L.; Darnell, J. *Molecular Cell. Biology*, 5th ed.; WH Freeman: New York, 2004.
- (10) Jaeger, K.-E.; Eggert, T. *Curr. Opin. Biotechnol.* **2004**, *15*, 305.
- (11) Hough, D. W.; Danson, M. J. *Curr. Opin. Chem. Biol.* **1999**, *3*, 39.
- (12) Ghosh, S.; Wu, A. X.; Fettingner, J. C.; Zavalij, P. Y.; Isaacs, L. *J. Org. Chem.* **2008**, *73*, 5915.
- (13) Corbett, P. T.; Sanders, J. K. M.; Otto, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 8858.
- (14) Ludlow, R. F.; Otto, S. *Chem. Soc. Rev.* **2008**, *37*, 101.
- (15) Peyralans, J. J. P.; Otto, S. *Curr. Opin. Chem. Biol.* **2009**, *13*, 705.
- (16) Nitschke, J. R. *Nature* **2009**, *462*, 736.
- (17) Wagner, N.; Ashkenasy, G. *J. Chem. Phys.* **2009**, *16907*, 1.
- (18) Elemans, J.; Lei, S. B.; De Feyter, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 7298.
- (19) Kramer, R.; Lehn, J.-M.; Marquisrigault, A. *Proc. Nat. Acad. Sci. U.S.A.* **1993**, *90*, 5394.
- (20) Wu, A. X.; Isaacs, L. *J. Am. Chem. Soc.* **2003**, *125*, 4831.
- (21) Mukhopadhyay, P.; Wu, A. X.; Isaacs, L. *J. Org. Chem.* **2004**, *69*, 6157.
- (22) Shivanyuk, A.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 12074.
- (23) Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **1999**, *121*, 11538.
- (24) Jiang, W.; Winkler, H. D. F.; Schalley, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 13852.
- (25) Jolliffe, K. A.; Timmerman, P.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 933.
- (26) Corbin, P. S.; Lawless, L. J.; Li, Z. T.; Ma, Y. G.; Witmer, M. J.; Zimmerman, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5099.
- (27) Ma, Y. G.; Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 13757.
- (28) Caulder, D. L.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1997**, *36*, 1440.
- (29) Enemark, E. J.; Stack, T. D. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 932.
- (30) Stiller, R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1998**, 977.
- (31) Albrecht, M.; Schneider, M.; Röttle, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 557.
- (32) Schultz, D.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2453.
- (33) Legrand, Y. M.; van der Lee, A.; Barboiu, M. *Inorg. Chem.* **2007**, *46*, 9540.
- (34) Barboiu, M.; Dumitru, F.; Legrand, Y. M.; Petit, E.; van der Lee, A. *Chem. Commun.* **2009**, 2192.
- (35) Nitschke, J. R. *Acc. Chem. Res.* **2006**, *40*, 103.
- (36) Shaller, A. D.; Wang, W.; Gan, H. Y.; Li, A. D. Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 7705.
- (37) Bilgiçer, B.; Xing, X.; Kumar, K. *J. Am. Chem. Soc.* **2001**, *123*, 11815.
- (38) Schnarr, N. A.; Kennan, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 667.
- (39) Rehm, T.; Schmuck, C. *Chem. Commun.* **2008**, 801.
- (40) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651.
- (41) Hunter, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5310.
- (42) Zheng, Y. R.; Yang, H. B.; Ghosh, K.; Zhao, L.; Stang, P. J. *Chem.—Eur. J.* **2009**, *15*, 7203.
- (43) Northrop, B. H.; Zheng, Y. R.; Chi, K. W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554.
- (44) Addicott, C.; Das, N.; Stang, P. J. *Inorg. Chem.* **2004**, *43*, 5335.

- (45) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.
- (46) Whitesides, G. M.; Mathias, L. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
- (47) Misteli, T. *J. Cell Biol.* **2001**, *155*, 181.
- (48) Eliseev, A. V.; Nelen, M. I. *J. Am. Chem. Soc.* **1997**, *119*, 1147.
- (49) Fischer, E. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 2985.
- (50) Pérez, E. M.; Martín, N. *Chem. Soc. Rev.* **2008**, *37*, 1512.
- (51) Grimme, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3430.
- (52) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: San Diego, CA, 1991.
- (53) Atkins, P. W.; Overton, T. L.; Rourke, J. P.; Weller, M. T.; Armstrong, F. A. *Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 2010.
- (54) Chi, K. W.; Addicott, C.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16569.
- (55) Yang, H. B.; Ghosh, K.; Northrop, B. H.; Stang, P. J. *Org. Lett.* **2007**, *9*, 1561.
- (56) Zheng, Y. R.; Yang, H. B.; Northrop, B. H.; Ghosh, K.; Stang, P. J. *Inorg. Chem.* **2008**, *47*, 4706.
- (57) Zheng, Y. R.; Northrop, B. H.; Yang, H. B.; Zhao, L.; Stang, P. J. *J. Org. Chem.* **2009**, *74*, 3554.
- (58) Northrop, B. H.; Yang, H. B.; Stang, P. J. *Inorg. Chem.* **2008**, *47*, 11257.
- (59) Pinalli, R.; Cristini, V.; Sottili, V.; Geremia, S.; Campagnolo, M.; Caneschi, A.; Dalcanele, E. *J. Am. Chem. Soc.* **2004**, *126*, 6516.
- (60) Yamanaka, M.; Yamada, Y.; Sei, Y.; Yamaguchi, K.; Kobayashi, K. *J. Am. Chem. Soc.* **2006**, *128*, 1531.
- (61) Chen, Z. J.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, *38*, 564.
- (62) Würthner, F. *Chem. Commun.* **2004**, 1564.
- (63) Osswald, P.; Würthner, F. *J. Am. Chem. Soc.* **2007**, *129*, 14319.
- (64) Wang, W.; Bain, A. D.; Wang, L. Q.; Exarhos, G. J.; Li, A. D. Q. *J. Phys. Chem. A* **2008**, *112*, 3094.
- (65) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808.
- (66) Lagana, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844.
- (67) Kim, K.; Selvapalam, N.; Ko, Y. H.; Park, K. M.; Kim, D.; Kim, J. *Chem. Soc. Rev.* **2007**, *36*, 267.
- (68) Huang, W. H.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2008**, *130*, 8446.
- (69) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, *38*, 875.
- (70) Harada, A.; Hashidzume, A.; Yamaguchi, H.; Takashima, Y. *Chem. Rev.* **2009**, *109*, 5974.
- (71) Chen, Y.; Liu, Y. *Chem. Soc. Rev.* **2010**, *39*, 495.
- (72) Miyauchi, M.; Harada, A. *J. Am. Chem. Soc.* **2004**, *126*, 11418.
- (73) Miyauchi, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2005**, *127*, 2984.
- (74) Kuad, P.; Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 12630.
- (75) Yamauchi, K.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2008**, *130*, 5024.
- (76) Tomimatsu, N.; Kanaya, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2009**, *131*, 12339.
- (77) Liu, S. M.; Ruspic, C.; Mukhopadhyay, P.; Chakrabarti, S.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2005**, *127*, 15959.
- (78) Freeman, W. A.; Mock, W. L.; Shih, N. Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367.
- (79) Mock, W. L. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, U.K., 1996.
- (80) Rekharsky, M. V.; Mori, T.; Yang, C.; Ko, Y. H.; Selvapalam, N.; Kim, H.; Sobransingh, D.; Kaifer, A. E.; Liu, S. M.; Isaacs, L.; Chen, W.; Moghaddam, S.; Gilson, M. K.; Kim, K. M.; Inoue, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 20737.
- (81) Mukhopadhyay, P.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2006**, *128*, 14093.
- (82) Rekharsky, M. V.; Yamamura, H.; Ko, Y. H.; Selvapalam, N.; Kim, K.; Inoue, Y. *Chem. Commun.* **2008**, 2236.
- (83) Masson, E.; Lu, X. Y.; Ling, X. X.; Patchell, D. L. *Org. Lett.* **2009**, *11*, 3798.
- (84) Celtek, G.; Artar, M.; Scherman, O. A.; Tuncel, D. *Chem.—Eur. J.* **2009**, *15*, 10360.
- (85) Wang, F.; Han, C. Y.; He, C. L.; Zhou, Q. Z.; Zhang, J. Q.; Wang, C.; Li, N.; Huang, F. H. *J. Am. Chem. Soc.* **2008**, *130*, 11254.
- (86) Ashton, P. R.; Philp, D.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Chem. Commun.* **1991**, 1680.
- (87) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1996**, *2*, 709.
- (88) Wang, F.; Zheng, B.; Zhu, K. L.; Zhou, Q. Z.; Zhai, C. X.; Li, S. J.; Li, N.; Huang, F. H. *Chem. Commun.* **2009**, 4375.
- (89) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
- (90) De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687.
- (91) Yakovchuk, P.; Protozanova, E.; Frank-Kamenetskii, M. D. *Nucleic Acids Res.* **2006**, *34*, 564.
- (92) Timmerman, P.; Vreekamp, R. H.; Hulst, R.; Verboom, W.; Reinhoudt, D. N.; Rissanen, K.; Udachin, K. A.; Ripmeester, J. *Chem.—Eur. J.* **1997**, *3*, 1823.
- (93) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254.
- (94) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.
- (95) Mock, W. L. *Supramolecular Polymers*, 2nd ed.; Taylor Francis: New York, 2005.
- (96) Fox, J. D.; Rowan, S. J. *Macromolecules* **2009**, *42*, 6823.
- (97) Burd, C.; Weck, M. *Macromolecules* **2005**, *38*, 7225.
- (98) Ligthart, G.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 810.
- (99) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
- (100) Hirschberg, J.; Beijer, F. H.; van Aert, H. A.; Magusim, P.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **1999**, *32*, 2696.
- (101) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874.
- (102) Söntjens, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487.
- (103) Zhao, X.; Wang, X. Z.; Jiang, X. K.; Chen, Y. Q.; Li, Z. T.; Chen, G. J. *J. Am. Chem. Soc.* **2003**, *125*, 15128.
- (104) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 13986.
- (105) Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193.
- (106) Hecht, S. *Mater. Today* **2005**, *8*, 48.
- (107) Ilhan, F.; Gray, M.; Rotello, V. M. *Macromolecules* **2001**, *34*, 2597.
- (108) South, C. R.; Burd, C.; Weck, M. *Acc. Chem. Res.* **2006**, *40*, 63.
- (109) Garrett, J. T.; Lin, J. S.; Runt, J. *Macromolecules* **2002**, *35*, 161.
- (110) Koevoets, R. A.; Versteegen, R. M.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 2999.
- (111) Colombani, O.; Barioz, C.; Bouteiller, L.; Chaneac, C.; Fomperie, L.; Lortie, F.; Montes, H. *Macromolecules* **2005**, *38*, 1752.
- (112) Versteegen, R. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **2005**, *38*, 3176.
- (113) Chebotareva, N.; Bomans, P. H. H.; Frederik, P. M.; Sommerdijk, N. A. J. M.; Sijbesma, R. P. *Chem. Commun.* **2005**, 4967.
- (114) Wisse, E.; Govaert, L. E.; Meijer, H. E. H.; Meijer, E. W. *Macromolecules* **2006**, *39*, 7425.
- (115) Botterhuis, N. E.; Karthikeyan, S.; Veldman, D.; Meskers, S. C. J.; Sijbesma, R. P. *Chem. Commun.* **2008**, 3915.
- (116) Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867.
- (117) Ikeda, M.; Tanaka, Y.; Hasegawa, T.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 6806.
- (118) Yashima, E.; Maeda, K.; Furusho, Y. *Acc. Chem. Res.* **2008**, *41*, 1166.

- (119) Iida, H.; Shimoyama, M.; Furusho, Y.; Yashima, E. *J. Org. Chem.* **2010**, *75*, 417.
- (120) Maeda, T.; Furusho, Y.; Sakurai, S.-I.; Kumaki, J.; Okoshi, K.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 7938.
- (121) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647.
- (122) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469.
- (123) Avram, L.; Cohen, Y. *J. Am. Chem. Soc.* **2002**, *124*, 15148.
- (124) Shivanyuk, A.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 3432.
- (125) Shivanyuk, A.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 7662.
- (126) Shivanyuk, A.; Rebek, J., Jr. *Chem. Commun.* **2001**, 2424.
- (127) Ajami, D.; Schramm, M. P.; Volonterio, A.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2007**, *46*, 242.
- (128) Wyler, R.; de Mendoza, J.; Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1699.
- (129) Ajami, D.; Hou, J. L.; Dale, T. J.; Barrett, E.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10430.
- (130) Kubota, Y.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4854.
- (131) Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092.
- (132) Yoshizawa, M.; Nagao, M.; Kumazawa, K.; Fujita, M. *J. Organomet. Chem.* **2005**, *690*, 5383.
- (133) Zhao, L.; Northrop, B. H.; Zheng, Y. R.; Yang, H. B.; Lee, H. J.; Lee, Y. M.; Park, J. Y.; Chi, K. W.; Stang, P. J. *J. Org. Chem.* **2008**, *73*, 6580.
- (134) Braekers, D.; Peters, C.; Bogdan, A.; Rudzevich, Y.; Böhmer, V.; Desreux, J. F. *J. Org. Chem.* **2008**, *73*, 701.
- (135) Rudzevich, Y.; Rudzevich, V.; Klautzsch, F.; Schalley, C. A.; Böhmer, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 3867.
- (136) Rudzevich, Y.; Rudzevich, V.; Böhmer, V. *Chem.—Eur. J.* **2010**, *16*, 4541.
- (137) Mogck, O.; Paulus, E. F.; Böhmer, V.; Thondorf, I.; Vogt, W. *Chem. Commun.* **1996**, 2533.
- (138) Schalley, C. A.; Castellano, R. K.; Brody, M. S.; Rudzevich, D. M.; Siuzdak, G.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4568.
- (139) Pop, A.; Vysotsky, M. O.; Saadioui, M.; Böhmer, V. *Chem. Commun.* **2003**, 1124.
- (140) Molokanova, O.; Bogdan, A.; Vysotsky, M. O.; Bolte, M.; Ikai, T.; Okamoto, Y.; Böhmer, V. *Chem.—Eur. J.* **2007**, *13*, 6157.
- (141) Wang, L. Y.; Vysotsky, M. O.; Bogdan, A.; Bolte, M.; Böhmer, V. *Science* **2004**, *304*, 1312.
- (142) Zhang, C. J.; Li, S. J.; Zhang, J. Q.; Zhu, K. L.; Li, N.; Huang, F. H. *Org. Lett.* **2007**, *9*, 5553.
- (143) Ashton, P. R.; Claessens, C. G.; Hayes, W.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1862.
- (144) Ashton, P. R.; Ballardini, R.; Balzani, V.; Gómez-López, M.; Lawrence, S. E.; Martínez-Díaz, M. V.; Montalti, M.; Piersanti, A.; Prodi, L.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 10641.
- (145) Jiang, W.; Schalley, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10425.
- (146) Jiang, W.; Schafer, A.; Mohr, P. C.; Schalley, C. A. *J. Am. Chem. Soc.* **2010**, *132*, 2309.
- (147) Ghosh, S.; Li, X. Q.; Stepanenko, V.; Würthner, F. *Chem.—Eur. J.* **2008**, *14*, 11343.
- (148) Li, X.-Q.; Stepanenko, V.; Chen, Z.; Prins, P.; Siebbeles, L. D. A.; Würthner, F. *Chem. Commun.* **2006**, 3871.
- (149) Würthner, F.; Bauer, C.; Stepanenko, V.; Yagai, S. *Adv. Mater.* **2008**, *20*, 1695.
- (150) Moffat, J. R.; Smith, D. K. *Chem. Commun.* **2009**, 316.
- (151) Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192.
- (152) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.
- (153) Lehn, J.-M.; Eliseev, A. V. *Science* **2001**, *291*, 2331.
- (154) Langner, A.; Tait, S. L.; Lin, N.; Rajadurai, C.; Ruben, M.; Kern, K. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 17927.
- (155) Ulrich, S.; Lehn, J.-M. *Chem.—Eur. J.* **2009**, *15*, 5640.
- (156) Ulrich, S.; Lehn, J.-M. *J. Am. Chem. Soc.* **2009**, *131*, 5546.
- (157) Saur, I.; Scopelliti, R.; Severin, K. *Chem.—Eur. J.* **2006**, *12*, 1058.
- (158) Schmittle, M.; Kalsani, V.; Fenske, D.; Wiegrefe, A. *Chem. Commun.* **2004**, 490.
- (159) Mahata, K.; Schmittle, M. *J. Am. Chem. Soc.* **2009**, *131*, 16544.
- (160) De, S.; Mahata, K.; Schmittle, M. *Chem. Soc. Rev.* **2010**, *39*, 1555.
- (161) Mahata, K.; Schmittle, M. *Chem. Commun.* **2010**, 4163.
- (162) Mahata, K.; Saha, M. L.; Schmittle, M. *J. Am. Chem. Soc.* **2010**, *132*, 15933.
- (163) Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Soc. Rev.* **2010**, *39*, 2577.
- (164) Grimsdale, A. C.; Müllen, K. *Macromol. Rapid Commun.* **2007**, *28*, 1676.
- (165) Katz, H. E.; Bao, Z. N.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.
- (166) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037.
- (167) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.
- (168) Ponce Ortiz, R.; Facchetti, A.; Marks, T. J. *Chem. Rev.* **2010**, *110*, 205.
- (169) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489.
- (170) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
- (171) Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719.
- (172) Bredas, J. L.; Durrant, J. R. *Acc. Chem. Res.* **2009**, *42*, 1689.
- (173) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.
- (174) Otero, R.; Écija, D.; Fernández, G.; Gallego, J. M.; Sánchez, L.; Martín, N.; Miranda, R. *Nano Lett.* **2007**, *7*, 2602.
- (175) Würthner, F.; Meerholz, K. *Chem.—Eur. J.* **2010**, *16*, 9366.
- (176) Landauer, J.; McConnell, H. J. *J. Am. Chem. Soc.* **1952**, *74*, 1221.
- (177) Lawrey, D. M. G.; McConnell, H. J. *J. Am. Chem. Soc.* **1952**, *74*, 6175.
- (178) Briegleb, G. B. *Elektronen-Donator-Acceptor-Komplexe*; Springer: Berlin, 1961.
- (179) Smulders, M. M. J.; Schenning, A.; Meijer, E. W. *J. Am. Chem. Soc.* **2008**, *130*, 606.
- (180) de Greef, T. F. A.; Nieuwenhuizen, M. M. L.; Stals, P. J. M.; Fitie, C. F. C.; Palmans, A. R. A.; Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2008**, 4306.
- (181) Brunsveld, L.; Schenning, A.; Broeren, M. A. C.; Janssen, H. M.; Vekemans, J.; Meijer, E. W. *Chem. Lett.* **2000**, 292.
- (182) Tahara, K.; Fujita, T.; Sonoda, M.; Shiro, M.; Tobe, Y. *J. Am. Chem. Soc.* **2008**, *130*, 14339.
- (183) Ajayaghosh, A.; Vijayakumar, C.; Praveen, V. K.; Babu, S. S.; Varghese, R. J. *J. Am. Chem. Soc.* **2006**, *128*, 7174.
- (184) de la Escosura, A.; Martínez-Díaz, M. V.; Thordarson, P.; Rowan, A. E.; Nolte, R. J. M.; Torres, T. *J. Am. Chem. Soc.* **2003**, *125*, 12300.
- (185) Yoshizawa, M.; Nakagawa, J.; Kurnazawa, K.; Nagao, M.; Kawano, M.; Ozeki, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1810.
- (186) Klosterman, J. K.; Yamauchi, Y.; Fujita, M. *Chem. Soc. Rev.* **2009**, *38*, 1714.
- (187) Yamauchi, Y.; Yoshizawa, M.; Akita, M.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 960.
- (188) Murase, T.; Horiuchi, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 7864.
- (189) Sugiyasu, K.; Kawano, S. I.; Fujita, N.; Shinkai, S. *Chem. Mater.* **2008**, *20*, 2863.
- (190) Molla, M. R.; Das, A.; Ghosh, S. *Chem.—Eur. J.* **2010**, *16*, 10084.
- (191) Wicklein, A.; Ghosh, S.; Sommer, M.; Würthner, F.; Thelakkat, M. *ACS Nano* **2009**, *3*, 1107.
- (192) van Herrikhuyzen, J.; Syamakumari, A.; Schenning, A.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10021.
- (193) Würthner, F.; Chen, Z.; Hoeben, F. J. M.; Osswald, P.; You, C.-C.; Jonkhøj, P.; Herrikhuyzen, J. v.; Schenning, A. P. H. J.; van der

- Schoot, P. P. A. M.; Meijer, E. W.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611.
- (194) Jonkheijm, P.; Stutzmann, N.; Chen, Z. J.; de Leeuw, D. M.; Meijer, E. W.; Schenning, A.; Würthner, F. *J. Am. Chem. Soc.* **2006**, *128*, 9535.
- (195) Beckers, E. H. A.; Chen, Z.; Meskers, S. C. J.; Jonkheijm, P.; Schenning, A. P. H. J.; Li, X.-Q.; Osswald, P.; Würthner, F.; Janssen, R. A. J. *J. Phys. Chem. B* **2006**, *110*, 16967.
- (196) Chen, Z. J.; Baumeister, U.; Tschierske, C.; Würthner, F. *Chem.—Eur. J.* **2007**, *13*, 450.
- (197) Sadrai, M.; Bird, G. R.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr., Sect. C* **1990**, *46*, 637.
- (198) Kühnle, A.; Linderroth, T. R.; Hammer, B.; Besenbacher, F. *Nature* **2002**, *415*, 891.
- (199) Huang, W. H.; Zavalij, P. Y.; Isaacs, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7425.
- (200) Zehnacker, A.; Suhm, M. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6970.
- (201) Mohr, J. T.; Krout, M. R.; Stoltz, B. M. *Nature* **2008**, *455*, 323.
- (202) Lacour, J.; Linder, D. *Science* **2007**, *317*, 462.
- (203) List, B.; Yang, J. W. *Science* **2006**, *313*, 1584.
- (204) Reetz, M. T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5716.
- (205) Thomas, C. M.; Ward, T. R. *Chem. Soc. Rev.* **2005**, *34*, 337.
- (206) Pasteur, L. C. R. *Hebd. Seances Acad. Sci.* **1848**, *26*, 538.
- (207) Kondepudi, D. K.; Kaufman, R. J.; Singh, N. *Science* **1990**, *250*, 975.
- (208) Crusats, J.; Veintemillas-Verdaguer, S.; Ribó, J. M. *Chem.—Eur. J.* **2006**, *12*, 7776.
- (209) Fletcher, S. P.; Jagt, R. B. C.; Feringa, B. L. *Chem. Commun.* **2007**, 2578.
- (210) Blackmond, D. G. *Chem.—Eur. J.* **2007**, *13*, 3290.
- (211) McBride, J. M.; Tully, J. C. *Nature* **2008**, *452*, 161.
- (212) Hutin, M.; Cramer, C. J.; Gagliardi, L.; Shahi, A. R. M.; Bernardinelli, G.; Cerny, R.; Nitschke, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 8774.
- (213) Dumitru, F.; Legrand, Y. M.; Van der Lee, A.; Barboiu, M. *Chem. Commun.* **2009**, 2667.
- (214) Safont-Sempere, M. M.; Osswald, P.; Radacki, K.; Würthner, F. *Chem.—Eur. J.* **2010**, *16*, 9366.
- (215) Safont-Sempere, M. M.; Osswald, P.; Stolte, M.; Grüne, M.; Renz, M.; Kaupp, M.; Radacki, K.; Braunschweig, H.; Würthner, F. *J. Am. Chem. Soc.* **2011**, *133*, 9580.
- (216) Gut, D.; Rudi, A.; Kopilov, J.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2002**, *124*, 5449.
- (217) Wang, W.; Shaller, A. D.; Li, A. D. Q. *J. Am. Chem. Soc.* **2008**, *130*, 8271.
- (218) Amemiya, R.; Yamaguchi, M. *Org. Biomol. Chem.* **2008**, *6*, 26.
- (219) Trzaska, S. T.; Hsu, H. F.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 4518.
- (220) Gsänger, M.; Oh, J. H.; Könemann, M.; Hoffken, H. W.; Krause, A. M.; Bao, Z. N.; Würthner, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 740.
- (221) Ishida, Y.; Aida, T. *J. Am. Chem. Soc.* **2002**, *124*, 14017.
- (222) Isaacs, L.; Witt, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4028.
- (223) Mizumura, M.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5378.
- (224) Takacs, J. M.; Hrvatin, P. M.; Atkins, J. M.; Reddy, D. S.; Clark, J. L. *New J. Chem.* **2005**, *29*, 263.
- (225) Kim, T. W.; Lah, M. S.; Hong, J. I. *Chem. Commun.* **2001**, 743.
- (226) Rang, A.; Nieger, M.; Engeser, M.; Lützen, A.; Schalley, C. A. *Chem. Commun.* **2008**, 4789.
- (227) Chas, M.; Gil-Ramírez, G.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Ballester, P. *Org. Lett.* **2010**, *12*, 1740.
- (228) Vincent, J. M.; Philouze, C.; Pianet, I.; Verlhac, J. B. *Chem.—Eur. J.* **2000**, *6*, 3595.
- (229) Lacour, J.; Jodry, J. J.; Ginglinger, C.; Torche-Haldimann, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 2379.
- (230) Maury, O.; Lacour, J.; Le Bozec, H. *Eur. J. Inorg. Chem.* **2001**, 201.
- (231) Jodry, J. J.; Frantz, R.; Lacour, J. *Inorg. Chem.* **2004**, *43*, 3329.
- (232) Bergman, S. D.; Frantz, R.; Gut, D.; Kol, M.; Lacour, J. *Chem. Commun.* **2006**, 850.
- (233) Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jodry, J. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3695.
- (234) Shi, X. D.; Fettingner, J. C.; Cai, M. M.; Davis, J. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3124.
- (235) Shi, X. D.; Fettingner, J. C.; Davis, J. T. *J. Am. Chem. Soc.* **2001**, *123*, 6738.
- (236) Hwang, I. W.; Kamada, T.; Ahn, T. K.; Ko, D. M.; Nakamura, T.; Tsuda, A.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2004**, *126*, 16187.
- (237) Kamada, T.; Aratani, N.; Ikeda, T.; Shibata, N.; Higuchi, Y.; Wakamiya, A.; Yamaguchi, S.; Kim, K. S.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2006**, *128*, 7670.
- (238) Maeda, C.; Kamada, T.; Aratani, N.; Sasamori, T.; Tokitoh, N.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 9681.
- (239) Maeda, C.; Kamada, T.; Aratani, N.; Osuka, A. *Coord. Chem. Rev.* **2007**, *251*, 2743.
- (240) Helmich, F.; Lee, C. C.; Nieuwenhuizen, M. M. L.; Gielen, J. C.; Christianen, P. C. M.; Larsen, A.; Fytas, G.; Leclere, P.; Schenning, A.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 3939.
- (241) Ryu, J. H.; Hong, D. J.; Lee, M. *Chem. Commun.* **2008**, 1043.
- (242) Pal, A.; Karthikeyan, S.; Sijbesma, R. P. *J. Am. Chem. Soc.* **2010**, *132*, 7842.
- (243) Percec, V.; Wilson, D. A.; Leowanawat, P.; Wilson, C. J.; Hughes, A. D.; Kaucher, M. S.; Hammer, D. A.; Levine, D. H.; Kim, A. J.; Bates, F. S.; Davis, K. P.; Lodge, T. P.; Klein, M. L.; DeVane, R. H.; Aqad, E.; Rosen, B. M.; Argintaru, A. O.; Sienkowska, M. J.; Rissanen, K.; Nummelin, S.; Ropponen, J. *Science* **2010**, *328*, 1009.
- (244) van Esch, J. H. *Nature* **2010**, *466*, 193.