

Self-Optimizing Charge-Transfer Energy Phenomena in Metallosupramolecular Complexes by Dynamic Constitutional Self-Sorting

Yves-Marie Legrand,[†] Arie van der Lee,[†] and Mihail Barboiu^{*†}

Adaptative Supramolecular Nanosystems Group, Institut Européen des Membranes - UMR-CNRS 5635, Place Eugène Bataillon, CC 047, F-34095 Montpellier, Cedex 5, France

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In this paper we report an extended series of 2,6-(iminoarene)pyridine-type Zn^{II} complexes $[(L_{ii})_2Zn]^{II}$, which were surveyed for their ability to self-exchange both their ligands and their aromatic arms and to form different homoduplex and heteroduplex complexes in solution. The self-sorting of heteroduplex complexes is likely to be the result of geometric constraints. Whereas the imine-exchange process occurs quantitatively in 1:1 mixtures of $[(L_{ii})_2Zn]^{II}$ complexes, the octahedral coordination process around the metal ion defines spatial-frustrated exchanges that involve the selective formation of heterocomplexes of two, by two different substituents; the bulkiest ones (pyrene in principle) specifically interact with the pseudoterpyridine core, sterically hindering the least bulky ones, which are intermolecularly stacked with similar ligands of neighboring molecules. Such a self-sorting process defined by the specific self-constitution of the ligands exchanging their aromatic substituents is self-optimized by a specific control over their spatial orientation around a metal center within the complex. They ultimately show an improved charge-transfer energy function by virtue of the dynamic amplification of self-optimized heteroduplex architectures. These systems therefore illustrate the convergence of the combinatorial self-sorting of the dynamic combinatorial libraries (DCLs) strategy and the constitutional self-optimized function.

Introduction

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

organization by design is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry. The selection of one or more components occurs as function of either internal (such as the nature and the geometry of the binding subunits of the ligand, the stoichiometry, etc.) or external factors (such as the nature of the medium and the presence of specific molecules or anions, etc.). In view of the lability of the coordination bond, numerous coordination processes may present a number of novel features such as cooperativity, diversity, selection, or adaptation. Thus, coordination equilibria might allow the generation of dynamic libraries (mixtures) of metal complexes presenting features such a

* To whom correspondence should be addressed. E-mail: mihai.barboiu@iemm.univ-montp2.fr.

[†] Institut Européen des Membranes.

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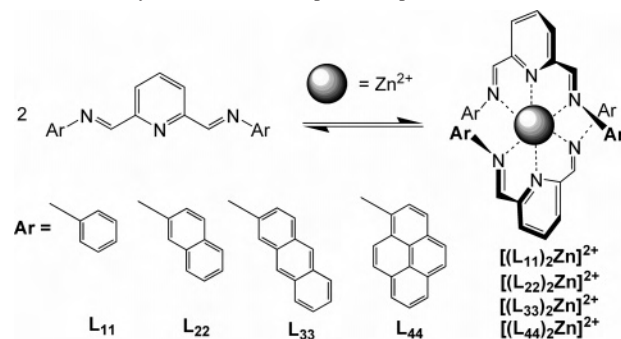
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self-selection, solid-state selection of a constituent of an equilibrating collection of complexes, and reversible switching between different coordination arrays.^{2–9} Starting with seminal publications by groups of Lehn² and Sanders,³ dynamic combinatorial chemistry has emerged as a powerful tool for the development of new receptors, drugs, catalysts, and materials. Recently, the dynamic features of supramolecular devices serve to bring into play the constitutional evolution of such species that the groups of Stang,⁴ Severin,⁵ and Lehn⁶ made during the last 3 years. These species represent a crucial advancement, and they provided useful insights in this field.

One of the key issues in designing complex dynamic combinatorial libraries (DCLs) is the choice of reversible processes that can interconvert the constitutional components. A number of such reactions have been tested including imine exchange, thiol–disulfide exchange, esterification, and ligand exchange in coordination complexes.^{2,3} Combination of two such reversible reactions in double-level dynamic combinatorial libraries using orthogonal^{7a} and communicative^{7b} exchange processes have been reported. More precisely, if the reversible processes occur independently, they might be addressed as *orthogonal*. When two levels of dynamic exchange cross over, they are considered as *communicative*. Coordination equilibria may allow the amplification from the dynamic mixtures of very specific metallosupramolecular architecture with a unique network topology.⁸ Several types of supplementary features, such as coordination behavior and geometry, stacking interactions, inter- and intramolecular space hindrance, are some of the parameters identified as being responsible for the amplification of topologically favored architectures in equilibrium of the DCLs. Indeed, such complicated topologies have attracted tremendous interest because of their simple one-pot synthesis from simple molecular components. Examples presenting features such as structural self-selection (self-sorting),^{4–6} reversible switching between different coordination arrays,^{7,8} or solid-state selection⁹ are becoming increasingly feasible.

We are interested in the possibility to use DCLs to self-sort specific metallosupramolecular architectures containing suitable molecular instructions for specific-based functions. We therefore decided to synthesize and study an extended

Scheme 1. Synthesis of Homoduplex Complexes $[(L_{ii})_2Zn]^{II}$, $i = 1–4$



series of 2,6-(iminoarene)pyridine-type Zn^{II} complexes $[(L_{ii})_2Zn]^{II}$, which were surveyed for their ability to self-exchange their aromatic arms and to form different homoduplex and heteroduplex complex aggregates in solution. Then they are self-sorted on the basis of intramolecular interactions, which ultimately show an improved charge-transfer energy function by virtue of the dynamic amplification of self-optimized heteroduplex architectures. These systems therefore illustrate the convergence of the combinatorial self-sorting of DCL strategy and the constitutional self-optimized function.

Results and Discussions

Ligand Design and Synthesis. For the reasons mentioned above, simple 2,6-(iminoarene)pyridine building blocks $L_{11}–L_{44}$, carrying two iminoarene chromophores, were chosen as synthetic precursors to constitute the double-level DCLs. They were synthesized from 2,6 diformylpyridine and the corresponding aromatic amine (CH_3CN , Δ , 5h), to afford $L_{11}–L_{44}$ after crystallization. We restricted our studies to benzene L_{11} , naphthalene L_{22} , anthracene L_{33} , and pyrene L_{44} groups, and common aromatic groups (Scheme 1).

This strategy using 2,6-(iminoarene)pyridine ligands gives easy access to functional pseudoterpyridine-type octahedral complexes in the presence of Zn^{II} ions.^{9a,10} A set of four homoduplex *parent complexes* $[(L_{ii})_2Zn]^{II}$, $i = 1–4$, have been synthesized by using L_{ii} , $i = 1–4$ ligands and zinc triflate (Scheme 1). The mixtures of 4:1, Zn^{II}/L_{ii} , $i = 1–4$ resulted in a 90% conversion to monoligand complexes $[L_{ii}Zn]^{II}$. The 1H NMR spectra of homoduplex $[(L_{ii})_2Zn]^{II}$ and monoligand $[L_{ii}Zn]^{II}$, $i = 1–4$ complexes consisted of a series of sharp peaks, indicating high symmetry. The spectra showed a deshielding of the para proton of the pyridine moieties due to the Zn^{II} ion complexation. We observe a gradual deshielding of the proton signals of the imine moieties of the complexes $[(L_{ii})_2Zn]^{II}$, $i = 1–3$ and $[L_{ii}Zn]^{II}$, $i = 1–4$, following the electron-withdrawing character of the aromatic substituents. For the pyrene-based homoduplex complex $[(L_{44})_2Zn]^{II}$, the proton signal of the imine moieties was shielded with respect to complexes $[(L_{22})_2Zn]^{II}$ and

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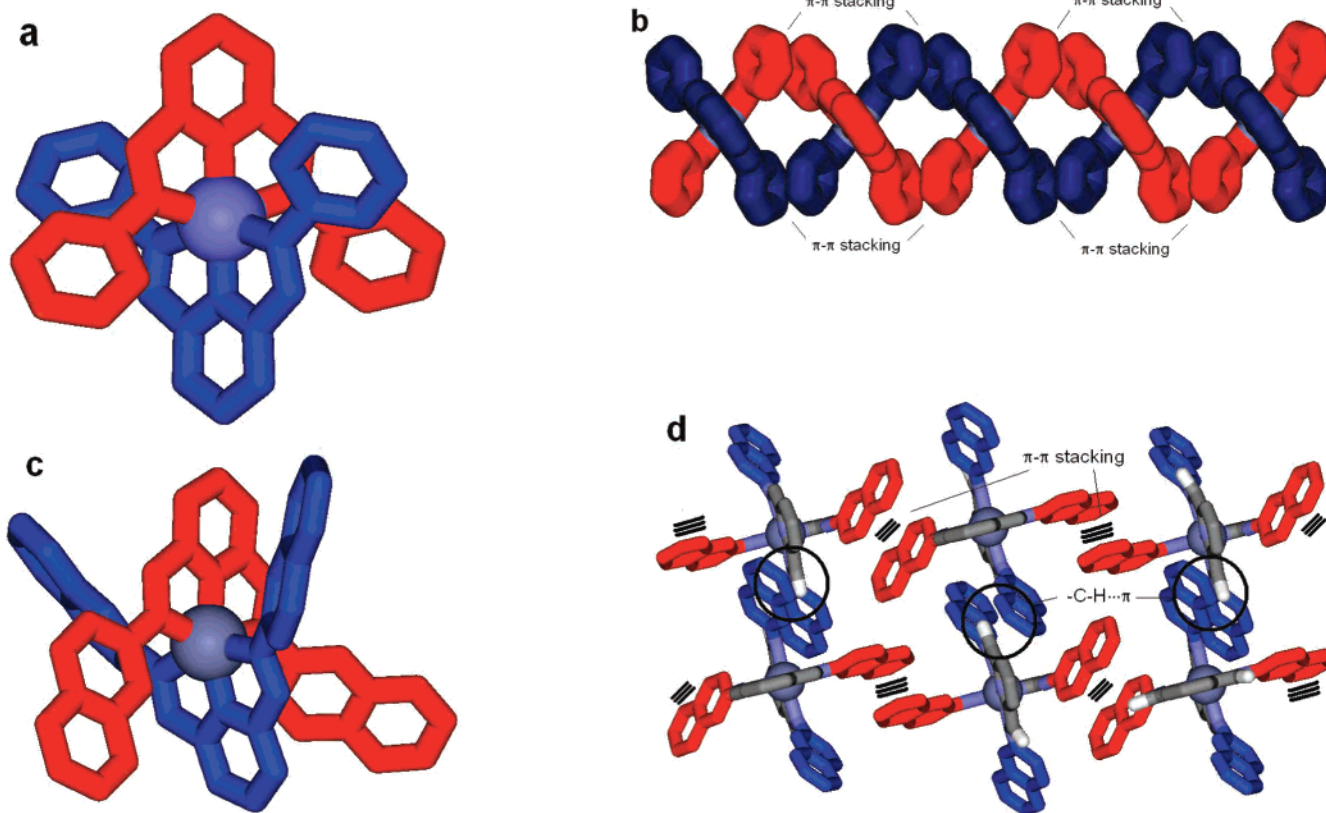


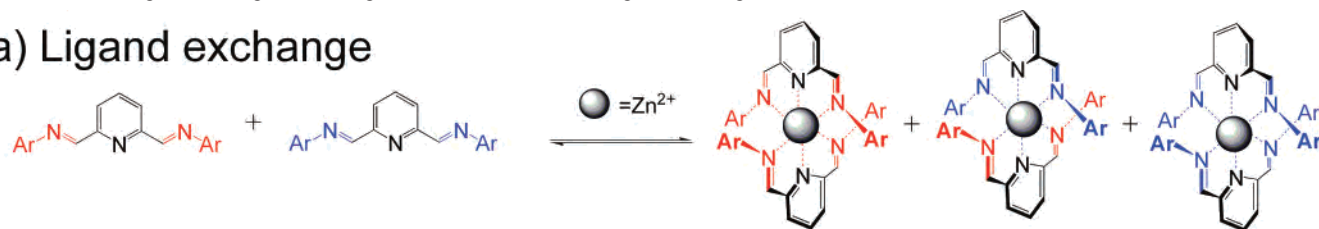
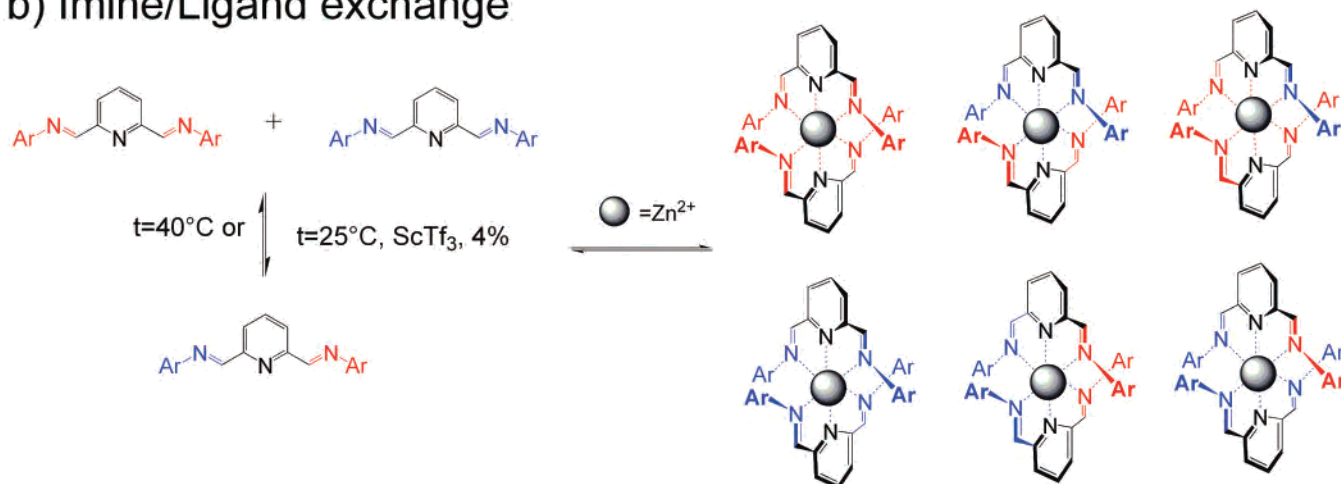
Figure 1. Crystal structure of $[(L_{11})_2Zn]^{II}$ and $[(L_{22})_2Zn]^{II}$: (a) and (c) view of the homoduplex complexes, (b) and (d) representation of the crystal packing in stick representation. The Zn^{II} ions are shown as blue spheres.

$[(L_{33})_2Zn]^{II}$. This suggests strong intramolecular $CH \cdots \pi$ interactions between the $N=CH$ proton and the pyrene moieties of the second coordinated ligand. This effect is likely to be the result of geometric features. Whereas in homoduplex complexes the phenyl, 2-naphthyl and 2-anthracenyl substituents are oriented in such a way that they are not interacting with the pseudoterpyridine core; the 2-pyrenyl complex with an angular orientation can tightly overlap with the central core of the complex. The ESI-MS spectra of homoduplex $[(L_{ii})_2Zn]^{II}$, $i = 1-4$ complexes showed strong doubly charged molecular peaks at $M_w/2$.

Solid-State Structures of the $[(L_{11})_2Zn]^{II}$ and $[(L_{22})_2Zn]^{II}$ Homoduplex Complexes. The crystal structures of the complexes were determined from crystals obtained from acetonitrile/*i*-propylether solutions at room temperature. The molecular and crystal-packing structures are presented in Figure 1. In both structures, the Zn^{II} ion is octahedrally coordinated by two ligands. The average $Zn^{II}-N_{\text{Pyridine}}$ and $Zn^{II}-N_{\text{imine}}$ distances are 2.04 and 2.25 Å, respectively. The crystal structure of $[(L_{11})_2Zn]^{II}$ has been previously reported.^{9a} The unit cell of the complex $[(L_{11})_2Zn]^{II}$ was found to contain two homoduplex complexes together with four triflate counterions and four acetonitrile molecules. In the structure, the two ligands of the duplex are arranged into two intertwined strands, which are held together in a double-helix form (0.5 turn/duplex) by the Zn^{II} cation (parts a and b of Figure 1). Each duplex of one helical sense is π - π stacked with two duplexes of the same helix (part b of Figure 1). Each duplex presents a tight contact with the two

neighboring ones, by the stacking of the terminal symmetrically disposed phenyl moieties (centroid-centroid distance of 3.68 Å). This pattern generates infinite double helix stacks of $[(L_{11})_2Zn]^{II}$ units of one helical sense with a helical pitch of about 15.3 Å. Accordingly, chiral double-helical channels are generated in the solid state with an interior void of about 1.8 Å (considering a projection in a plane and taking into account the van der Waals radii of diagonally located N_{imine} and CH_{imine} sites). The zinc ions are arranged into an approximately linear array that is tightly fitting into the central cavity of the helical channel. The double-helical entity is reminiscent of other double-stranded dinuclear Ag^+ helicates described earlier.^{8c}

The unit cell of the complex $[(L_{22})_2Zn]^{II}$ was found to contain two homoduplex complexes together with four triflate counterions and four acetonitrile molecules. In the crystal structure, the two ligands are not stereochemically equivalent. Each $[(L_{22})_2Zn]^{II}$ duplex, which the two pseudoterpyridines arrange into two orthogonal planes (part c of Figure 1), are associated by naphthalene-naphthalene interactions. These interactions are restricted to one direction, and each duplex presents a tight contact with the two neighboring ones (average π - π stacking centroid-centroid distances of 3.90 Å), forming parallel layers, which are alternatively stratified (part d of Figure 1). π interactions in the other direction are disrupted, with the other two naphthalene moieties not being involved in intermolecular π - π stacking, but present a short $CH \cdots \pi$ distance ($d_{H-\text{centroid}} = 2.9$ Å) between the plane of the rings and the imine protons of an adjacent complex

Scheme 2. Single-Level Ligand-Exchange and Double-Level Imine/ligand Exchange DCLs**a) Ligand exchange****b) Imine/Ligand exchange**

molecule. Having established that ligands L_{11} – L_{44} can be used to form octahedral assemblies with Zn^{II} ions in acetonitrile, scrambling exchange reaction were investigated.

Single-Level Ligand Exchange Scrambling Experiments. The ligand exchange between Zn^{II} complexes $[(L_{ij})_2Zn]^{II}$, $i = 1-4$ was first studied in the reaction of stoichiometric binary mixtures (1:1, mol/mol) of homoduplex complexes in acetonitrile at room temperature (Scheme 2). In all of the reactions, the signals of symmetrical complexes and those of the crossover heteroduplex products were monitored by 1H NMR (part a of Figure 2, remaining data can be found in the Supporting Information) and ESI-MS (part b of Figure 2). The 1H NMR spectra of binary mixtures of two different parent complexes $[(L_{ij})_2Zn]^{II}$, $i = 1-4$ show four sets of sharp proton resonances, which consist of the two initial homoduplex complexes together with two signals, one for each ligand, corresponding the heteroduplex $[(L_{ij}L_{ji})Zn]^{II}$, $i = 1-4$, $j = 1-4$ mixed species. The composition of the binary mixtures has been characterized on the basis of the integration of imine 1H NMR signals of the homo- and heteroduplex complexes, using the solvent peak as a reference (Table 1). Very good reproducibility for the quantitative analysis of homo- and heterocomplexes in a complex dynamic library can be obtained by 1H NMR, giving us great confidence that NMR technique is a reliable method.

A closer look at the data reveals that simple mixing of two homoduplex complexes bearing substituents that are formed by phenyl, naphthyl, and anthracenyl aromatic rings results in the formation of mixtures following the statistical distribution 1:2:1. (Table 1, entries 1, 2, 4). Analysis of the dynamic mixtures resulting from the addition of pyrene-based

homoduplex complex $[(L_{44})_2Zn]^{II}$ with other homoduplex complexes $[(L_{ii})_2Zn]^{II}$, $i = 1-3$ reveals that a self-sorting process occurs, with a $\sim 50\%$ amplification of the heteroduplex complexes $[(L_{ii}L_{44})Zn]^{II}$, $i = 1-3$ (Table 1, entries 3, 5, 6). In these heteroduplex complexes, whereas the proton signals of the imine moieties of phenyl, naphthyl, and anthracenyl-substituted ligands were shielded overall (~ -0.2 ppm), the proton signals of the imine moieties of pyrenyl-substituted ligands were overall deshielded ($\sim +0.25$ ppm) with respect to the homoduplex complexes. This suggests that the intramolecular $CH\cdots\pi$ interactions between the $N=CH$ protons of the phenyl, naphthyl, and anthracenyl substituted ligands and the pyrenyl moieties of a second coordinated ligand are maintained when heteroduplex complexes form. The pyrenyl substituents are spatially close to the pseudoterpyridine center, whereas the phenyl, naphthyl, and anthracenyl terminals are stereochemically excluded from the proximity of the coordination center. These are involved in intermolecular $\pi-\pi$ stacking interactions with ligands of the same type. This suggests that intermolecular $\pi-\pi$ stacking interactions between phenyl, naphthyl, and anthracenyl groups observed in the solid-state structure of $[(L_{22})_2Zn]^{II}$ play an important role in the aggregation process of these compounds in solution. Similar trends are observed upon the formation of terpyridine complexes bearing naphthalene groups.¹¹ The formation of three-component DCLs was furthermore confirmed by ESI-MS (part b of Figure 1). The mass spectra showed the formation of dominant cross-

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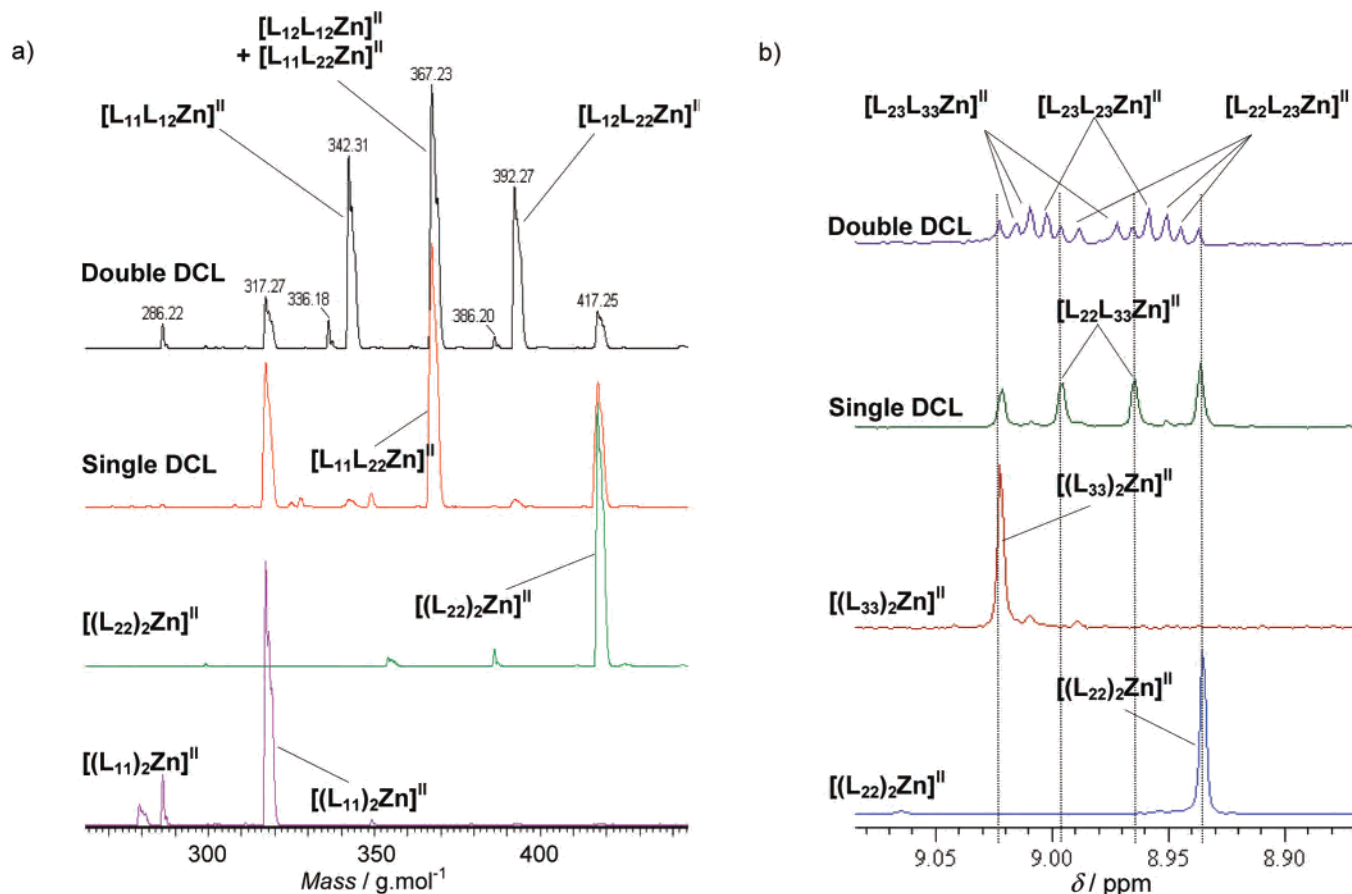


Figure 2. (a) ESI-MS and (b) ^1H NMR show evidence of different complexes exchanging in solution.

Table 1. Statistical and Experimental Abundance of Each Complex (Obtained from ^1H -NMR Spectroscopies) in the Single-Level Libraries and Corresponding Amplifications (Highlighted) in Some Cases

	$\text{L}_{ii} \text{L}_{jj}$	$(\text{L}_{ii})_2$	$(\text{L}_{ii})(\text{L}_{jj})$	$(\text{L}_{jj})_2$
	statistical distribution %	25	50	25
		Amplification %		
1.	$\text{L}_{11} \text{L}_{22}$	25,0	50,0	25,0
2.	$\text{L}_{11} \text{L}_{33}$	25,0	50,0	25,0
3.	$\text{L}_{11} \text{L}_{44}$	15,0	70,0	15,0
4.	$\text{L}_{22} \text{L}_{33}$	25,0	50,0	25,0
5.	$\text{L}_{22} \text{L}_{44}$	12	76,0	12
6.	$\text{L}_{33} \text{L}_{44}$	12	76,0	12

^a We speak about *amplification* when the experimental abundance is higher than the statistical one. It is calculated using the difference between the experimental and the statistical abundances as follows, for example in case 3.: $40\% = [(70-50)/50] \times 100$.

products, in all of the reactions, after a rapid equilibration of the 1:1 solutions of the homoduplex complexes.

Double-Level Imine/Ligand Exchange Scrambling Experiments. Next we investigated a more complex exchange process. The imine/ligand exchange around the central pseudoterpyridine moiety (Scheme 2) is expected to act simultaneously, leading to a more complex exchanging species in solution. The increase in the imine exchange rate is easily done by simply increasing the temperature of the sample or by using scandium triflate (ScTf_3) as a catalyst.⁶ Although the rate of reaction for the single-level exchange

is very fast (instantaneous) at 20 °C, it is dependent on temperature and slightly on substituent size for the double-level exchange. A thermal treatment of the mixtures for 2 h at 40 °C gave in all of the cases double-level exchanged libraries, which are thermodynamically stable at room temperature. The addition/elimination steps are consistent with the transimination mechanism in the presence of Zn^{II} /temperature^{6c} and Sc^{III} ^{6f} recently proposed by Giuseppone et al. In this context, our strategy was to employ stoichiometric binary mixtures (1:1, mol/mol) of homoduplex complexes in acetonitrile at 40 °C or to add ScTf_3 (4% M) to generate the interconversion of all of the possible stoichiometries and geometries around the metal center, thereby forming a library of six hetero- and homonuclear complexes (Table 2).

Imine exchange kinetics between the homoligands L_{ii} and L_{jj} is typically rapid in the presence of Zn^{II} ions, facilitating the equilibration of the heteroligand L_{ij} .^{6e,7a,b} For example, in the series of $[\text{L}_{ii}\text{Zn}^{\text{II}}]$ 1:1 complexes,¹² after 2 h at 40 °C the mixtures follow a statistical distribution $[\text{L}_{ii}\text{Zn}^{\text{II}}]/[\text{L}_{ij}\text{Zn}^{\text{II}}]/[\text{L}_{jj}\text{Zn}^{\text{II}}] = 1:2:1$. As shown in Figure 1, the ^1H NMR spectra of binary mixtures of two different *parent complexes* $[(\text{L}_{ii})_2\text{Zn}^{\text{II}}]$, $i = 1-4$ and $[(\text{L}_{jj})_2\text{Zn}^{\text{II}}]$, $j = 1-4$ show two sets of six sharp proton resonances and consist of the two initial homoduplex complexes together with the heteroduplex

(12) The 1:1 $[\text{L}_{ij}\text{Zn}^{\text{II}}]$ complexes may be obtained almost quantitatively by using an excess (minimum $\text{L}_{ij}/\text{Zn}^{\text{II}}$, 1:4, mol/mol) of ZnTf_2 in acetonitrile.

Table 2. Statistical and Experimental Abundance (Obtained from ^1H -NMR Spectroscopies) of Each Complex in the Double-Level Libraries and Corresponding Amplifications (Highlighted) in Some Cases

	$L_{ii}L_{jj}$	$(L_{ii})_2$	$(L_{ii})(L_{jj})$	$(L_{ii})(L_{jj})$	$(L_{ij})_2$	$(L_{ij})(L_{jj})$	$(L_{ii})_2$
	statistical distribution %	6.25	25	12.5	25	25	6.25
		Amplification %					
1.	$L_{11}L_{22}$	8	24	17	19	24	8
				36			
2.	$L_{11}L_{33}$	11	18	12	30	18	11
		76			20		76
3.	$L_{11}L_{44}$	3	25	13	31	25	3
					24		
4.	$L_{22}L_{33}$	6	25	13	25	25	6
5.	$L_{22}L_{44}$	2	24	16	32	24	2
				28	28		
6.	$L_{33}L_{44}$	0	27	10	36	27	0
			8		44	8	

complex $[(L_{ii}L_{jj}Zn)]^{II}$ and the heteroduplex complexes formed by the heteroligand L_{ij} , that is $[(L_{ii}L_{ij})Zn]^{II}$, $[(L_{ij}L_{ij})Zn]^{II}$, and $[(L_{ij}L_{jj})Zn]^{II}$, $i = 1-4$, $j = 1-4$. This is reliable with a double-level imine/ligand exchange DCL (Scheme 2).

Analysis of the resulting dynamic mixtures of homoduplex complexes $[(L_{ii})_2Zn]^{II}$ and $[(L_{jj})_2Zn]^{II}$, $i = 1-4$, $j = 1-4$ by ^1H NMR and ESI-MS revealed that, in all of the cases except one (Table 2, entry 4), the same self-sorting process occurs. In fact, the spectra showed that the heteroduplex complexes $[(L_{ii}L_{ij})Zn]^{II}$ and $[(L_{ij})_2Zn]^{II}$, $i = 1-4$, $j = 1-4$ are predominantly identified in the mixtures (Table 2; entries 1-3, 5, 6).

The NMR spectra of the scrambled heterocomplexes (Supporting Information) show that the bulkiest substituents are spatially close to the pseudoterpyridine center, whereas the least bulky aromatic groups stereochemically excluded from the proximity of the coordination center, are involved in intermolecular $\pi-\pi$ stacking interactions with ligands of the same type. Moreover, the self-sorting process is really selective in the case of L_{33} , anthracenyl, and L_{44} pyrenyl-derived ligands; the ^1H NMR and ESI-MS spectra showed the heteroduplex complexes formed by the heteroligand L_{34} identified for $[(L_{33}L_{34})Zn]^{II}$, $[(L_{34}L_{34})Zn]^{II}$, and $[(L_{34}L_{44})Zn]^{II}$ to be exclusively formed (Table 2, entry 6).

The self-sorting of heteroduplex complexes is likely to be the result of geometric constraints. Whereas the imine-exchange process occurs quantitatively in 1:1 mixtures of $[(L_{ii})_2Zn]^{II}$, $i = 1-4$ complexes, the octahedral coordination process around the metal ion defines spatial-frustrated exchanges involving the selective formation of heterocomplexes of two, by two different substituents; the bulkiest ones (pyrene in principle) specifically interact with the pseudoterpyridine core, sterically hindering the other least bulky ones, which are intermolecularly stacked with similar ligands of neighboring molecules. The self-sorting process defined by the specific self-constitution of the ligands exchanging their aromatic substituents is self-optimized by a specific control over their spatial orientation around a metal center within the complex.

Photophysical Properties of Single- and Double-level DCLs. The fluorescence spectra of homoduplex complexes

$[(L_{ii}Zn)]^{II}$, $i = 1-4$ and of their single- and double-level DCLs in acetonitrile are shown in Figure 3. Complexation with $d^{10}Zn^{II}$ ions does not usually introduce low-energy metal-centered or charge-transfer states into the ligand, so that MC (Metal Centered), MLCT (Metal to Ligand Charge Transfer), or LMCT (Ligand to Metal Charge Transfer) bands are not expected to be present in the absorption spectrum of Zn^{II} complexes. As a consequence, the absorption spectra of homo- and heterocomplexes should be regarded as perturbed by metal-ion complexation and $\pi-\pi$ stacking interactions among them.¹³

The overall effect can be explained as the intrinsic feature of such terpyridine-type aromatic complexes,¹⁴ by taking into account two different phenomena; the first one is due to the complexation with the metal ion, which decreases the electronic density on the pseudoterpyridine moiety and, as a consequence, perturbs the electronic structure of the arene unit, leading to the observed blue shift of the band.¹⁴ Second, this process makes the pseudoterpyridine unit easier to be reduced, so that a charge-transfer transition from the aromatic chromophore becomes possible. A charge-transfer transition was also observed in the Ru^{II} ^{14a} and Zn^{II} ^{14b,c} complexes, which have as a ligand a terpyridine covalently linked to a pyrene unit.

As a general rule, when single-level and double-level DCLs are formed from equimolar mixtures of homocomplexes $[(L_{ii})_2Zn]^{II}$, the fluorescence bands of naphthyl, anthracenyl, and pyrenyl chromophores $i = 1-3$, centered at 410, 480, and 420 nm respectively, show reduced intensity (Figure 3). The fluorescence band of the single-level DCL and double-level DCL complexes can in theory be attributable, because of its shape and energy, to (i) a charge-transfer transition from the chromophore moiety to the coordinated pseudoterpy unit, (ii) the formation of intramolecular excimers (involving the two pyrene chromophore of the same ligand), or (iii) the formation of exciplexes (involving the pyrene chromophores of one ligand and the pseudoterpy moiety of a second ligand). This latter term is clearly absent, and the typical excimer fluorescence from a couple of chromophores lies at much higher energies. In addition, as it can be clearly observed by NMR and the X-ray structure of $[(L_{22})_2Zn]^{II}$, metal-ion complexation brings the aromatic chromophore moieties of L_{ii} and the pseudoterpyridine unity of the second ligand in close proximity, so that π stacking interactions between those three units can be established. Interactions of this kind are expected to cause a broadening and a decrease in the bands of the chromophore involved, as is indeed observed. In agreement with the results above, the decrease in the fluorescence bands of the bulkiest aromatic chromophore of the single-level and double-level DCLs can be attributed, because of its shape and energy, to

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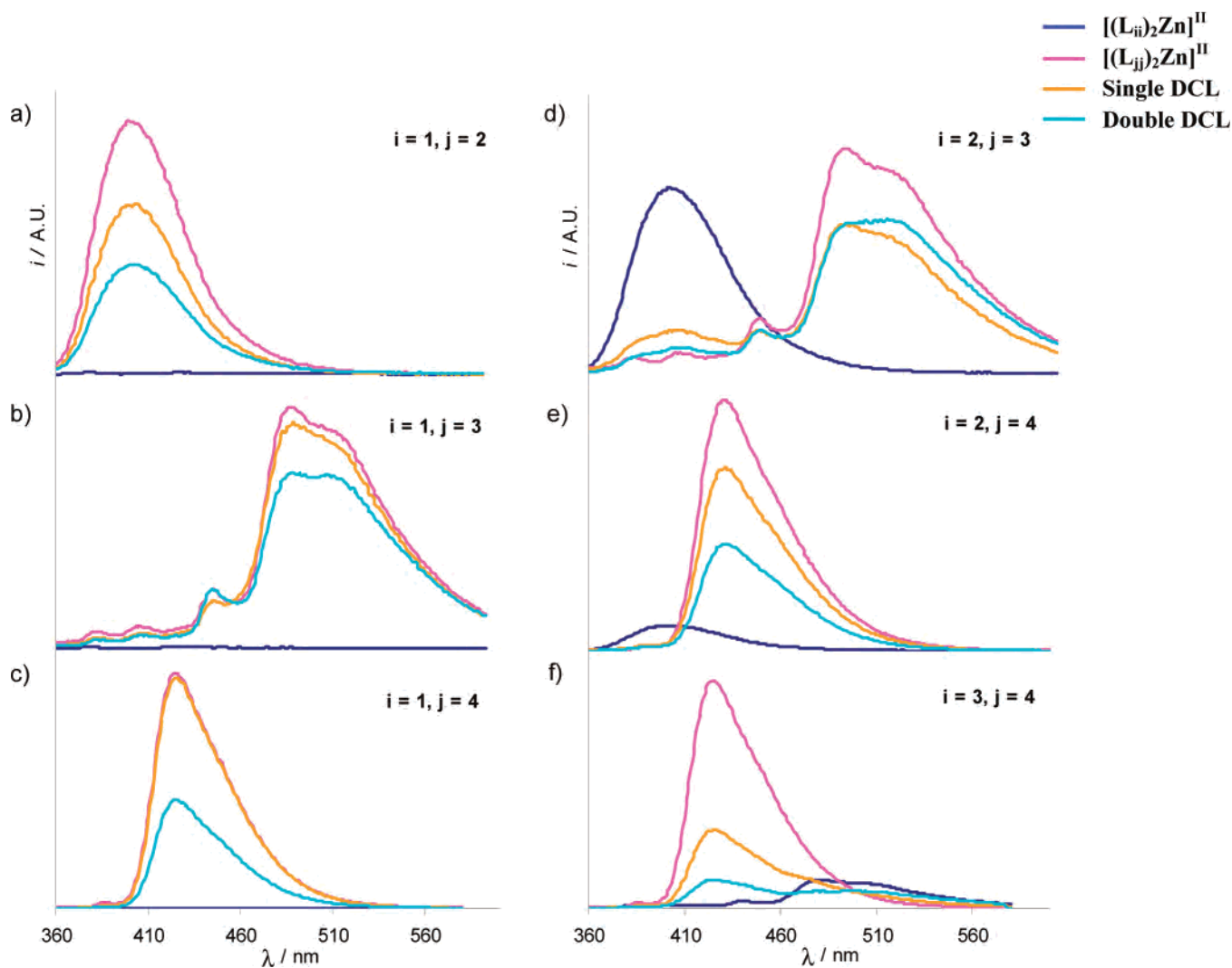


Figure 3. Fluorescence emission spectra recorded in acetonitrile at 293 K of (a) $[(L_{11})_2Zn]^{II}/[(L_{22})_2Zn]^{II}$, (b) $[(L_{11})_2Zn]^{II}/[(L_{33})_2Zn]^{II}$, (c) $[(L_{11})_2Zn]^{II}/[(L_{44})_2Zn]^{II}$, (d) $[(L_{22})_2Zn]^{II}/[(L_{33})_2Zn]^{II}$, (e) $[(L_{22})_2Zn]^{II}/[(L_{44})_2Zn]^{II}$, and (f) $[(L_{33})_2Zn]^{II}/[(L_{44})_2Zn]^{II}$, with excitation at 344 nm.

a charge-transfer transition from the chromophore moiety interacting with the coordinated pseudoterpyridine units.

The double (imine/ligand) exchange in double-level DCLs compared with the single-level DCLs generates an increased charge-transfer energy by optimizing the constitutional rearrangement of the chromophoric arms around the metal center. In very general terms, the homoduplex complexes solutions emit more than the single-level DCLs, which emit more than the double-level DCLs. In most cases, the quenching of fluorescence ranges between a third and a half of the most fluorescent homoduplex complex.

Conclusion

Over the last few years, dynamic combinatorial chemistry has been used as a powerful tool to discover new receptors, drugs, catalysts, and materials.^{1–3} The dynamic features of molecular and supramolecular systems serve more recently to bring into play the constitutional evolution of such systems,^{4–9} and new selection rules can be beneficial for control over the self-assembly and dynamic component exchange for the selection of specific fittest architectures.

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

From a conceptual point of view, the constitutional evolution of the dynamic coordination systems toward the selection of mixtures of heteroduplex architectures instead a specific amplified architecture is of special interest for the improvement of their specific charge-transfer energy function. For each combination of two homoduplex complexes, the fluorescence intensity of initial compounds systematically decreases for single-level ligand exchange mixtures and then

for double-level imine/ligand heterocomplexes. Such collective reorganization of the system allows the self-sorting of specific heterocomplex architectures, presenting an intrinsic property of energy transfer specifically amplified under the pressure of internal structural factors. Similar examples of self-sensing^{6c} or self-extracting^{7b} structurally complex systems self-optimizing their function through their constitutional self-assembly have been recently reported. The self-sorting processes are very common in selective-functional self-assembly of multicomponent biological,^{16a,b} polymeric,^{16c} or DCL⁵ systems. The systems described here represent a novel example of dynamic-instructed mixtures of coordination compounds, where the concept of constitutional self-sorting and a specific function (charge-transfer energy) might be associated in principle.

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Supporting Information Available: Experimental methods, including synthesis, crystallographic informations, spectral characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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