

# Self-Assembly of Pseudo[1]rotaxanes by Palladium (II)/Platinum(II)-Directed Integrative Social Self-Sorting: Is the Metal Required?

Tamara Rama, Arturo Blanco-Gómez, Carlos Peinador,\* and Marcos D. García\*<sup>[a]</sup>

New results are presented on the multicomponent supramolecular synthesis of pseudo[1]rotaxanes, achieved by designing pairs of structurally matching *N*-monoalkyl-4,4'-bipyr-idinium/2,7-diazapyrenium-based ligands having complementary  $\pi$ -donor/acceptor features, and intended to self-assemble into the targeted supramolecules by following integrative self-sorting processes. In all the studied cases, it was found that the envisioned species, characterized by NMR spectroscopy and MS

#### Introduction

On its journey from structure to function, current synthetic chemistry is progressively shifting its attention from the kinetically-controlled construction of static molecular complexity,<sup>[1,2]</sup> to the design and study of dynamic multicomponent aggregates prepared by self-assembly.<sup>[2,3]</sup> In this regard, Nature has a head start of a few billion years as chemist, being able to create functional matter by spatiotemporally-controlled self-assembly of a limited number of different molecular constituents.<sup>[4]</sup> In sharp contrast, abiotic self-assembly typically relies on the use of identical elements, producing highly symmetric aggregates under the guidance of directional intermolecular interactions.<sup>[5]</sup> Consequently, there is still a substantial margin for the design of efficient self-assembly strategies, able for instance to produce discrete asymmetrical entities by integrative social self-sorting of structurally-diverse building blocks.<sup>[6,7]</sup>

Following these ideas and our interest on the self-assembly of dynamic host-guest systems,<sup>[8,9]</sup> we have recently described the multicomponent supramolecular synthesis in aqueous media of a series of heterodimeric pseudo[1]rotaxanes.<sup>[10]</sup> This type of host-guest complexes is of high current interest for a series of reasons. Firstly, aggregation can be produced intermolecularly with the species acting as AB-type heteroditopic monomers, which have been extensively used for the development of supramolecular polymers.<sup>[11]</sup> On the other hand, intramolecular association can take place leading to self-

[a]	Dr. T. Rama, Dr. A. Blanco-Gómez, Prof. Dr. C. Peinador,
	Prof. Dr. M. D. García
	Departamento de Química and Centro de Investigacións Científicas
	Avanzadas (CICA), Facultade de Ciencias
	Universidade da Coruña
	A Coruña 15071 (Spain)
	E-mail: carlos.peinador@udc.es
	marcos.garcia1@udc.es
	Supporting information for this article is available on the WWW under

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spectrometry, arise as the main products of the self-assembly in aqueous media by using palladium(II)/platinum(II) metal centers as the guiding force. Crucially, we have also found that by improving the  $\pi$ -donor/acceptor properties of the matching pairs of ligands ( $L_4$  and  $L_5$ ), the integrative self-sorting processes prevail even in the absence of metallic ions to afford the heterodimeric species with an association constant being 756 $\pm$  43 M<sup>-1</sup>.

inclusion complexes, which have demonstrated is applicability as precursors of a variety of interlocked structures,<sup>[12]</sup> or in the development of indicator displacement assays for analyte sensing.<sup>[13]</sup>

In our specific case (Scheme 1),<sup>[10]</sup> we found that pseudo[1] rotaxanes (±)-**S**<sub>1a,b</sub> could be efficiently prepared in water by Pd (II)/Pt(II)-directed self-assembly, using the L-shaped ligand **L**<sub>1</sub> and its matching amphiphilic counterpart (±)-**L**<sub>2</sub>, which owns an electron-rich dioxophenylene subunit attached though a flexible polyethylene glycol-based linker to the common  $\pi$ -deficient *N*-monoalkyl-4,4'-bipyridinium moiety found in both ligands. Remarkably, (±)-**S**<sub>1a,b</sub> were the only products detected on the **M**<sub>1</sub>/**M**<sub>2</sub>-directed self-assembly processes, with no observation of the homodimeric species (±)-**S**<sub>2a,b</sub> and (±)-**S**<sub>3a,b</sub>. This integrative self-sorting phenomenon was rationalised on the basis of the enthalpic gain produced by optimization of  $\pi$ - $\pi$ , C–H··· $\pi$  and hydrophobic interactions between complementary ligands and, crucially, because of the maximization of the number of those weak interactions per cavity of receptor.

Based on these previous results, we planned to expand our initial study to the self-assembly of two new pairs of matching ligands, namely  $L_1/(\pm)-L_3$  and  $(\pm)-L_4/L_5$  (Scheme 1). Compared to our preceding systems, those studied herein would have enhanced  $\pi$ -donor/acceptor characteristics in at least one of the building blocks, improving in that manner the non-covalent interactions previously argued to be the guiding forces of the self-sorting processes.

## **Results and Discussion**

The new amphiphilic ligands  $(\pm)$ -L<sub>3-4</sub> were adequately synthesised in an analogous fashion as previously reported for  $(\pm)$ -L<sub>2</sub>,<sup>[10,14]</sup> by using our in-house methodology for the preparation of functionalized ditopic *N*-monoalkyl-4,4'-bipyridinium-based

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Scheme 1. Depiction of the  $M_1/M_2$ -directed self-assembly processes discussed in this work. Top: previously reported integrative social self-sorting of complementary ligands  $L_1$  and  $(\pm)-L_2$ . Bottom: New metal-directed self-assembly processes studied in this work. Other potential non-occurring species have been attenuated.

derivatives (Scheme 2 and Supporting Information for synthetic procedures and characterization).<sup>[15]</sup>

Having all the building blocks in our hands,<sup>[16]</sup> we planned to study independently the Pd(II)/Pt(II)-directed self-assembly in water of the potential homodimeric species resulting from the use of each of the ligands.<sup>[16,17]</sup> In this context, (en)Pd(ONO<sub>2</sub>)<sub>2</sub> (**M**<sub>1</sub>) and (PEt<sub>3</sub>)<sub>2</sub>Pt(ONO<sub>2</sub>)<sub>2</sub> (**M**<sub>2</sub>),<sup>[18-20]</sup> were chosen as appropriate square-planar metal complexes able to guide the self-assembly of rectangular **M**<sub>2</sub>**L**<sub>2</sub> species.

Nevertheless, prior to the discussion on the self-assembly of the homodimeric aggregates, it is worth noting the potential complexity of the conformational/stereochemical outcome of these processes. Firstly, *syn-/anti*- diastereoisomers can arise due to the racemic nature of  $(\pm)$ -L<sub>3</sub>/L<sub>4</sub> and, depending on the absolute stereochemical configuration of the building blocks joined by the metal centers (Figure 1).<sup>[15]</sup>

Furthermore, the long and flexible polyethylene glycolbased linker connecting the two aromatic subunits can provoke



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Scheme 2. Synthesis of the amphiphilic ligands  $(\pm)$ -L<sub>3,4</sub>.



(±)-syn-down-endo (±)-syn-down-exo (±)-syn-up-endo (±)-syn-up-exo

Figure 1. Schematic depiction of the potential isomers arising from the Pd (II)/Pt(II)-directed homodimeric self-assembly of  $(\pm)$ -L\_3-4 (exemplified for  $(\pm)$ -L\_4).

the observation of different stable conformers by NMR techniques, as demonstrated in similar systems.<sup>[21]</sup> Consequently, the dihydroxynaphthalene (DHN) subunit could be introduced into the cavity of the receptor above or below its plane, resulting into what we have labelled as *up* and *down* conformers. Finally, two different insertion modes for the DHN moiety into the receptor are possible relative to the connector, resulting in *endo* or *exo* conformations.<sup>[22]</sup>

Proceeding with the study on the self-assembly of homodimeric species, we observed how the reaction in aqueous media of an equimolar 5 mM mixture of ligand  $(\pm)$ -L<sub>3</sub> and complex M<sub>1</sub>, instantaneously produced a <sup>1</sup>H-NMR spectrum with a set of broad signals for the ligand. Generally, this result implies two situations: the appearance of oligomers and/or an equilibrium state near coalescence for the components of the aggregate.<sup>[23]</sup> In order to discard the former situation, we carried out the study of the speciation of the system by <sup>1</sup>H-NMR and UV-Vis, on



a concentration window ranging from 5–0.08 mM.<sup>[14]</sup> The NMR experiments showed no changes upon dilution, with the set of signals initially observed at 5 mM remaining unaffected. Furthermore, we noticed how the addition of metal center **M**<sub>1</sub> to a yellowish solution of  $(\pm)$ -L<sub>3</sub>, instantaneously produced an intense orange coloration, with the appearance of a charge-transfer band centered at  $\lambda_{max}$ =470 nm on the UV-Vis spectrum, accounting for the establishment of new  $\pi$ - $\pi$  interactions on the system. Crucially, a linear correlation could be verified between the concentration of  $(\pm)$ -L<sub>3</sub> and the absorbance at the charge-transfer band,<sup>[14]</sup> indicating a unimolecular process and discarding therefore higher order equilibria.<sup>[21]</sup>

Once the non-existence of oligomeric species on the self-assembly concentration window, we proceeded to avoid the observed coalescence by performing <sup>1</sup>H-NMR experiments at variable temperature. In essence, on increasing the temperature, we detected a situation closer to rapid equilibrium for the system, with chemical shifts for the sole set of signals of the ligand at 80 °C, being in good agreement with the formation of the expected homodimeric self-inclusion complex ( $\pm$ )-**S**<sub>sa</sub> (Figure 2).

Although the signals corresponding to the DHN moiety are still near coalescence at 80 °C, their shielded chemical shifts relative to the free ligand confirm its insertion into the hydrophobic cavity formed upon the self-assembly of  $(\pm)$ -**S**<sub>sa</sub>. Furthermore, signals assigned to protons H<sub>a</sub>, H<sub>f</sub> and H<sub>g</sub> within the bipyridinium moieties are consistently deshielded, as a consequence of both the coordination with the Pd(II) centers and the establishment of C–H… $\pi$  interactions, between the pyridines on the short sides of the receptor and H<sub>4</sub>/H<sub>8</sub> on the DHN unit. Conversely, protons H<sub>b-c</sub> are clearly shielded because of their transient insertion within the cavity of the host.

In order to further confirm the metal-directed self-assembly of the homodimeric supramolecule obtained from  $(\pm)$ -L<sub>3</sub>, the kinetic lability of the Pd(II) species was surpassed by preparing the Pt(II) analogue  $(\pm)$ -S<sub>5b</sub>·6NO<sub>3</sub>, which was self-assembled in aqueous media starting from the ligand and M<sub>2</sub>. The experiment produced a <sup>1</sup>H-NMR consistent with the homodimeric species for the mixture at 80 °C. Precipitation of the obtained



Figure 2. <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O, 80 °C) spectra for: a) 2.5 mM (±)-L<sub>3</sub>, and b) S<sub>5a</sub> (5 mM (±)-L<sub>3</sub> and M<sub>1</sub>).

compound from the aqueous solution with excess KPF<sub>6</sub> allowed to obtain  $S_{5b}$ ·6PF<sub>6</sub>, which was submitted to HR-ESI-MS in acetone, showing a fragment at m/z = 1427.4263 for  $[S_{5b}-2PF_6]^{2+}$ with mass and isotopic distributions in good agreement with those peaks theoretically calculated for the species (Figure 3).

Turning our attention to the  $M_1$ -guided self-assembly of the diazapyrene-containing ligand  $(\pm)$ - $L_4$ , we found that the 2.5 mM equimolar mixture of ligand and complex in  $D_2O$  at r.t. produced, as anticipated,<sup>[22]</sup> a very complex NMR spectrum (Figure 4).

As for  $(\pm)$ -**S**<sub>5a</sub>, dilution experiments for equimolar mixtures of  $(\pm)$ -**L**<sub>4</sub> and **M**<sub>1</sub>, monitored by NMR and UV-Vis,<sup>[14]</sup> allowed to discard the formation of oligomeric species or equilibria other than unimolecular,<sup>[21]</sup> pointing out that the most likely explanation for the complex spectra observed would be a slow exchange regime on the NMR timescale which, in turn, account







Figure 4. <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 25 °C) spectra for: a) 2.5 mM (±)-L<sub>4</sub>, and b) (±)-S<sub>8a</sub> (2.5 mM (±)-L<sub>4</sub> and M<sub>1</sub>).

for the potential diastereoisomers and conformers arising from the self-assembly of  $(\pm)$ - $S_{8a}$  (vide supra). To add insult to injury, the insertion of one of the 1,5-DHN moieties into the cavity of the supramolecule produces a loss of symmetry on the corresponding inclusion complex, making the nuclei on the upper and lower regions of the metallacyclic subunit chemically non-equivalent but with, arguably, quite similar chemical shifts.

All these factors would certainly account for the complex situation observed on the spectrum. Even though, a COSY experiment recorded for the mixture rendered quite interesting information. Specifically, groups of proton signals, rather than individual nuclei, correlate in agreement with the proposed structure  $(\pm)$ -**S**<sub>8a</sub>·6NO<sub>3</sub>. Furthermore, following the same methodology described for  $(\pm)$ -**S**<sub>sa,b</sub>, the Pt(II) analogue  $(\pm)$ -**S**<sub>8b</sub>·6PF<sub>6</sub> was self-assembled from  $(\pm)$ -L<sub>4</sub> and **M**<sub>2</sub>, allowing for the identification by means of HR-ESI-MS of a diagnostic peak at m/z = 1474.4163 for  $[\mathbf{S}_{8b}$ -2PF<sub>6</sub>]<sup>2+</sup>, with mass and isotopic distribution in good agreement with that calculated for the proposed structure (Figure 3).

With the information gathered on the self-assembly of the homodimeric species  $(\pm)$ - $S_{s_{a,b}}$  and  $(\pm)$ - $S_{a_{a,b}}$  in our hands, as well as that previously reported by our group on the structures of non-functionalized metallacycles  $S_{2a,b}$  and  $S_{7a,b}$ ,<sup>[16]</sup> we then proceeded to study the  $M_1/M_2$ -directed self-assembly involving each of the designed matching pairs of complementary ligands. As for the homodimeric species, the prospective analysis by NMR spectroscopy of the targeted hetero pseudo[1]rotaxanes would be as well conditioned by the structural features of the ligands. However, in the case of the heterodimeric species, the absence of *syn-/anti*- diasteromers, reduces the number of potential isomers resulting from the self-assembly (Figure 5).

As previously observed for  $(\pm)$ - $S_{sar}$  the reaction of a stoichiometrically-adjusted mixture of  $(\pm)$ - $L_3$  (2.5 mM),  $L_1$  (2.5 mM) and  $M_1$  (5 mM) in D<sub>2</sub>O, instantaneously produced a <sup>1</sup>H NMR with broad signals at r.t. Dilution experiments monitored by <sup>1</sup>H-NMR and UV-Vis for the mixture within the concentration window 2.5–0.08 mM,<sup>[14]</sup> supported again the non-existence of oligomeric species on the observed dynamic equilibrium.

Once more, VT <sup>1</sup>H-NMR experiments allowed us to overcome the initial observed coalescence, showing a single set of signals for each of the ligands in very good agreement with the Pd(II)-directed self-sorting of  $(\pm)$ -**S**<sub>4a</sub>. As shown in Figure 6, the experiment recorded at 60 °C shows a situation of rapid interconversion between the DHN units inside/outside the receptor, as well as all the potential *up/down* and *endo/exo* isomers associated to the self-inclusion process. Regarding the



Figure 5. Schematic depiction of the potential isomers resulting from the Pd (II)/PtII)-directed heterodimeric self-sorting of (±)-L<sub>3</sub>/L<sub>1</sub> and (±)-L<sub>4</sub>/L<sub>5</sub> (exemplified for (±)-L<sub>3</sub>/L<sub>1</sub>).



Figure 6. <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O, 60 °C) spectra for: a) 2.5 mM L<sub>1</sub>, b) 2.5 mM (±)-L<sub>3</sub>, c) (±)-S<sub>4a</sub> (2.5 mM (±)-L<sub>3</sub>, 2.5 mM L<sub>1</sub> and 5 mM M<sub>1</sub>), d) DOSY NMR for solution c).

relative chemical shifts, assigned with the aid of a COSY experiment at 60 °C,<sup>[14]</sup> those showed the expected deshielding of protons H<sub>a</sub>, H<sub>g</sub> and H<sub>f</sub> in each of building blocks because of coordination to **M**<sub>1</sub> and C–H··· $\pi$  interactions with H<sub>4</sub>/H<sub>8</sub>, with these protons of the guest part of  $(\pm)$ -L<sub>3</sub> appearing massively shielded by circa 4 ppm regarding the free ligand. The remaining protons on the system appear consistently shielded, because of the concurrence of the expected host-guest interactions. A DOSY experiment recorded at 60 °C also supported the formation of the heteromer  $(\pm)$ -S<sub>4a</sub>, with all the signals for the building blocks diffusing as a whole (Figure 6d). Furthermore, the **M**<sub>2</sub>-directed self-assembly of the matching pair allowed us to obtain crucial HR-ESI MS data, in good agreement with the formation of the self-sorted Pt(II) analogue  $(\pm)$ -S<sub>4b</sub> (Figure 3).

Regarding the study of the  $M_1$ -directed self-sorting of the matching pair  $L_5/(\pm)-L_4$ , the analysis of the results by means of NMR spectroscopy was hampered by very similar reasons to those obscuring the study of the homodimeric self-assembly of  $(\pm)-L_4$  itself (*vide supra*). In consequence, the <sup>1</sup>H-NMR in D<sub>2</sub>O recorded for the mixture of the components needed for the assembly of 5 mM  $(\pm)$ -S<sub>6a</sub> was certainly complex, to say the least.<sup>[14]</sup>

In this situation, we found only subtle clues pointing out to the heterodimeric self-assembly of the intended pseudo[1] rotaxane. First, the NMR spectra for the mixture remained unchanged within the 5–0.08 mM concentration window. Furthermore, a linear correlation was found between the absorbance attributed to the charge-transfer band ( $\lambda_{max}$  = 470 nm), and the concentration of components on the same range, accounting for the non-occurrence of oligomeric species. Additionally, the COSY NMR of the mixture allowed for the observation of <sup>1</sup>H–<sup>1</sup>H correlation peaks between groups of signals that can be attributed (for instance, by analogy with



pseudorotaxane  $(\pm)$ - $S_{4a}$  and other similar inclusion complexes),<sup>[10,15-17]</sup> to a DHN moiety inserted into the cavity of metallacyclic receptor. Specifically, Figure 7 shows correlation peaks on the COSY NMR between 3 pairs of DHN doublets that can be clearly assigned to H<sub>4</sub>/H<sub>8</sub>, accounting for the appearance of at least 3 different conformers in slow interconversion for  $(\pm)$ -S<sub>6a</sub>. Conversely, the region on the spectra between 6–7 ppm conveniently lacks the appearance of signals attributable to a DHN moiety outside the cavity (see for instance Figure 4), suggesting that the homodimeric species (±)- $\boldsymbol{S}_{8a}$  is not favoured in this occasion. Finally, further evidence of the likely self-assembly of (±)- $\boldsymbol{S}_{6a}$  were obtained by studying the  $\boldsymbol{M}_2\text{-}$ directed self-assembly of  $(\pm)$ -L<sub>4</sub>/L<sub>5</sub>, which allowed for the identification by HR ESI-MS of the Pt(II) analogue  $(\pm)$ - $S_{6b}$ (Figure 3).

Reached this point in our study, we wondered whether the robust  $\pi$ -donor/acceptor characteristics of our designed matching pairs  $L_1/(\pm)-L_3$  and  $L_5/(\pm)-L_4$ , would be sufficient to promote the observed social self-sorting even in the absence of the directing force of the metal cations. In the case of  $L_1/(\pm)-L_3$ , we found that, as previously observed for  $L_1/(\pm)-L_2$ ,<sup>[10]</sup> the metal centers were imperative for the self-sorting leading to  $(\pm)$ -S<sub>5a,b</sub>. Consequently, <sup>1</sup>H-NMR experiments recorded within the concentration window studied for the self-assembly of those pseudo[1]rotaxanes, using equimolar mixtures of the abovementioned matching pairs were congruent with nothing but the sum of the individual spectra, accounting for the lack of intermolecular interactions between the complementary ligands on the absence of the Pd(II)/Pt(II) complexes. Needless to say, dilution experiments monitored by <sup>1</sup>H-NMR of the individual amphiphilic ligands (±)-L2 and (±)-L3, showed as well a concentration-independent behaviour on the concentration range studied.



Figure 7. Partial COSY NMR (400 MHz, D\_2O, r.t.) spectrum for (±)- $S_{6a}$  (2.5 mM (±)-L4, 2.5 mM  $L_5$  and 5 mM  $M_1$ ).

On the other hand, we found a profoundly different comportment for the diazapyrenium matching pair  $L_5/(\pm)-L_4$ . Whilst the <sup>1</sup>H-NMR spectrum in  $D_2O$  of  $L_5$  was found to be concentration-independent in the self-assembly concentration range, dilution experiments for the amphiphile  $(\pm)$ -L<sub>4</sub> showed a significant concentration dependence on the 2.5-0.04 mM range. Furthermore, it should be notice that, for instance, the <sup>1</sup>H-NMR of the species at 1.25 mM (Figure 8c), clearly shows a strong intramolecular donor-acceptor interaction, with protons H<sub>a-d</sub> on the diazapyrenium moiety being consistently shielded if compared with the non-functionalized analogue  $L_5$ , and those on the aromatic donor  $H_{2\text{--}4}\!/H_{6\text{--}8}$  substantially deshielded if compared with, for instance, free 1,5-DHN. Taken together, these facts pointed out to the dimerization of the amphiphile on the self-assembly concentration window producing  $((\pm)-L_4)_2$ . The non-linear fitting of the chemical shifts for  $(\pm)-L_4$  as a function of its concentration, allowed for the estimation of the dimerization equilibrium (narcissistic self-sorting) constant in water as  $K_{4\cdot4} = 439 \pm 32 \text{ M}^{-1}$  (see Supporting Information).

With this information in our hands, we proceeded to study whether the dimerization of  $(\pm)$ -L<sub>4</sub> can be precluded in the presence of the matching partner  $L_5$ , implying therefore an integrative social self-sorting of the pair even in the absence of the metal ion. As shown on Figure 8, the <sup>1</sup>H-NMR in D<sub>2</sub>O of a 1:1 mixture of both ligands at 1.5 mM gives rise to compelling changes on the chemical shifts of both species. The <sup>1</sup>H/<sup>13</sup>C nuclei of both partners on the 1:1 mixture could be assigned on the basis of 1D/2D NMR experiments,<sup>[14]</sup> clearly showing how the previously observed concentration-independent chemical shifts of L<sub>5</sub>, appear now greatly modified by the presence of its functionalized counterpart  $(\pm)$ -L<sub>4</sub>. In essence, the new resonances observed for  $\boldsymbol{L}_{\!\scriptscriptstyle 5}$  are consistent with a strong interaction with the DHN moiety of the amphiphile, with shielded relative chemical shifts for protons H<sub>a-d</sub> on the long side of the ligand, accounting for intermolecular  $\pi$ -stacking interactions. Interestingly, protons on the short side of  $L_5$  ( $H_{f-\alpha}$ ), appear deshielded



Figure 8.  $^1H$ -NMR spectra (500 MHz,  $D_2O,$  r.t.) for a) 2.5 mM  $L_5,$  b) 1.25 mM  $L_5,$  1.25 mM  $(\pm)$ -L\_4, and c) 2.5 mM  $(\pm)$ -L\_4.



compared with the free ligand, a clear evidence of the establishment of C–H··· $\pi$  interactions with the  $\pi$ -donor moiety of (±)-L<sub>4</sub>, a fact that in turn implies the creation of a hydrophobic (pseudo)cavity between the matching partners. The relative chemical shifts of (±)-L<sub>4</sub> in the presence of its matching pair, are as well consistent with the formation of the integrative species.

In order to estimate the extent of narcissistic vs social aggregation of the matching pair, we performed an <sup>1</sup>H-NMR titration experiment, keeping constant the global concentration of  $(\pm)$ -L<sub>4</sub> at 0.25 mM and varying that of L<sub>5</sub>. The nonlinear fitting of the observed chemical shifts for the ligands against the total concentration of  $L_{5'}^{[14]}$  was achieved explicitly considering the above-discussed dimerization process for  $((\pm)-L_4)_2$ . The obtained data fitted well to a competing equilibrium (see Supporting Information), where the amphiphilic ligand is consumed both on its dimerization an on the establishment of the heterodimeric species (integrative self-sorting) (±)- $L_4 \cdot L_5$  ( $K_{4.5} = 756 \pm$ 43 M<sup>-1</sup>). The selectivity of the social/narcissistic self-sorting process between  $(\pm)$ -L<sub>4</sub> and L<sub>5</sub> can be expressed by [Equation (1)] where  $K_{4\cdot4}$  and  $K_{5\cdot5}$  represent the equilibrium constants for the dimerization of  $(\pm)\text{-}L_4$  and  $L_5\text{,}$  respectively. It should be noted that the observed selectivity is due more to the very small self-association constant of  $L_5$  than to the fact that  $K_{4.5}$  is higher than  $K_{4\cdot 4}$ .<sup>[26]</sup>

$$K_{sel} = \frac{K_{4.5}^2}{K_{4.4} \cdot K_{5.5}} \tag{1}$$

#### Conclusion

In the work presented herein we have discussed the Pd(II)/Pt(II)directed self-assembly of structurally matching pairs of Nmonoalkyl-4,4'-bipyridinium-based ligands. The obtained results are consistent with our previously reported data,<sup>[10]</sup> suggesting the predominance of integrative social self-sorting processes in the designed systems, promoted by the enthalpic gain caused by the optimization of intermolecular interactions per selfassembled molecular receptor, and leading to the multicomponent self-assembly of pseudo[1]rotaxanes. Furthermore, we found that the fine-tuning of the structural features of the matching pairs, by implementing DNP-diazapyrenium donoracceptor interactions on the system, results on a situation where competitive narcissistic and integrative social self-sorting coexist without the aid of the metal centers. The small selfassociation constant of L<sub>5</sub> (narcissistic self-sorting), determines the prevalence of the integrative self-sorting process between  $(\pm)$ -L<sub>4</sub> and L<sub>5</sub>.

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### **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** host-guest systems • pi interactions • rotaxanes • self-sorting • supramolecular chemistry

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lacyclic receptors,<sup>[9–10,15–17]</sup> and in particular with those involving  $S_2$  and  $S_7$  and aromatic substrates,<sup>[16]</sup> we can anticipate that the improvement on the donor-acceptor interactions correlates quite well with the rate of exchange between interacting and non-interacting guest. In essence, the larger the aromatic surface of the host and/or guest, the slower this exchange regime on the NMR timescale.

- [23] In the metal-directed self-assembly of ditopic ligands,<sup>[24]</sup> the smallest macrocyclic species typically appears as the main product of the process under a given set of temperature and solvent conditions, only in a certain concentration window between the so-called *lsac* (lower self-assembly concentration) and *EM* (effective molarity),<sup>[25]</sup> since monomer and linear oligomers prefer to exist in the lower and higher concentration ranges, respectively. In the case of the Pd(II)-directed self-assembly of our *N*-monoalkyl-4,4'-bipyridinium-based ditopic ligands, the macrocyclic species typically appear as the main products of the self-assembly on the concentration window 10–0.1 mM.<sup>[9–10,15–17]</sup>.
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