

Supramolecular Chemistry | Hot Paper |

Nickel-Cornered Molecular Rectangles as Polycyclic Aromatic Hydrocarbon Receptors

Víctor Martínez-Agramunt, Sheila Ruiz-Botella, and Eduardo Peris*^[a]

Abstract: Two nickel-cornered organometallic metalla-rectangles containing a pyrene-linked-di-*N*-heterocyclic carbene have been prepared. The dimensions of one side of the rectangle were modulated by either using pyrazine or 4,4'-bipyridine. The two molecules were tested as hosts for the recognition of seven small polycyclic aromatic hydrocarbons (PAHs) in [D₆]acetone. By using ¹H NMR spectroscopy titrations, it could be established that the host-guest stoichiometries of the inclusion complexes formed were 1:1 for the pyrazine-based host, and 1:2 for the host containing bipyridine, in accordance with the larger dimensions of the latter. The molecular structure of the inclusion complex consisting

of the bipyridine-containing host and pyrene was determined by X-ray crystallography, which confirms the 1:2 host-guest stoichiometry of this species. The determination of the association constants indicate that the binding strengths are in the order: Perylene < naphthalene < phenanthrene < anthracene < pyrene < triphenylene, ranging from 130–4400 M⁻¹ in the case of the smaller host, thus indicating that larger PAHs show higher binding strengths than smaller ones, except for the case of perylene, which exceeds the size for an optimum dimensional fitting within the cavity. As a proof of concept, the pyrazine host was used as a PAH-scavenger in heptane.

Introduction

The basis for metallo-supramolecular design is the availability of rigid ligands with two or more binding sites, which in combination with suitable metals form symmetrical structures with a variety of shapes and sizes.^[1] Supramolecular coordination complexes (SCCs)^[2] are often referred to as “molecular flasks”,^[3] because they show well-defined nanoscopic cavities. It is precisely the presence of such cavities that makes SCCs suitable for important applications in catalysis,^[4] molecular recognition,^[5] the stabilization of highly reactive species,^[6] and as drug delivery/release vectors.^[7]

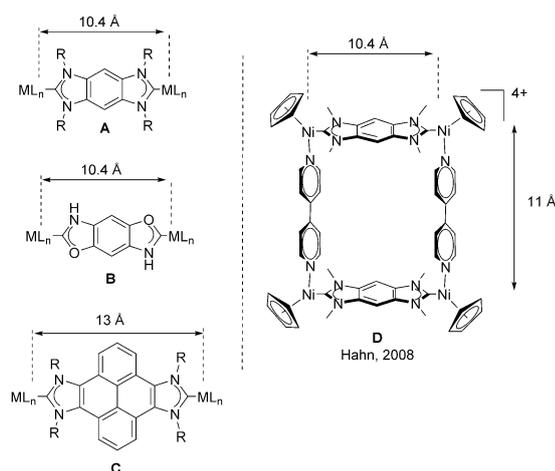
The structural outcome of metallo-supramolecular synthesis is largely dependent on the nature of the metal ions and ligands. From a design perspective, the ligand is arguably considered as the most important component, because its topological features and binding abilities determine the size, geometry and functionality of the resulting metallo-supramolecules. This, combined with the predictable and well-defined coordination geometries of transition metals, gives metallo-supramolecules some advantages over traditional organic receptors,^[8] which often require highly sophisticated multistep synthetic procedures to achieve similar goals.

Most of the known metallo-supramolecular molecules are based on the use of *N*- or *O*-donor Werner-type polydentate ligands. Only recently, organometallic ligands—largely based on poly-*N*-heterocyclic carbenes (NHCs)^[9]—have been used for the preparation of a diverse type of SCCs, including molecular squares, rectangles and triangles,^[10] cylinders^[11] and organometallic polymers.^[12] Most of the known organometallic molecular squares and rectangles are based on the use of the well-known benzo-di(imidazolylidene) ligand (**A**) described by Bielawski and co-workers in 2005.^[12e,13] The benzo-di(oxazolylidene) ligand (**B**), described by Hahn and co-workers, also allowed for the preparation of a number of molecular squares.^[10d,e,14] The same group recently described an example of a M₄L₄ molecular square with four bridging benzo-di(imidazolylidene)s, which was obtained by a single-step procedure.^[15] These examples demonstrate the great potential of Janus-di-NHCs for the construction of metallo-supramolecular assemblies, but also illustrate the limited number of organometallic ligands that are currently available for preparing metallo-supramolecular assemblies. In fact, the use of either **A** or **B** establishes a metal-to-metal separation of 10.4 Å, which in most cases is too small to build cavities of the appropriate size for hosting organic guests. This may be the reason why none of the aforementioned organometallic metallo-supramolecules have been used as receptors for organic molecules; this may also explain why organometallic host-guest chemistry is so rare, despite the increasing number of known organometallic assemblies. During the last few years, we developed a series of Janus di-NHC ligands in order to construct SCCs with longer metal-to-metal distances.^[16] We also found that these di-NHCs with extended polyaromatic linkers imparted unique catalytic

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properties that we ascribed to supramolecular interactions between aromatic substrates and the polyaromatic cores of the ligands.^[17] Because rectangle-like species have demonstrated unique binding abilities and selectivities for planar aromatic guests,^[8b] we thought that our nanosized Janus-di-NHCs may introduce interesting applications for host-guest chemistry, and for this reason we became interested in developing a series of molecular rectangles for the selective recognition of organic molecules. In particular, we predicted that the structural features of the pyrene-linked di-NHC ligand **C** (Scheme 1),^[16a]

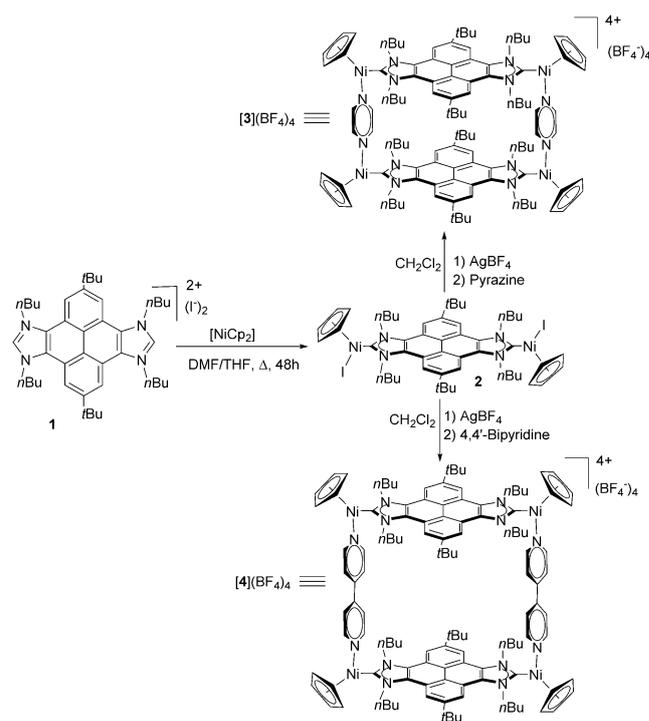


Scheme 1. **A** and **B**, Janus di-NHC used for the preparation of known molecular rectangles. **C**, the di-NHC used in this work. **D**, previously published nickel-cornered rectangle.

could be used for the preparation of molecular rectangles with the potential to recognize polycyclic aromatic hydrocarbons (PAHs) by means of π - π -stacking interactions. Low molecular weight PAHs ranging from naphthalene ($M_w = 128.16$) to coronene ($M_w = 300.36$) are hazardous materials that have gathered significant environmental concern.^[18] Smaller unsubstituted PAHs (2–3 rings) exhibit acute toxicity, whereas many of the 4- to 7-ring PAHs are less toxic but carcinogenic to a variety of organisms. Therefore, there is a great interest in developing host molecules for PAH detection. Several metallo-supramolecular rectangles have been used for the recognition of PAHs,^[19] although all the known examples refer to the Werner-type coordination cages with second- and third-row transition-metals. Based on these precedents, herein we describe the preparation of two nickel-cornered molecular rectangles based on the pyrene di(imidazolylidene) ligand **C**, for the selective recognition of a range of small PAHs.

Results and Discussion

The synthetic procedure that we used is depicted in Scheme 2. The reaction of the pyrene di(imidazolium) diiodide **1** with nickelocene in a mixture of DMF/THF afforded the dimetallic complex **2** in 73% yield. Then the reaction of complex **2** with pyrazine and two equivalents of AgBF_4 leads to the air-stable



Scheme 2. Synthesis of nickel-cornered rectangles.

tetranickel complex $[3](\text{BF}_4)_4$ in 75% yield. By following a similar procedure, but adding 4,4'-bipyridine instead of pyrazine, complex $[4](\text{BF}_4)_4$ was obtained in 80% yield. Complexes **2**, $[3](\text{BF}_4)_4$ and $[4](\text{BF}_4)_4$ were characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

The molecular structure of complex **2** was confirmed by single crystal X-ray diffraction (Figure 1). The molecule consists of a pyrene-linked di(imidazolylidene) connecting two nickel centers. The coordination sphere about the metals is completed by one iodine and one cyclopentadienyl ligand. The relative disposition of the two metal complex fragments is *anti*, with the two iodine ligands pointing in opposite directions. The metal complex fragments are oriented in the less-hindered position, with the Ni–I bonds quasi-perpendicular with respect to

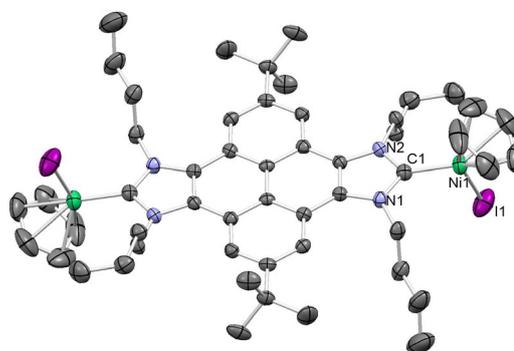


Figure 1. Molecular structure of complex **2**. Ellipsoids at 50% probability. Hydrogen atoms and solvent (chloroform) omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ni(1)–C(1) 1.890(3), Ni(1)–I(1) 2.4838(6), C(1)–Ni(1)–I(1) 96.60(11).

the plane of the imidazolylidene. The Ni–C_{carbene} distance is 2.131 Å, and the separation between the two metals is 12.989 Å, similar to the M–M distances of other dimetallic complexes bridged by the same pyrene di(imidazolylidene) ligand.^[16a,20]

We then tested our molecular rectangles [3](BF₄)₄ and [4](BF₄)₄ for the recognition of small PAHs. Our initial prediction was that the metal-to-metal distance established by the pyrene di(imidazolylidene) ligand of around 13 Å, should introduce a size cutoff of PAHs up to pyrene or triphenylene (4 rings), whereas larger PAHs such as coronene (7 rings), with a larger size of 11.3 Å, should not fit inside the cavity of either of the two rectangles. The choice of the *N*-heterocyclic linker (pyrazine or 4,4'-bipyridine), should determine whether one or two layers of the polyaromatic guests are accommodated inside the cavity, according to the Ni–Ni distances established along the heterocyclic linkers, which we estimated as 7 and 11 Å, for pyrazine and 4,4'-bipyridine, respectively. We also envisioned that the tetra-cationic nature of the two rectangles, together with the presence of the pyrene linker, should favor the incorporation of electron-rich PAHs through π – π stacking interactions.

The recognition abilities of complexes [3](BF₄)₄ and [4](BF₄)₄ were studied by ¹H NMR titration experiments, by monitoring the change in chemical shift of the ligand signals upon addition of solutions of the different polyaromatic guests. For our studies we chose [D₆]acetone, because it provided the best solubility for hosts and guests, and produced ¹H NMR spectra with sharp signals of the hosts. Most studies for the determination of the association constants between coordination cages and PAHs were performed in acetonitrile, but the recent shortage of this solvent and its higher toxicity makes acetone a much greener and convenient alternative,^[21] especially if further practical applications are pursued. The titrations were performed at constant concentrations of the hosts (typically 1 mM). In general, the addition of the solutions of the guests induced important perturbations in the ¹H NMR spectra, indicating the formation of inclusion complexes that showed fast kinetics on the NMR timescale. However, when [3](BF₄)₄ was used as host, the NMR titrations with the larger PAHs produced a significant broadening of the host signals, suggesting that the kinetics of aggregate formation occur on the NMR timescale. This observation is in agreement with the findings reported by Stoddart and co-workers, in the sense that smaller PAHs form inclusion complexes faster than the larger ones.^[22]

Figure 2 shows the ¹H NMR spectra resulting from the titration of [3](BF₄)₄ with naphthalene. As can be observed, the addition of guest to the host solution produces a significant upfield shift of the host pyrene linker proton signals, together with a gradual downfield shift of the pyrazine proton signals. This behavior clearly confirms that the guest occupies the hollow gap in the molecule, which is the only region where the chemical shifts of the two linkers of [3](BF₄)₄ can be simultaneously perturbed. The stoichiometry of the host–guest complexes formed was found to be 1:1, for all the cases in which host [3](BF₄)₄ was used. This assumption was based on the analysis of the binding isotherms resulting from the titrations of host

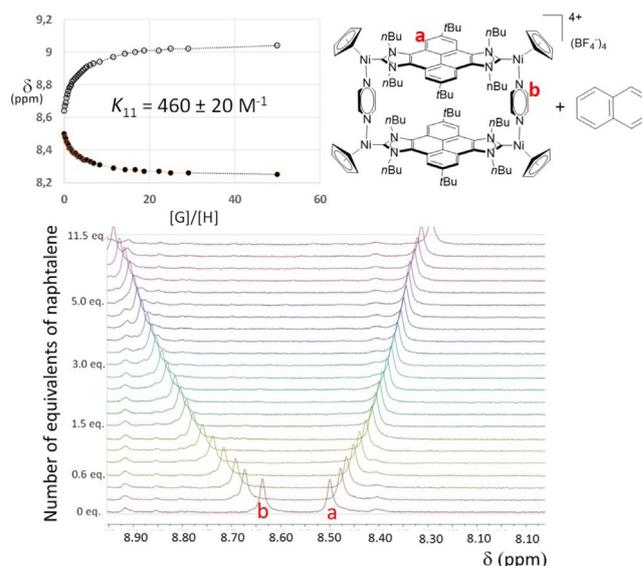


Figure 2. Representative region of the ¹H NMR (400 MHz) spectra of the titration of [3](BF₄)₄ with naphthalene. The spectra were recorded at a constant concentration of [3](BF₄)₄ (1 mM). The plot represents the binding isotherm, with the resulting association constant obtained from the nonlinear regression analysis.

[3](BF₄)₄ with all the polyaromatic guests. In all cases, the 1:1 stoichiometry gave the lowest residuals compared to any other stoichiometry.^[23] A Job plot was also carried out to confirm the formation of the 1:1 complex (Figure 3 shows a representative Job plot for the case of [3](BF₄)₄ and triphenylene). The association constants (K_{11}) were calculated by global nonlinear regression analysis.^[23,24]

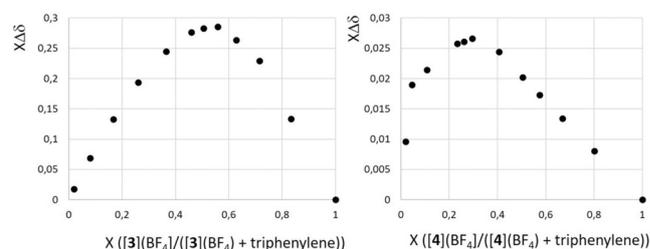


Figure 3. Left: Job plot for the inclusion complex formed between [3](BF₄)₄ and triphenylene (1:1 stoichiometry). Right: Job plot for the inclusion complex formed between [4](BF₄)₄ and triphenylene (1:2 stoichiometry).

A different situation arises when [4](BF₄)₄ is used as host. For this molecule, we performed the titrations with pyrene and triphenylene. In both cases, the titration curves were best fitted to a 1:2 host–guest stoichiometry. The corresponding Job plots also confirmed this stoichiometry (Figure 3). This result is consistent with the larger size of the cavity formed when 4,4'-bipyridine was used instead of pyrazine, which should allow two guests molecules to be accommodated within the hollow space of the rectangle.

The analysis of the ¹H NMR spectra also allowed for the determination of the host–guest association constants, which are shown in Table 1. The results indicate that the binding affinities

Entry	Host	Guest	H:G	K_{11} [M^{-1}]	K_{12} [M^{-1}]
1	[3](BF ₄) ₄	naphthalene	1:1	460 ± 20	–
2	[3](BF ₄) ₄	phenanthrene	1:1	1540 ± 110	–
3	[3](BF ₄) ₄	anthracene	1:1	2600 ± 350	–
4	[3](BF ₄) ₄	triphenylene	1:1	4400 ± 500	–
5	[3](BF ₄) ₄	pyrene	1:1	3450 ± 400	–
6	[3](BF ₄) ₄	perylene	1:1	130 ± 25	–
6	[4](BF ₄) ₄	triphenylene	1:2	181 ± 30	40 ± 10
7	[4](BF ₄) ₄	pyrene	1:2	18 ± 3	4 ± 1
8	[3](BF ₄) ₄	coronene	–	–	–

[a] K_{11} and K_{12} values calculated by global nonlinear regression analysis.^[23,24] Titrations were carried out using constant concentrations of host (1 mM in [D₆]acetone at 298 K). Errors refer to the regression fittings.

of the PAHs guests are in the order perylene < naphthalene < phenanthrene < anthracene < pyrene < triphenylene. The binding constants for [4](BF₄)₄ are in accordance with a classical stepwise non-cooperative binding, for which $K_{11} \approx 4K_{12}$, as expected for a situation in which the binding sites are identical and independent of each other.^[25] It has to be taken into account that, despite the good fittings, the association constants related to [4](BF₄)₄ have to be taken as a crude estimation due to their low values, which indicate a very low degree of inclusion complex formation throughout the titration.

The association constants for [3](BF₄)₄ are higher than those observed for [4](BF₄)₄, probably as a consequence of the closer distance between the two pyrene walls in [3](BF₄)₄, which facilitates an optimized π -stacking interaction with the planar PAH molecules. According to Rebek's rule, the binding between the host and the guest is expected to be favorable when the guest occupies about 55% of the host volume.^[26] However, this rule has exceptions when the structures are open to the exterior, as in a molecular rectangle. Also, it is difficult to make an estimation of the internal (or guest-accessible) volumes of our molecules [3](BF₄)₄ and [4](BF₄)₄. For hosts with very large voids, Stoddart found that the affinity between the host and the PAHs guest followed and approximately linear trend of increasing $\log K_a$ values with increasing number of π -electrons in the guests.^[22,27] As the PAH π -electron density increases, the π - π binding between host and guest becomes more effective, and the association constant increases. This situation is also observed for the affinity trends shown by [3](BF₄)₄, although in our case we found a trend between the representation of the association constants and the number of guest π -electrons, as shown by the plot shown in Figure 4a. An excellent linearity is followed by guests in the range of 10–18 π -electrons, except for the case of phenanthrene, which probably deviates from the optimum face-to-face π - π overlap with [3](BF₄)₄. These PAHs have a suitable size to fit within the gap of the host. Perylene, with 20 π -electrons and a larger size than pyrene and triphenylene, exceeds the optimum volume to fit within the cavity of the host. In this case, the favorable π - π -stacking interactions may be accompanied by an unfavorable steric strain, which turns into a reduced binding constant. The overall

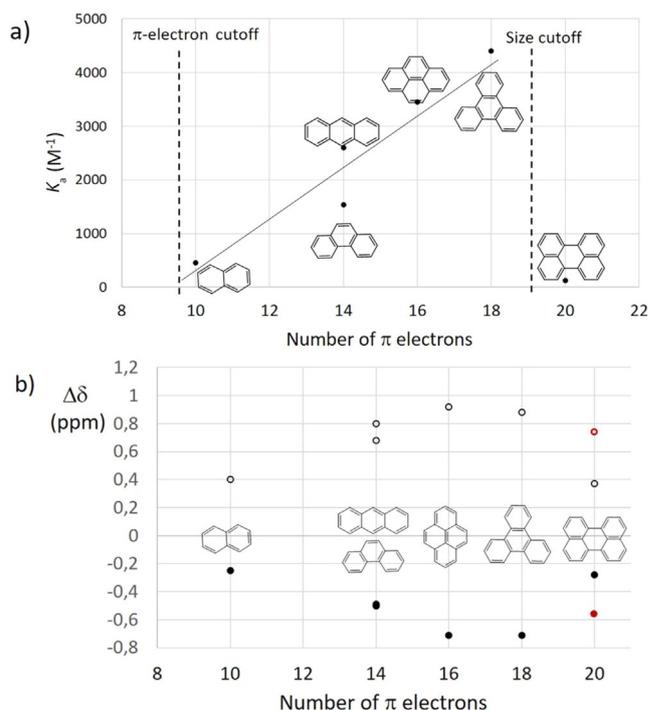


Figure 4. a) Plot of the association constants (K_a) in [D₆]acetone between [3](BF₄)₄ and the number of π -electrons of the six PAHs used in this study (the straight line is just to guide the eye). b) Maximum chemical shift differences (experimental) plotted against the number of electrons present in the different PAHs. The values in red represent the estimated maximum chemical shift difference, as obtained from the non-linear regression fitting.

picture is that [3](BF₄)₄ behaves as an excellent host for the selective recognition of the smaller PAHs, with a higher affinity to the four-fused-ring PAHs, triphenylene and pyrene. This selectivity is determined by the stereoelectronic nature of the PAHs, which establish clear interaction and size limits. In a similar line, the plot of the maximum chemical shift differences between the pyrene core and the pyrazine ligand protons of host [3](BF₄)₄ reflects a similar trend (Figure 4b), although in this case the chemical shift differences found for the two 14 electron PAHs (phenanthrene and anthracene) are almost identical. In the case of perylene, the experimental value obtained is lower than the value estimated by regression analysis (red dots in Figure 4b), because signal saturation was not reached during the NMR titration for this guest. Overall, the plot illustrates the combined effect of the binding affinities together with the shielding/deshielding effect of the PAH guests.

In the same direction, the ¹H NMR titrations carried out with coronene as guest did not show any signal shifting; thus we assumed that our hosts do not show any binding affinity with coronene due to its larger size, which exceeds the hollow space of both hosts. Similarly, the titrations using benzene as guest demonstrated that the binding affinity of our two metal-rectangles to benzene is negligible. These findings illustrate the great selectivity of our rectangles to bind only to smaller PAHs.

Single crystals suitable for X-ray analysis of [4](BF₄)₄⋅(pyrene)₂ were obtained by slow evaporation of a so-

lution of the aggregate in acetone. The molecule crystallized in a triclinic $P\bar{1}$ space group. The metalla-rectangle is composed by two dinuclear $[\text{Ni}_2\text{Cp}_2(\mu\text{-pyrene-di}\{\text{imidazolylidene}\})]^{2+}$ clips connected by two 4,4'-bipyridine ligands (Figure 5). The Ni–Ni

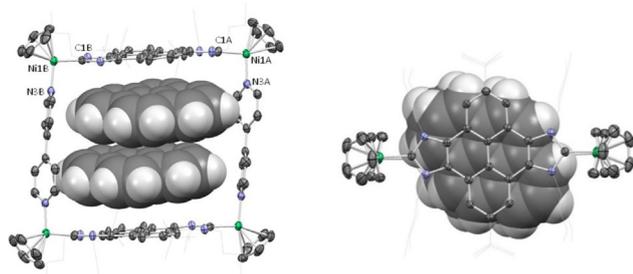


Figure 5. Two perspectives of the molecular structure of complex $[\mathbf{4}](\text{BF}_4)_4\text{C}(\text{pyrene})_2$. Ellipsoids at 50% probability. Hydrogen atoms, solvent (acetone) and counter-anions (BF_4^-) omitted for clarity. The molecules of pyrene are represented with the space-filling diagrams, and the *n*-butyl and *tert*-butyl groups of $[\mathbf{4}](\text{BF}_4)_4$ are represented in the wireframe form. Selected bond distances (Å) and angles ($^\circ$): Ni(1A)–C(1A) 1.905(4), Ni(1A)–N(3A) 1.908(3), Ni(1B)–C(1B) 1.892(4), Ni(1B)–N(3B) 1.897(3), C(1A)–Ni(1A)–N(3A) 97.88(15), C(1B)–Ni(1B)–N(3B) 94.46(16).

distances are 12.941 and 10.876 Å through the pyrene di-NHC and the 4,4'-bipyridine bridging ligands, respectively. The N–Ni–C angles are significantly larger than 90° , and the two parallel pyrene di-NHC ligands are slightly displaced relative to each other. The metalla-rectangle contains two parallel-displaced molecules of pyrene, which are separated from each other by 3.682 Å. The torsion angle between the planes of the pyrene molecules and the pyrene core of the di-NHC ligand is 6.21° , and the average distance between these two fragments is 3.79 Å. These parameters indicate that an effective π – π -stacking interaction is established both between the two pyrene guest molecules, and between the pyrene guests and the pyrene core of the di-NHC ligand. The longest axis of the pyrene molecules are disposed at an angle of 29.71° with respect to the axis formed by the two nickel centers linked by the di-NHC ligand.

Finally, we tested $[\mathbf{3}](\text{BF}_4)_4$ as a PAH-scavenger. For this, we dissolved 1.1×10^{-3} mmol of the PAH in heptane (0.4 mL) together with anisole as a nonbinding standard. For the experiment performed with pyrene, the irradiation of the solution with a UV lamp (365 nm) generates a strong blue emission due to the presence of the fluorescent PAH. Then $[\mathbf{3}](\text{BF}_4)_4$ (1.3×10^{-3} mmol) was added to the solution, and the suspension was sonicated over 3 h. UV irradiation of the resulting suspension showed that the emission disappeared, thus indicating that pyrene had been extracted from the heptane solution (Figure 6) by forming the insoluble inclusion complex $[\mathbf{3}](\text{BF}_4)_4\text{Cpyrene}$. In order to quantify the removal of pyrene, the solid was filtered off and the filtrate solution was examined by ^1H NMR spectroscopy. The analysis indicated that the majority of pyrene was removed from the original heptane solution (> 90% removed, Figure 7). In the case of the experiment carried out with $[\mathbf{3}](\text{BF}_4)_4$ and naphthalene, the analysis of the so-



Figure 6. Samples irradiated with UV light (365 nm). Both tubes contain 1.1×10^{-3} mmol of pyrene in 0.4 mL of heptane. The tube on the left also contains 1.3×10^{-3} mmol of $[\mathbf{3}](\text{BF}_4)_4$, and the picture was taken after 1 h of sonication. The image shows how the addition of $[\mathbf{3}](\text{BF}_4)_4$ quenches the emission of pyrene.

lution after being sonicated for three hours indicated that less than 10% of naphthalene remained in the heptane solution, thus this smaller PAH was extracted to a similar extent as pyrene. In order to compare the extracting ability of this scavenger, more pyrene (1.1×10^{-3} mmol) was added to the suspension containing $[\mathbf{3}](\text{BF}_4)_4\text{Cnaphthalene}$, and the suspension was subjected to sonication for another three hours. The NMR spectroscopic analysis of the resulting solution indicated that naphthalene was replaced by pyrene inside the scavenger

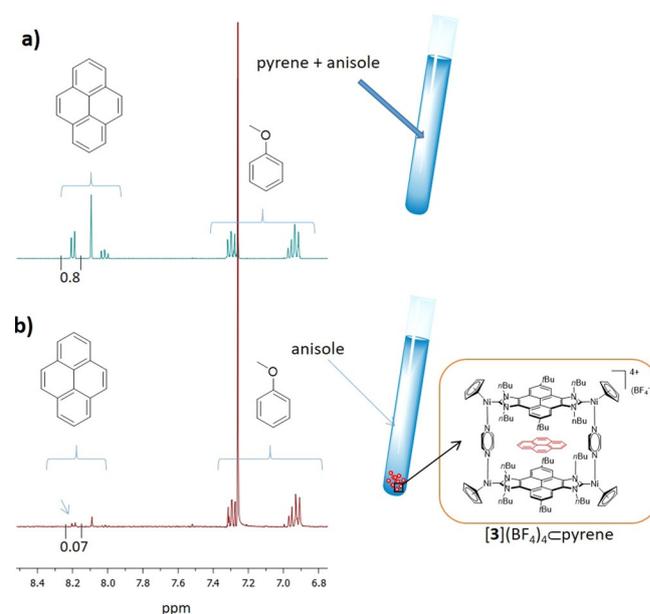


Figure 7. Selected region of the ^1H NMR spectra (CDCl_3 , 400 MHz) of the samples prepared for analysis of the scavenging properties of $[\mathbf{3}](\text{BF}_4)_4$. a) ^1H NMR spectrum of the sample before addition of $[\mathbf{3}](\text{BF}_4)_4$. b) ^1H NMR spectrum of the sample after addition of $[\mathbf{3}](\text{BF}_4)_4$ and after 3 h of sonication. The numbers below both spectra indicate the integrals of the reference signals of pyrene. The flux diagram indicates the experimental procedure.

(Figure 8). This selectivity experiment indicates that, in accordance with the affinity studies performed by ^1H NMR titrations, $[\mathbf{3}](\text{BF}_4)_4$ shows higher affinity to pyrene under these experimental conditions.

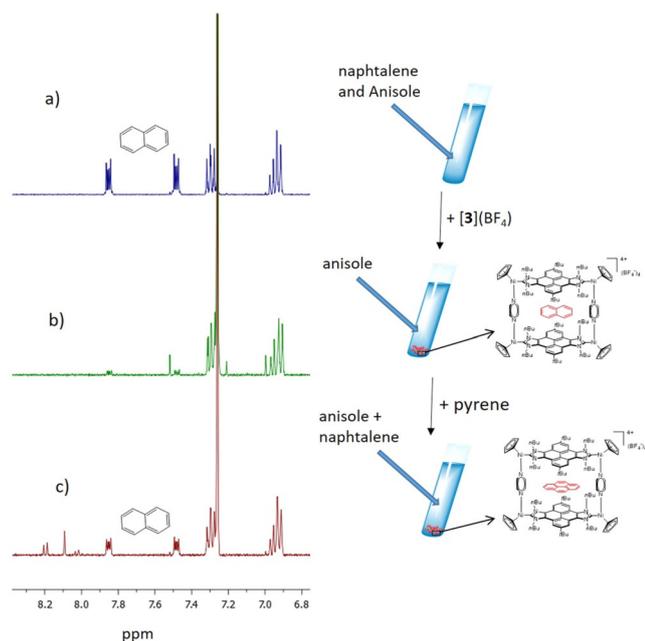


Figure 8. Selectivity experiment of extraction of naphthalene and pyrene. a) ^1H NMR spectrum of the sample containing naphthalene before addition of $[\mathbf{3}](\text{BF}_4)_4$. b) ^1H NMR spectrum of the sample after addition of $[\mathbf{3}](\text{BF}_4)_4$ and after 3 h of sonication. c) ^1H NMR spectrum of the sample after addition of pyrene and after 3 h of sonication. All experiments at room temperature. The sequence of images illustrate how $[\mathbf{3}](\text{BF}_4)_4$ scavenges naphthalene from the solution, and then how pyrene replaces naphthalene from the inclusion complex formed.

Conclusion

In summary, we prepared two new nickel-cornered supramolecular coordination rectangles using a pyrene bis-NHC ligand. The length of one of the sides of the rectangle was modified by using pyrazine or 4,4'-bipyridine. The two rectangles were used as receptors for the recognition of seven, potentially harmful, polycyclic aromatic hydrocarbons. The rectangle with pyrazine was able to host one guest molecule, whereas the rectangle with bipyridine was able to host up to two guest molecules. The binding constants were determined by means of ^1H NMR titration in $[\text{D}_6]$ acetone, and higher affinities were found for the smaller PAHs. The highest binding constants were produced by the inclusion complexes with pyrene and triphenylene, probably as a consequence of their best dimensional matching. A relationship between the size of the PAH and the binding constant could be established by correlating the number of electrons of the guest with their association constants.

An important achievement of our work is that we were able to use both rectangles as effective PAH scavengers in heptane. The PAH is trapped inside the receptor, and its disappearance from the solution can be detected by simply irradiating the so-

lution with a UV lamp (in the case of pyrene), and quantified by ^1H NMR spectroscopy. Considering the harmful effects of many of the smaller PAHs in the environment, we believe that these findings may have important implications for providing effective ways for the extraction of PAHs from apolar organic solvents. The introduction of metal centers in the design of molecular receptors may provide some benefits compared to the use of the more widely used organic-based receptors, because coordination chemistry often provides predictable and well-defined structures to create tailored metallacycles for the dimensional matching of PAHs. In our case, the introduction of nickel in the structure of the receptor introduces further benefits, firstly because this metal is inexpensive compared to the most widely used metal cages that use noble transition metals, and secondly because nickel centers in organometallic complexes often behave as reversible redox centers, thus the affinity properties of the molecule could be modulated electrochemically. This, together with the existing number of rigid di- and tri-NHC ligands that now can be found in the literature, which could enlarge the number of rectangles with various shapes and sizes, opens up a vast research field that hopefully inspires the work of future researchers in the area of metal-based PAH receptors and scavengers.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: host-guest systems · nickel · polycyclic aromatic hydrocarbons · scavengers · supramolecular coordination complexes

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