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Platinum-Based Organometallic Folders for the Recognition of Electron-Deficient Aromatic Substrates

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Dedicated to the Laboratoire Hétérochimie Fondamentale et Appliquée-LHFA (CNRS-Paul Sabatier University) on the occasion of its 50th anniversary

Abstract: A series of platinum complexes with *cis*-oriented polyaromatic N-heterocyclic carbene ligands were prepared and characterized. The relative disposition of the polyaromatic ligands about the metal cause these compounds to behave as metallofolders, featuring a cavity defined by the void space between the polyaromatic functionalities. The complexes were used as receptors of organic molecules, whereby selective affinity was displayed for electron-deficient aromatic substrates, such as 1,2,4,5-tetracyanobenzene (TCNB), 2,4,7-trinitro-9-fluorenone (TNFLU), and 1,4,5,8-naphtalenetetracarboxylic dianhydride (NTCDA). The binding affinities of two of the metallofolders with these substrates were determined by means of ^{1}H NMR titrations. Electrospray mass spectrometry (ESI-MS) was also used to assess the affinities. The molecular structure of one of the platinum folders was determined in the presence of TCNB, showing the clear interaction between this guest molecule and the folder formed by the two mutually *cis*-oriented polyaromatic ligands. This work demonstrates how the presence of the mutually *cis*-oriented polyaromatic ligands may be a very useful tool for the preparation of metal-based receptors.

Introduction

Metallosupramolecular chemistry was defined by Constable in 1994 as chemistry involving the combination of bridging organic ligands with metal units in order to synthesize discrete or polymeric assemblies.[1] Hence, the basis for metallosupramolecular design is the availability of (often rigid) ligands with two or more binding sites that are able to combine with suitable metal fragments to form symmetrical structures with a variety of shapes and sizes.[2] The two most commonly used strategies for metallosupramolecular design are based on directional bonding and symmetry interactions,[3] both of which rely on the combination of polytopic rigid ligands and metal fragments with available coordination sites. The mixing of soluble metal and ligand precursors results in the formation of metal–ligand bonds that generate the thermodynamically favored products in a process known as coordination-driven self-assembly;[2b,3c,g,4] for this reason, metallosupramolecules are often referred to as supramolecular assemblies. The resulting products display highly symmetrical structures with well-defined cavities,[5] which impart unique reactivity and suitability towards applications in catalysis,[6] molecular recognition,[7] and the stabilization of highly reactive species.[8] Most efforts in the design of metallosupramolecules are based on forming well-defined hydrophobic cavities, thereby mimicking enzymes.[9] For the formation of the cavities, an array of several metals is needed; this is the reason why metal-organic molecules with cavities (metallocavitands) have been defined as "multimetallic complexes", whereby metal coordination is necessary for cavity formation.[5b] Therefore, by definition, metallocavitands bearing only one metal are rare, and mostly consist of metal-based molecular tweezers.[10]

We recently described a series of N-heterocyclic carbene (NHC)-based cylinder-like structures with hollow central cavities, which were prepared by a metal-controlled self-assembly methodology.[11] Parallel to this research, we also designed a series of di- and tritopic NHC ligands bearing rigid polyaromatic linkers,[12] and found that the catalytic performances of the corresponding metal complexes were highly influenced by supramolecular effects, which we attributed to the π–π stacking interactions between the polyaromatic spacers of the ligands and the aromatic substrates.[13] In order to study the nature of these supramolecular interactions, a series of complexes with monodentate NHC ligands with rigid polyaromatic backbones were obtained,[14] and by well-known host-guest chemistry approaches, we were able to determine the nature

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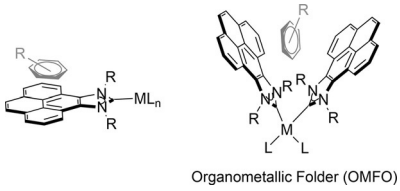
of the supramolecular interactions, and also quantify the extent of the non-covalent binding.[14b] The binding affinities that we found between the π-stacking additives and the metal complexes were low,[12d,14b] because the host–guest interactions were produced on the open surface of the metal complex, rather than in the interior of a cavity. From our point of view, these results established the basis for the use of monometallic complexes as receptors for molecular recognition, as an alternative to using the common self-assembly polymetallic architectures. We thought that we could improve the binding affinities (and thus the receptor properties) of monometallic compounds by building a well-defined pocket by coordinating two polyaromatic-based ligands *cis* to each other in a pseudo-square planar metal complex (Scheme 1). The resulting folder-



Scheme 1. Two systems with polyaromatic NHC ligands.

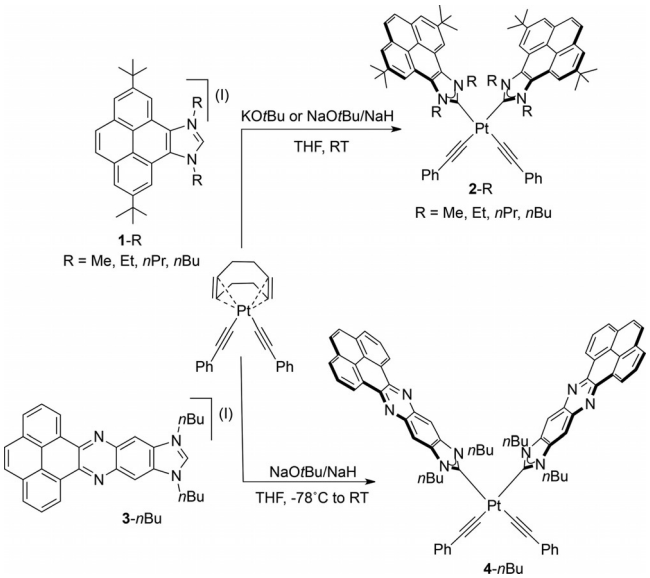
shaped complex, or organometallic folder (OMFO), should show enhanced guest affinity within a cavity formed by two mutually large *cis*-oriented polyaromatic ligands.

We herein describe a family of *cis*-platinum(II) complexes with pyrene- and phenanthrophenazine-NHC ligands, which we used as receptors for a series of organic molecules. This demonstrates how the presence of the *cis* polyaromatic ligands constitutes a very useful tool for the preparation of metal-based receptors.

Results and Discussion

The complexes prepared in this work contain a platinum center with two *cis*-NHC ligands decorated with a pyrene or a phenanthrophenazine fragment. The resulting molecules display a folder-type structure, in which the two NHC ligands (functionalized with the rigid polyaromatic fragment) define the void space. The depth of the folder is defined by the nature of the polyaromatic ligand; it is therefore deeper in the case of the phenanthrophenazine-substituted imidazolylidene. The pyrene-imidazolium salts **1**-R (R = Et, *n*Pr, or *n*Bu) were obtained according to the method previously described for **1**-Me.[15] The reaction of **1**-R with *cis*-[Pt(CCPh)$_2$(COD)] (CCPh = phenylacetylide, COD = 1,5-cyclooctadiene) in the presence of a base (see Scheme 2) in THF, afforded the *cis*-pyrene-NHC Pt^{II} complexes **2**-Me, **2**-Et, **2**-*n*Pr and **2**-*n*Bu in moderate to excellent yields.

Complexes **2**-R were successfully characterized by NMR spectroscopy, mass spectrometry (ESI-MS) and elemental analyses. The NMR spectra of all three complexes were consistent with the twofold symmetry of the molecules. The ^{13}C NMR spectra showed the diagnostic signal due to the presence of



Scheme 2. Synthesis of the complexes.

the metallated carbene carbon atoms at 178.1, 178.1, 178.6 and 178.3 ppm, and the signals due to the metallated carbons of the acetylide appeared at 107.2, 107.7, 106.9 and 106.9 ppm for **2**-Me, **2**-Et, **2**-*n*Pr and **2**-*n*Bu, respectively.

By using the same synthetic protocol, but using the phenanthro[4,5-abc]phenazine-imidazolium salt **3**-*n*Bu, complex **4**-*n*Bu was obtained in 45% yield. The NMR spectra of the complex were consistent with its binary symmetry. The ^{13}C NMR spectrum showed the signal for the magnetically equivalent carbene carbons at 190.5 ppm. The electrospray mass spectrum of the complex displayed a peak at *m*/*z* 1333.6, attributed to $[M+Na]^+$.

The molecular structure of **2**-Me was confirmed by single crystal X-ray diffractometry (Figure 1, left). The molecule consists of a platinum center with two pyrene-imidazolylidene ligands and two phenylacetylides in a *cis* disposition. The two pyrene-imidazolylidenes and the two phenylacetylides are sym-

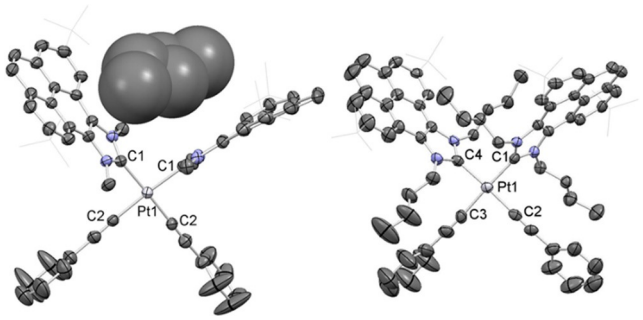
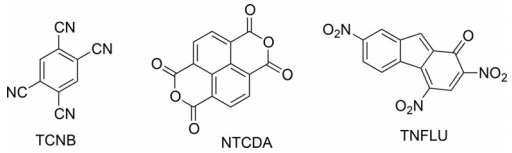


Figure 1. Molecular structures of complexes **2**-Me (left) and **2**-*n*Bu (right). Ellipsoids at the 50% probability level. *tert*-Butyl groups shown as wireframes. Hydrogen atoms omitted for clarity. In **2**-Me two molecules of $CHCl_3$ omitted, and hexane is represented in the space-filling diagram. Selected bond distances (Å) and angles (°) for **2**-Me: Pt(1)–C(1) 2.041(4), Pt(1)–C(2) 2.031(5), C(2)–C(3) 1.163(7), C(1)-Pt(1)-C(1) 92.8(2), C(2)-Pt(1)-C(2) 89.4(3). For **2**-*n*Bu: Pt(1)–C(1) 2.048(4), Pt(1)–C(4) 2.027(4), Pt(1)–C(2) 2.016(5), Pt(1)–C(3) 2.037(5), C(1)-Pt(1)-C(4) 92.00(16), C(2)-Pt(1)-C(3) 86.99 (17).

metry-related. The Pt–C(carbene) bond distance is 2.041(4) Å. The torsion angle formed by the imidazolylidene ring and the metal coordination plane is 66.95°, which is far from being perpendicular. The pyrene fragments of the carbene ligands show a bow-shaped distortion, in which their concave sides are facing each other. Interestingly, one molecule of hexane occupies the cavity formed by the two pyrene-imidazolylidene ligands, indicating that the pocket generated by these two ligands tends not to remain empty. This suggests that this folder-type molecule may be used as a host in the recognition of selected organic molecules. This structure can be compared with the molecular structure of complex **2**-*n*Bu (Figure 1, right). In this case, the average torsion angle established between the pyrene-imidazolylidene ligands and the coordination plane is 66.92°, very similar to that found in **2**-Me. The Pt–C(carbene) bond distances are 2.027(4) and 2.048(4) Å. Interestingly, the folder formed by the two pyrene-imidazolylidene ligands does not trap a solvent molecule, but it does not remain empty, because two N-*n*Bu wingtips from each of the imidazolylidene ligands occupy the void space of the cavity.

The ^{1}H NMR spectra of **2**-Me and **2**-*n*Bu were recorded in $CDCl_3$, C_6D_6, and [D_6]DMSO. The ^{1}H NMR spectra of **2**-Me were concentration-dependent in $CDCl_3$ and C_6D_6. As the concentration of the complex increased, the signals associated to the protons of the pyrene ring were shifted upfield, and those related to the phenyl ring of the phenylacetylide ligand were shifted downfield, as a consequence of the formation of self-associated assemblies. Plotting the chemical shift changes versus the concentration of the complexes allowed us to calculate the dimerization constants. These constants were 40 and 3900 M^{-1}, for the dimerization of **2**-Me in $CDCl_3$ and C_6D_6, respectively (see Supporting Information for more details). These results suggest that the association constants decrease with the polarity of the solvent, in the order $C_6D_6 > CDCl_3 >$ [D_6]DMSO, indicating the increased ability of polar solvents to solvate the planar electron-rich surfaces of the pyrene-functionalized complex. This affinity of the polar molecules of the solvent with the complexes is also reflected by the mass spectra of complexes **2**-Me and **2**-*n*Bu in DMSO, which in all cases displayed intense peaks assigned to $[M+\text{DMSO}+\text{Na}]^+$. For the case of **2**-*n*Bu, we observed that the ^{1}H NMR spectra did not show concentration dependence in any of the three solvents used, therefore suggesting that self-association for this complex is negligible.

We thought that the pyrene fragments in complexes **2**-Me, **2**-*n*Bu and **4**-*n*Bu, could provide an electron-rich environment that could be used for the recognition of electron-deficient aromatic guests. Since the two metal complexes with the *n*Bu substituents showed a reduced tendency to self-associate, we considered **2**-*n*Bu and **4**-*n*Bu to be the best choices of host. The aromatic guests that we chose for our study were 1,2,4,5-tetracyanobenzene (TCNB), 2,4,7-trinitro-9-fluorenone (TNFLU), and 1,4,5,8-naphtalenetetracarboxylic dianhydride (NTCDA) (Scheme 3). For the titrations, we chose [D_6]DMSO as the optimum solvent, because it provided the highest solubility of all guests used. TNFLU is also very soluble in chloroform, thus for this guest we also performed the titration in $CDCl_3$ in order to compare the result with that obtained in [D_6]DMSO.



Scheme 3. Electron-deficient aromatic guests used in this study.

Some interesting features about the structures of the host–guest complexes could be directly extracted from the ^{1}H NMR spectra taken from our titration experiments. Figure 2 shows some representative spectra from the titration of **4**-*n*Bu with TNFLU in $CDCl_3$. As can be seen from the spectra, the addition of the guest resulted in an upfield shift of the signals due to the protons of the phenanthrophenazine fragment of the NHC ligand (a, b, c, d and e), whereas the signals due to the protons of the phenylacetylide remained unchanged. A maximum negative shift of 0.26 ppm was achieved for the case of proton a. This result is consistent with the interaction of the guest with the polyaromatic fragments of the NHC ligands within the inner cavity of the metallofolder, rather than with the phenyl ring of the phenylacetylide. A π–π stacking interaction between the polyaromatic moiety of the NHC ligand and the molecule of TNFLU could be the driving force for the encapsulation. Similar results could be obtained for the titrations with all other guests, and for the titrations using complex **2**-*n*Bu.

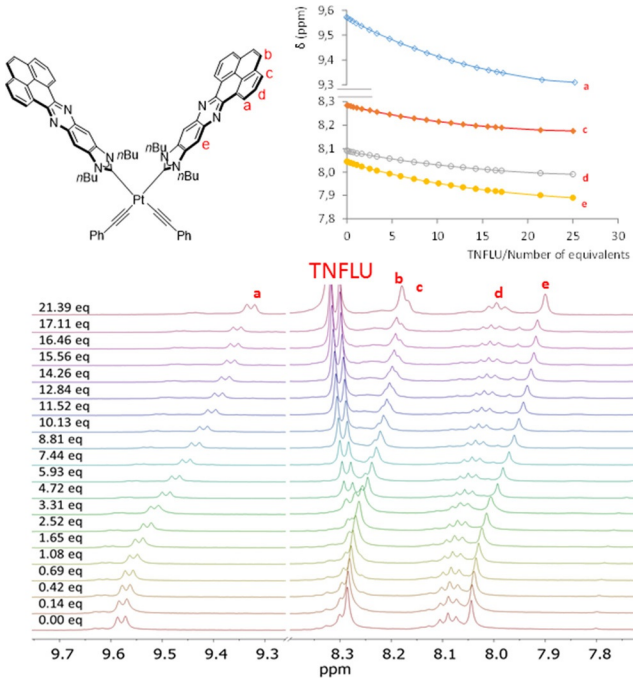


Figure 2. Representative region of the ^{1}H NMR (500 MHz) titration spectra of **4**-*n*Bu with TNFLU in $CDCl_3$. The spectra were recorded using a constant concentration of **4**-*n*Bu (1 mM) at 298 K. The inset plot represents the binding isotherms.

Analysis of the ^{1}H NMR titrations allowed the stoichiometry and association constants (K_a) of the host–guest adducts to be determined.[16] The analysis of the binding isotherms showed that the curve fittings were best represented by the formation of 1:1 complexes. This conclusion was also supported by the fact that fitting to a 1:1 stoichiometry gave the lowest residuals compared to other potential stoichiometries. The 1:1 association constants, K_{11}, were calculated by global nonlinear regression analysis, in which all protons showing chemical shift variations were simultaneously included.[16a,17] The association constants that we obtained are shown in Table 1. In most cases, the titrations were performed in [D$_6$]DMSO, in which the guests showed higher solubility. Only in the case of the titration of TNFLU could the experiments also be carried out in $CDCl_3$, due to its higher solubility. For the titration of **4**-*n*Bu with TCNB in DMSO, the chemical shift variations were so low ($\Delta\delta_{max} \approx 0.04$ ppm) that we could not determine an accurate value of the association constant. The association constants were higher in $CDCl_3$ than in [D$_6$]DMSO, in agreement with the higher ability of DMSO to solvate the electron-rich surfaces of the ligands in **2**-*n*Bu and **4**-*n*Bu (compare entries 2 and 3 for titrations with TNFLU). As can be seen from the results, both **2**-*n*Bu and **4**-*n*Bu show low to moderate affinities for electron-deficient aromatic substrates ($1\ M^{-1} > K_{11} > 22\ M^{-1}$), and also show no tendency to bind an electron-rich polyaromatic substrate such as pyrene. The metallofolder with a larger cavity, **4**-*n*Bu, consistently produced higher binding constants. Among the electron-deficient substrates, TNFLU gave the highest association constants for both complexes under study, as expected according to its higher electron deficient character compared to the rest of the substrates. On the contrary, TCNB showed the lowest (measurable) affinity. It is worth mentioning that for the titrations with this guest, the phenyl ring proton signals from the phenylacetylide ligands were also upfield shifted. This indicates that for TCNB, the guest interacts simultaneously with the inner part of the folder (formed by the two pyrene-imidazolylidene ligands), and also with the phenylacetylide ligands.

Table 1. Binding constants of **2**-*n*Bu and **4**-*n*Bu with different electron-deficient arenes (DMSO, 25 °C).[a]

Entry	Guest	Solvent	K_{11}, [M^{-1}] **2**-*n*Bu	**4**-*n*Bu
1	TCNB	[D$_6$]DMSO	1 ± 0.5[b]	n.d.[c]
2	TNFLU	[D$_6$]DMSO	9 ± 1	22 ± 1
3	TNFLU	$CDCl_3$	21 ± 1	47 ± 1
4	NTCDA	[D$_6$]DMSO	8 ± 1	10 ± 1
5	pyrene	[D$_6$]DMSO	≈ 0	≈ 0

[a] K_{11} values calculated by global nonlinear regression analysis.[16a,17] Titrations were carried out at 298 K using constant concentrations of host. [b] For this case, the curve-fitting program generates a more precise value of $0.8 \pm 0.1\ M^{-1}$. However, the binding is very weak, so the fitting is based only on the early part of the binding, with less than 50% of the complex formed. Accordingly, for this specific case we prefer to give a value of $1 \pm 0.5\ M^{-1}$ to this constant. [c] n.d. = not determined; $\Delta\delta$ were too low to make an accurate estimation of the constant.

In addition to the ^{1}H NMR titrations, we also evaluated the affinity of hosts **2**-*n*Bu and **4**-*n*Bu with the different electron-deficient aromatic guests by mass spectrometry. ESI-MS is one of the most versatile and widespread techniques for this purpose, because it allows noncovalent complexes to be gently transferred from solution to gas phase.[18] The ESI-MS spectra of complexes **2**-*n*Bu and **4**-*n*Bu, with an excess of the different guests and in the presence of NaI, showed prominent peaks corresponding to $[M+I+X]^-$ in the negative mode (in which X is the corresponding guest molecule). These results are in agreement with the 1:1 host–guest stoichiometry found by the NMR titrations. We next addressed the potential of the ESI technique to qualitatively elucidate the relative binding affinities of **4**-*n*Bu towards all electron-deficient aromatic guests. ESI-MS-based methods are known to be very useful for quantitatively evaluating host–guest binding events.[18b,19] In competitive ESI-MS experiments, the ESI mass spectrum of a selected host is investigated in the presence of a set of potential guests, so that different host–guest complexes can be simultaneously identified and quantified. The competitive ESI mass spectrum (negative scan mode) taken from solutions of **4**-*n*Bu with three equivalents of guest in a CH_2Cl_3/CH_3CN mixture is shown in Figure 3. In this negative ESI mass spectrum, we observed the formation of the supramolecular complexes formed between **4**-*n*Bu and all substrates used. Ion abundances indicate the tendency of TNFLU and NTCDA to preferably bind with **4**-*n*Bu, whereas the adduct with TCNB shows a much less-intense peak as a consequence of its lower affinity, in agreement with the results obtained by the NMR methods.

We were able to obtain single crystals of **2**-*n*Bu suitable for X-ray diffraction analysis from a [D$_6$]DMSO solution containing TCNB. The resulting structure showed the co-crystallization of **2**-*n*Bu and TCNB (Figure 4). The asymmetric unit cell contains one molecule of **2**-*n*Bu and one molecule of TCNB, with 50% occupancy at each side of the metal complex. The structure also shows one molecule of DMSO trapped inside the pyrene-based folder of the metal complex. The metric parameters of the molecule are very similar to those shown by **2**-*n*Bu in Figure 1. For example, the Pt–C(carbene) bond lengths are 2.040 and 2.024 Å. The average torsion angle established between the pyrene-imidazolylidene and the coordination plane of the molecule is 70.47°, thus slightly larger than that in the structure of **2**-*n*Bu depicted in Figure 1. The torsion angle between the two NHC ligands is 92.10(13)° (taken as the measurement of the C(1)-Pt(1)-C(4) angle), which is almost identical to the corresponding angle shown for **2**-*n*Bu shown in Figure 1 [92.00(16)°]. Similarly, the angles established by the two phenylacetylide ligands are very similar in the structures of **2**-*n*Bu, both with and without the tetracyanobenzene guest (88.86° and 86.99°, respectively). These parameters indicate that the orientation of the ligands is rather rigid, with little flexibility to favor an interaction with the guest. The most significant feature of the structure is the presence of the molecules of TCNB, which show clear π–π stacking interactions with one of the pyrene walls, and a phenyl ring of one of the phenylacetylide ligands, featuring interplanar distances of 3.425 and 3.443 Å, respectively. This interaction of the two faces of the molecule

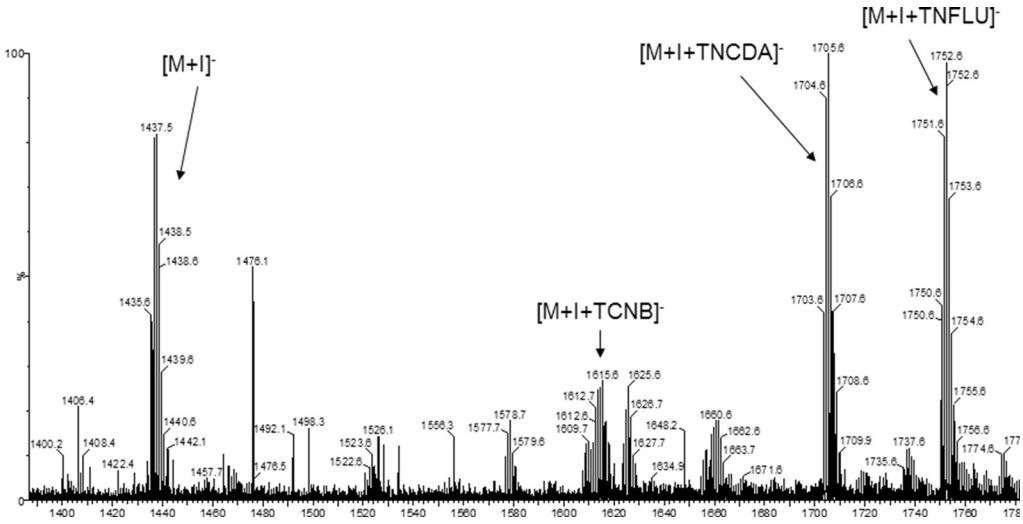


Figure 3. Selected region of the ESI-MS spectrum (negative scan mode) of a mixture of **4**-*n*Bu and three equivalents of TCNB, NTCDA and TNFLU. Non-assigned peaks correspond to solvated forms of the complexes, such as $[M+I+2CH_3CN]^-$, $[M+I+TCNB+CH_3CN]^-$, etc.

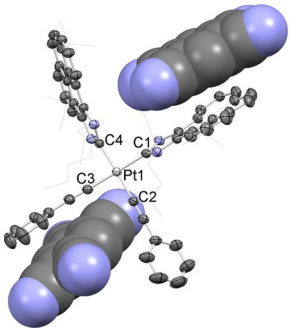


Figure 4. Molecular structure of complex **2**-*n*Bu–TCNB. Ellipsoids at the 50% probability level. Hydrogen atoms and solvent (DMSO) omitted for clarity. *tert*-Butyl groups shown as wireframes for clarity. Two molecules of tetracyanobenzene shown as space-filling diagrams. Selected bond distances (Å) and angles (°): Pt(1)–C(1) 2.040(3), Pt(1)–C(4) 2.024(3), Pt(1)–C(2) 2.010(3), Pt(1)–C(3) 1.990(4), C(1)-Pt(1)-C(4) 92.10(13), C(2)-Pt(1)-C(3) 88.86(12).

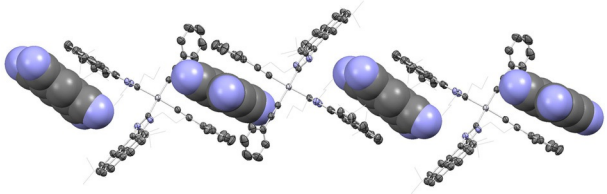


Figure 5. Crystal packing of complex **2**-*n*Bu–TCNB. The array of molecules is represented along the *c* axis.

was already predicted by the NMR titrations (vide supra); the overall stoichiometry of the adduct formed is 1:1, considering the 50% occupancy of each TCNB molecule. Another interesting feature of the structure is that each molecule of tetracyanobenzene is trapped by two host molecules. This presents an optimal assembly, in which the TCNB molecule is trapped by two host molecules, thereby forming two rectangular cages; one consisting of two pairs of phenylacetylenes, and one consisting of two pairs of phenanthrophenazine fragments. This arrangement is shown in Figure 5.

Conclusions

In summary, we prepared a series of organometallic folders (OMFOs) for the recognition of aromatic substrates within the cavity formed by the *cis*-oriented polyaromatic-based ligands. As shown by their molecular structures, these molecules tend to fill the void space formed by the folder. The molecules were tested for the recognition of aromatic substrates, for which they showed a selective affinity for electron-deficient molecules. Although the host–guest association constants were low, our molecules were able to effectively discriminate between electron-rich and electron-deficient aromatic substrates. Although the binding affinities found are not as high as those observed for other organic-based molecules tailor-made for the recognition of similar systems, we believe that the simplicity of the preparation of these complexes together with their great potential may soon make organometallic folders into highly competitive systems. By simply changing the nature of the metal, its oxidation state, the nature of the co-ligands, or the net-charge of the complex, we believe that the recognition abilities of metallofolders could be easily tuned, so that highly efficient and selective systems may soon be developed. This, combined with the simplicity of the preparation of our new types of receptors, may trigger the inspiration of researchers in the field of organometallic supramolecular chemistry.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: host–guest chemistry · N-heterocyclic carbenes · organometallic folder · platinum · supramolecular chemistry

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