



'Pincer-tweezer' tetraimidazolium salts as hosts for halides

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ABSTRACT

In this work we describe the preparation of two tetracationic molecular tweezers that were used as hosts for the recognition of chloride, bromide and iodide. These two hosts contain a rigid bis-alkynyl spacer that connects two arms built with two pincer bis-imidazolium units. The nature of the spacer confers distinct structural features to these two molecular 'pincer-tweezers'. The tweezer with the anthracenyl linker has a quasi-parallel disposition of the two arms of the tweezer, while in the carbazolyl-linked tweezer the two arms are significantly more separated. The study of the binding affinities of these two hosts with the three target halides showed substantial differences depending on the tetra-imidazolium tweezer used. In particular, the carbazolyl-based tweezer follows a 1:2 host:guest binding model, while the binding of the anthracenyl-linked tweezer is best explained using a 1:1 model. The different behavior is ascribed to the subtle different structural features of the two tetra-azolium receptors. The comparison of the affinities of the two tetracationic hosts with the related bis-imidazolium mono-pincer host indicates significantly enhanced association constants shown by the pincer-tweezer hosts, which are ascribed to a combination of the larger electrostatic attraction provided by the use of the tetracations together with the converging orientation of the two pincer bis-imidazoliums in the structure of the tweezers. These new tweezer-shaped tetra-imidazolium receptors are significantly different to other traditional tetrazoliums used as hosts for anions, which are mostly based on cyclic and more flexible structures. The pincer-tweezer hosts are acyclic and nevertheless more rigid than most of the poly-azolium-based receptors used until now.

1. Introduction

Anion recognition by synthetic receptors has become a fundamental pillar of supramolecular chemistry due to the important role of anions in numerous biological and environmental processes [1–11]. Imidazolium groups have been used as the basis for designing a numerous group of anion receptors due to their strong affinity to anions through (C–H)⁺...X[–] interactions, which occur by a combination of strong hydrogen bonding with favorable electrostatic interactions [12–24]. Imidazolium-based receptors are also advantageous due to their relative simple synthesis, which facilitates their integration into a variety of acyclic and macrocyclic structural frameworks built to complement the size and shape of target anion guests. Compared to monotopic molecular receptors that only recognize a single ion, anion receptors with multiple recognition sites normally show enhanced binding affinity leading to interesting applications in many fields [25–28], and have attracted great interest in supramolecular chemistry because they are prone to showing cooperative interactions [29–37]. Understanding the mechanisms that govern

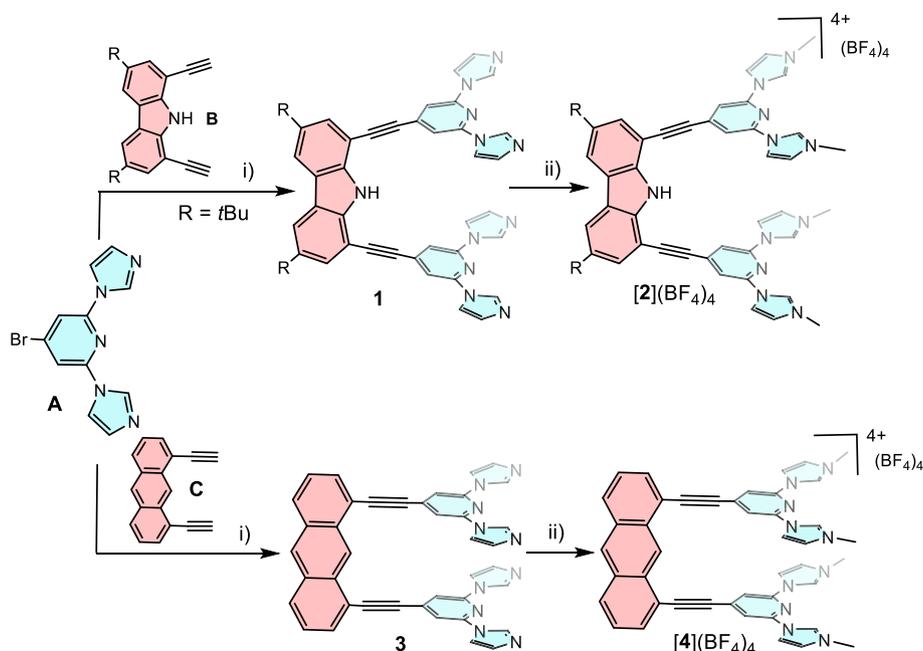
supramolecular cooperativity is of great importance because cooperative interactions play a very significant role in many natural processes where information between biological complexes takes place [38–40].

Bis(imidazolium)-substituted molecules acting as dicationic π -conjugated anion receptors usually form 1:1 complexes with anions [41–43], and the binding sites of the host normally converge on the anion in a pincer-like fashion [44]. In addition, computational and experimental evidences have revealed that pincer or tweezer shapes are beneficial for anion binding hosts, because anions require a large vacant space for stabilizing their excess of electron density [45,46]. Pyridine-connected bisazoliums have been used for constructing several anion receptors [47], most of them based on macrocyclic systems, as the so-called 'Texas-sized' molecular boxes [48–51]. All this prompted us to design two molecular tweezers bearing two arms equipped with two pyridine-connected bis-imidazolium pincers. As spacers, we used two rigid bis-alkynyl- based linkers, as shown in Scheme 1. We thought that these anion receptors could provide a good opportunity for studying the cooperative effects associated to the 1:2 host:guest complexation. In

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Scheme 1. Synthesis of the tetra-imidazolium receptors $[2](\text{BF}_4)_4$ and $[4](\text{BF}_4)_4$. i) $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, DIPA, THF, 80 °C; ii) $[(\text{CH}_3)_3\text{O}](\text{BF}_4)$, CH_3CN , RT.

principle, the spatial arrangement of the two arms of the tweezer should generate improved binding affinities with anions due to the enforced proximity of the four positive charges of the imidazolium units. In addition, the use of the two hosts with the two different relatively rigid spacers should provide interesting information about the influence of the separation of the two pincers on the binding properties of the receptors. The design of these pincer-tweezer anion receptors connects well with our previous studies on the synthesis of molecular tweezers [52–56] and azolium-based anion receptors [57–60]. The present study describes the use of these two tetraimidazolium-based molecular tweezers as receptors for a selection of three anion guests (Cl^- , Br^- and I^-). As will be discussed below, these receptors showed significant enhanced affinities when compared with those shown using the related mono-pincer dicationic receptor. In addition, the structural differences between the two tetra-imidazolium tweezers lead to substantially different anion recognition behaviors.

2. Results and discussion

The two tetra-imidazolium-based molecular tweezers $[2](\text{BF}_4)_4$ and $[4](\text{BF}_4)_4$ were obtained according to the method depicted in Scheme 1. The palladium-catalysed Sonogashira coupling of 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole (**B**) with 4-bromo-2,6-imidazolyl-pyridine (**A**) afforded the neutral tetra-imidazolyl tweezer-shaped compound **1** as a brownish insoluble product in quasi-quantitative yield (93%). The tetramethylation of **1** with trimethyloxonium tetrafluoroborate in acetonitrile at room temperature allowed the generation of the tetraimidazolium salt $[2](\text{BF}_4)_4$ as a pale brown solid in 50% yield. Both the ^1H and ^{13}C NMR patterns of the compound are consistent with the pseudo- C_{2v} symmetry of the tetracation. The ^1H NMR spectrum of $[2](\text{BF}_4)_4$ ($\text{DMSO}-d_6$) shows the distinctive resonance due to the C2–H protons at 10.28 ppm. The signal due to the N–H proton of the carbazolyl linker appears at 11.67 ppm. The Electrospray Mass spectrum (ESI-MS) shows m/z peaks at 201, 297 and 490, assigned to $[2]^{4+}$, $[2 + \text{BF}_4]^{3+}$ and $[2+2\text{BF}_4]^{2+}$, respectively.

The preparation of the anthracenyl-connected tetraimidazolium tweezer $[4](\text{BF}_4)_4$, was performed following a similar procedure as that described for $[2](\text{BF}_4)_4$, but using 1,8-diethynyl-anthracene (**C**) instead. The reaction yields for **3** and $[4](\text{BF}_4)_4$ were 77 and 60%, respectively. The ^1H and ^{13}C NMR spectra of $[4](\text{BF}_4)_4$ are consistent with its pseudo-

C_{2v} symmetry. The ^1H NMR spectrum of $[4](\text{BF}_4)_4$ in $\text{DMSO}-d_6$ shows the distinctive resonance at 10.18 ppm, attributed to the four equivalent C2–H protons of the imidazolium units. A relevant feature of the ^1H NMR spectrum is that the five signals due to the protons of the anthracenyl spacer appear in the region between 7.7 and 9.5 ppm, thus clearly indicating that the tetra-cation exists as a monomer in DMSO . These protons would be significantly shielded if the anthracenyl spacer were participating in a π – π -stacking event, as we have observed before [55,61,62]. In addition to this, by recording the $\text{DMSO}-d_6$ ^1H NMR spectra of $[4](\text{BF}_4)_4$ at different concentrations, we did not observe any perturbation of the resonances of the protons of the compound, thus indicating that this tetraimidazolium does not self-associate in DMSO . This information is particularly relevant due to the high level of self-complementarity of the molecule, which is reflected by its solid state structure, as will be described below. The ESI-MS shows m/z peaks at 176, 263, 439 and 965, assigned to $[4]^{4+}$, $[4 + \text{BF}_4]^{3+}$, $[4+2\text{BF}_4]^{2+}$ and $[4+3\text{BF}_4]^+$, respectively.

Both $[2](\text{BF}_4)_4$ and $[4](\text{BF}_4)_4$ constitute a new type of tetraimidazolium molecular tweezers, in which the spatial separation between the two pyridine-bis-imidazolium units is controlled by the nature of the spacer. While the anthracenyl-bis-alkynyl linker **C** allows a quasi-parallel arrangement of the two arms of the tweezer [55,62], the carbazolyl-bis-alkynyl linker **B**, with its two diverging alkynyl units allows establishing a larger separation between the two bis-imidazolium groups [53,56]. The structure of compound $[4](\text{BF}_4)_4$ was confirmed by single crystal X-diffraction studies (Fig. 1). The structure consists of an anthracenyl unit with two alkynyl groups that connect to two pyridyl-bis-imidazolium fragments. The most interesting feature of the structure is that the cation forms a self-aggregated duplex structure, $[4_2]^{8+}$, in which the anthracenyl spacers are sandwiched between the two panels formed by the pyridine-bis-imidazolium units of the complementary molecule. The distance between the two planes formed by the pyridine-bis-imidazolium groups is 6.97 Å, and the distance between each of these planes and the anthracenyl spacer of the complementary molecule is of 3.47 Å, therefore reflecting a significant π – π -stacking interaction. The formation of this dimer is a clear indication of the high degree of self-complementarity of the molecule, a feature that we have found in other molecular tweezers bearing rigid bis-alkynyl spacers [52, 55,61].

We next explored the ability of $[2](\text{BF}_4)_4$ and $[4](\text{BF}_4)_4$ to behave as

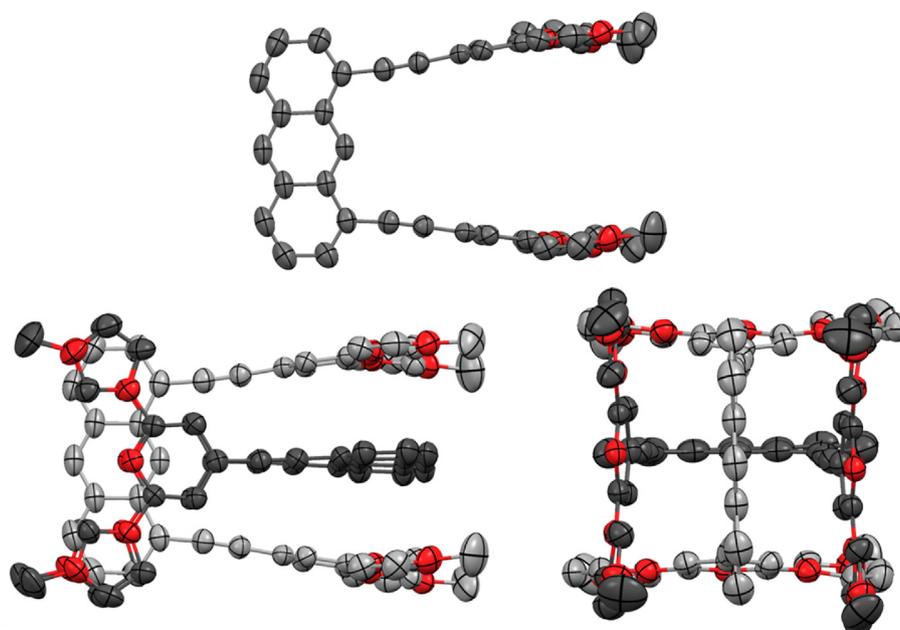


Fig. 1. Molecular structure of the tetracationic tweezer $[4]^{4+}$. Hydrogen atoms and counterions are omitted for clarity. The figure on the top shows only one of the components of the self-aggregated dimer that is formed in the solid state structure. The two figures below show two perspectives of the self-aggregated dimer $[4_2]^{8+}$ as found in the structure.

anion receptors. The recognition and binding properties of both hosts were studied by ^1H NMR titration experiments, monitoring the perturbations produced in the selected NMR resonances upon addition of the tetrabutylammonium salts of the investigated anion guests. All titrations were performed in $\text{DMSO-}d_6$, using a constant concentration of the tetracationic hosts. For the study, we selected chloride, bromide and iodide. For the titrations performed using $[2](\text{BF}_4)_4$ we observed that the series of spectra were indicative of the presence of fast exchange kinetics on the NMR timescale. In this case, the addition of incremental amounts of the halides induced the downfield shift of the signal due to the four equivalent protons of the C2–H group of the imidazolium units, in a clear indication of the direct participation of these protons in the interaction established with all three different anions. The signals due to the four equivalent C–H protons of the two pyridine rings were also deshielded. For the titration with chloride, we also observed a significant downfield shift of the resonance due to the proton of the NH group, which suggests that the binding is also supported by a $\text{N-H}\cdots\text{Cl}$ hydrogen bonding interaction. Interestingly, the signal due to the NH group does not show such perturbation when the titrations were performed with bromide or iodide (Figures S23 and S24), most likely because these larger anions have a more difficult access to the inner cavity of the tweezer, and also due to the weaker hydrogen bonding interaction that might then be established with the NH group. As an illustrative example, Fig. 2 shows the series of spectra obtained for the titration of $[2](\text{BF}_4)_4$ with tetrabutylammonium chloride, where the shifting of the above mentioned three resonances is clearly observed.

A quick look at the spectra resulting from the titrations performed with $[4](\text{BF}_4)_4$ indicated a different behavior of this host. For the titrations performed with $[4](\text{BF}_4)_4$ with chloride, a slow exchange kinetics with respect to the NMR timescale was observed. As can be seen in Fig. 3, upon addition of increasing amounts of tetrabutylammonium chloride, the resonances due to the imidazolium C2–H groups and the N– CH_3 protons split into two new resonances each one. This indicates that the sequence of spectra allows identifying three different species formed along the experiment, which we assigned to free $[4]^{4+}$, and the 1:1 and 1:2 host-guest adducts, $(\text{Cl}^-)@[4]^{4+}$ and $(2\text{Cl}^-)@[4]^{4+}$. This slow kinetics is very likely due to the encapsulation of the chloride anion into the relatively rigid well-defined cavity formed by $[4]^{4+}$, which allows an

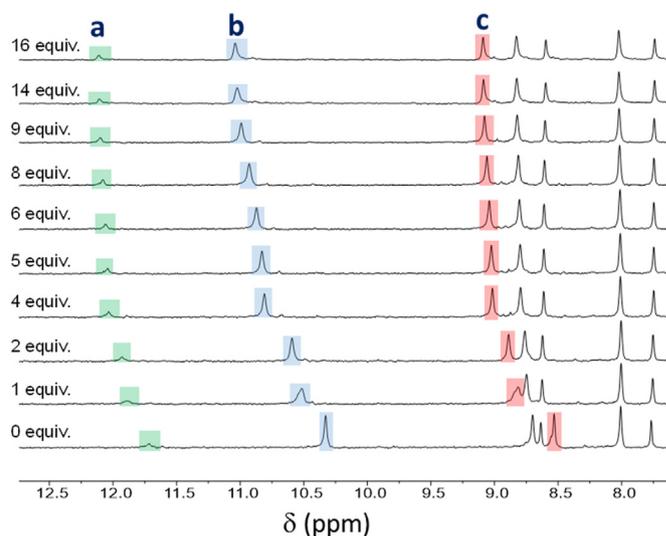


Fig. 2. Selected region of the series of ^1H NMR spectra ($\text{DMSO-}d_6$) obtained from the titration of $[2](\text{BF}_4)_4$ with tetrabutylammonium chloride. The resonances depicted as a, b and c, refer to the ones assigned to the N–H proton of the carbazolyl linker, the C2–H protons of the imidazolium units, and the protons of the pyridine rings of the host molecule, respectively.

effective interaction of the anion with all four imidazolium units of the host (see Fig. 3). This scenario resembles the situation that is established when macrocyclic hosts with well-defined cavities based on relatively rigid frameworks are used, for which slow exchange kinetics are normally observed [63]. The situation is different when $[2](\text{BF}_4)_4$ is acting as a host, because the larger separation of the two pincers may hamper the participation of all four imidazolium units in the stabilization of the 1:1 host:guest complexes. The titrations of $[4](\text{BF}_4)_4$ with bromide and iodide show fast exchange kinetics on the NMR timescale, although the resonances of the protons which experienced perturbations were significantly broader than those shown by spectra generated from the titrations performed with $[2](\text{BF}_4)_4$, thus indicating that the exchange kinetics for

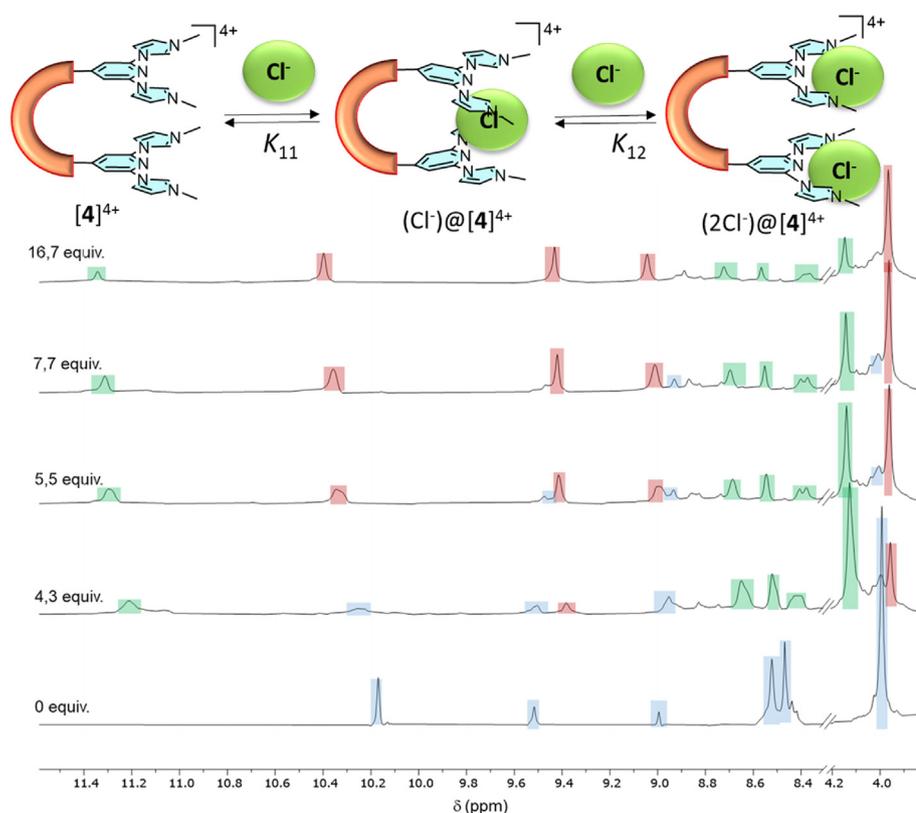


Fig. 3. Two selected regions of the series of ^1H NMR spectra (DMSO- d_6) obtained from the titration of $[\text{4}](\text{BF}_4)_4$ with tetrabutylammonium chloride. The series of spectra show how the resonances due to $[\text{4}]^{4+}$ (blue) disappear as new ones due to $(\text{Cl}^-)@[\text{4}]^{4+}$ (green) and finally $(2\text{Cl}^-)@[\text{4}]^{4+}$ (red) progressively appear. The spectrum on the top shows the formation of $(2\text{Cl}^-)@[\text{4}]^{4+}$ (resonances highlighted in red) as the major product. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

these two anions is slower for $[\text{4}](\text{BF}_4)_4$ than for $[\text{2}](\text{BF}_4)_4$, in agreement to what we already observed for the chloride guest.

The determination of the binding constants between $[\text{2}](\text{BF}_4)_4$ and the anion guests was performed by global non-linear regression analysis [64,65] of the data obtained from the ^1H NMR titrations. The binding of the host:guest complexes formed with chloride and bromide were best fitted to a 1:2 stoichiometry model. This conclusion was based on the analysis of the binding isotherms resulting from each of the titrations, and by comparing the distribution of residuals when assuming 1:1 and 1:2 stoichiometries. The 1:2 stoichiometry was also supported by the Job plot analysis (see ESI for details). For the titration with iodide, good fittings were obtained using both 1:1 and 1:2 binding models. However, both fitting models delivered very similar K_{11} values, but the value of K_{12} obtained using the 1:2 model was very small and was accompanied by a rather large error. Under these circumstances we considered more appropriate to consider that the 1:1 model depicts a more accurate picture for the binding of this anion. As can be observed from the data shown in Table 1, $[\text{2}](\text{BF}_4)_4$ shows large binding affinities with all three guests under study. The examination of the data shown in Table 1 reveals a number of important trends. The binding affinities of $[\text{2}](\text{BF}_4)_4$ with the halides follows the trend $\text{Cl}^- > \text{Br}^- > \text{I}^-$, in agreement with the basicity trend of the anions. For chloride and bromide, the cooperative factor α is less than 1, indicative of negative cooperativity. This is most likely due to electrostatic interactions related to the repulsion between the two anions, which inhibits the second binding event. For the case of the titration with iodide, the binding of the second iodide is negligible, as a consequence of the greater repulsion shown for this larger guest.

For $[\text{4}](\text{BF}_4)_4$, the K_{11} values obtained for the binding of bromide and iodide are of the same order of magnitude as those obtained for $[\text{2}](\text{BF}_4)_4$ (compare entries 2 with 4, and 3 with 5). In this case, the binding isotherms were best fitted to a 1:1 stoichiometry model, thus suggesting that for this host the second binding event is more affected by the electrostatic repulsion between the two anions than in the case of the use of $[\text{2}](\text{BF}_4)_4$. This situation arises from the shorter distance between the two bis-

Table 1

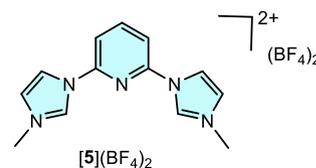
Association constants for the formation of host-guest complexes between $[\text{2}](\text{BF}_4)_4$, $[\text{4}](\text{BF}_4)_4$ and $[\text{5}](\text{BF}_4)_2$, and a series of three anions, in DMSO- d_6 at 25 °C.^a

Entry	Host	Guest	K_{11} (M^{-1})	K_{12} (M^{-1})	α^b
1	$[\text{2}](\text{BF}_4)_4$	Cl^-	2470 (7)	88 (2)	0.14
2	$[\text{2}](\text{BF}_4)_4$	Br^-	758 (4)	79 (4)	0.41
3	$[\text{2}](\text{BF}_4)_4$	I^-	211 (3)	–	–
4	$[\text{4}](\text{BF}_4)_4$	Br^-	675 (6)	–	–
5	$[\text{4}](\text{BF}_4)_4$	I^-	310 (6)	–	–
6	$[\text{5}](\text{BF}_4)_2$	Cl^-	124(1)	–	–
7	$[\text{5}](\text{BF}_4)_2$	Br^-	49(3)	–	–
8	$[\text{5}](\text{BF}_4)_2$	I^-	N/A	–	–

^a Association constants calculated by global nonlinear regression analysis. A 1:2 (H:G) binding model was assumed for the determination of the constants for $[\text{2}](\text{BF}_4)_4$ with chloride and bromide. A 1:1 (H:G) binding model was used for the determination of the constants for $[\text{4}](\text{BF}_4)_4$ and $[\text{5}](\text{BF}_4)_2$. The fittings were performed without parameter restrictions. All anions were added as tetrabutylammonium salts. All errors shown in parenthesis are given in percentage.

^b α is the cooperative factor, defined as $\alpha = 4K_{12}/K_{11}$.

azolium units of the quasi-parallel tweezer $[\text{4}](\text{BF}_4)_4$, compared to the distance between the bis-azoliums displayed by $[\text{2}](\text{BF}_4)_4$, for which the two alkynyl-connected pincer branches are oriented in a divergent manner. We also considered interesting to explore the binding affinities of the mono-pincer host $[\text{5}](\text{BF}_4)_2$ (Scheme 2). For this host the binding



Scheme 2. Mono-pincer $[\text{5}](\text{BF}_4)_2$.

isotherms were best fitted to a 1:1 model. For the case of the titrations with tetrabutylammonium iodide, the shift of the signal due to the C2–H protons of the imidazolium units was smaller than 0.1 ppm, so we considered that the binding affinity with this anion was negligible. The association constants obtained for the binding with chloride and bromide were significantly smaller than those obtained using the tetra-azolium tweezers [2](BF₄)₄ and [4](BF₄)₄, as a consequence of the combined effect produced by the larger electrostatic attraction produced by the tetracationic host for the anion, and by the orientation of the four imidazolium units that allow establishing a concerted interaction with the anion host.

3. Conclusions

In summary, in this work we prepared two molecular tweezers with two arms each one bearing a pincer bis-imidazolium unit. These two molecular ‘pincer-tweezers’ connect the two bis-imidazolium units through two different rigid bis-alkynyl linkers, which make the molecules to have structurally different topologies. The carbazolyl-based linker, with its two diverging alkynyl groups, allows that the two bis-imidazolium pincers are significantly separated compared to the situation arising from the use of the anthracenyl-based linker, for which the two alkynyl groups are quasi-parallel. This situation provides a high degree of self-complementarity to the anthracenyl-connected molecular tweezer-pincer, for which the solid state structure shows the formation of dimer aggregates.

The ability to bind anions by these two tetra-imidazolium salts was studied in DMSO. Although the binding affinities shown by the two hosts were essentially similar in terms of the association constants found, they showed interesting differences that can be related with their different structural features. In the case of the carbazolyl-based host ([2](BF₄)₄), all three anions tested showed fast exchange kinetics with respect to the NMR timescale, and the binding of the second anion was negatively affected by the first binding event, thus indicating a clear case of negative cooperativity. For the case of the anthracenyl-based host ([4](BF₄)₄), all titrations indicated slower exchange kinetics compared to those shown by [2](BF₄)₄. In addition, for the binding of [4](BF₄)₄ with bromide and iodide, the binding followed a 1:1 binding model, indicating that the host did not show any tendency to bind to a second anion. This situation contrasts with the 1:2 binding model followed for the titration of [2](BF₄)₄ with bromide, for which the binding of the second halide is feasible due to the larger distance between the two arms of the tweezer. This larger separation reduces the electrostatic repulsion between the two anions compared to the more unfavorable situation that would arise from binding two anions to the anthracenyl-based host [4](BF₄)₄.

Our studies also allow comparing the binding affinities of our two tetra-imidazolium hosts, with those found for the mono-pincer bisazolium host [5](BF₄)₄, for which the association constants are significantly smaller, thus highlighting the benefits provided by the combined action of two converging bis-imidazolium units in the recognition of anion guests. We think that our tweezer-shaped tetra-imidazolium receptors are significantly different to other traditional tetrazoliums used as hosts for anions, since most of the ones that have been reported so far are based on cyclic and more flexible structures. Our hosts are acyclic and nevertheless more rigid than most of the poly-azolium-based receptors used until now.

4. Experimental procedures

Full experimental procedures are provided in the Supplementary Information file.

Author contributions

Esteban Valencia performed the experiments. Macarena Poyatos

conducted and supervised the experiments and wrote the paper. Eduardo Peris supervised the results and wrote the paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tchem.2022.100018>.

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