

Towards hydrogen and halogen bonded frameworks based on 3,5-bis(triazolyl)pyridinium motifs

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We attempted to use hydrogen, iodo and seleno 3,5-bis(triazolyl)pyridinium (**btp**) motifs to form 3D supramolecular frameworks assembled by hydrogen, halogen or chalcogen bonding to anions. Initially, we prepared flexible ditopic and tetratopic receptors where the pyridinium nitrogen atom was functionalised with a benzylic group but were unable to crystallise extended frameworks. We subsequently developed the use of Zincke methodology to prepare rigid ditopic and tetratopic hydrogen and halogen bonding tectons, and were able to crystallise the sulfate derivative of a tetratopic receptor, although unfortunately this did not have the desired open framework. Several crystal structures were obtained with the receptors and monovalent anions, including one containing an unusually short iodotriazole...Cl⁻ halogen bond. Generally, the **btp** triazole groups show a tendency to rotate away from the desired conformation and it appears that this may contribute to difficulties in obtaining 3D frameworks even when the receptors have a rigid core.

Introduction

Three dimensional frameworks assembled by hydrogen bonding (sometimes referred to as hydrogen bonded organic frameworks, HOFs) have received significant research interest, particularly in the last decade or so.^{1,2} This is largely because the relatively weak nature of hydrogen bonds often gives rise to highly crystalline materials that can be prepared in milder conditions than those used to prepare coordination polymers/metal organic frameworks (CPs/MOFs)^{3,4} or covalent organic frameworks (COFs).^{5,6} A number of different hydrogen bonding motifs have been used to construct these frameworks, using either the self-recognition of a neutral component⁷⁻¹⁴ or the interaction between two charged tectons.¹⁵⁻²³ While many frameworks have been reported, these have typically used a relatively limited set of hydrogen bonding motifs.^{1,2}

Halogen bonding and chalcogen bonding are two other types of supramolecular interactions that can be relatively strong and are distinguished from hydrogen bonds by their more stringent linearity.²⁴⁻²⁸ Potentially this linearity would make them ideal motifs for the formation of supramolecular frameworks as it should lead to predictable structures. Despite this possible advantage, relatively few 3D frameworks assembled by halogen²⁹⁻³⁸ or chalcogen³⁹⁻⁴³ bonding have been reported. Indeed we are only aware of one halogen bonded framework³⁷ and one chalcogen bonded⁴² framework that are sufficiently stable to allow for solvent removal and subsequent gas sorption studies.

Given the lack of diversity in building blocks used to prepare hydrogen bonded frameworks, and the small number of halogen and chalcogen bonded materials known, we decided to investigate new tectons for the synthesis of supramolecular frameworks. To this end, we were attracted to the 3,5-bis(triazolyl)pyridinium (**btp**) motif, which was first reported by Li and Li in 2011,⁴⁴ and subsequently developed as an anion

recognition motif by Beer.⁴⁵ This motif contains a positive charge as well as potentially bidentate hydrogen bond donors, and variants containing halogen⁴⁶ and chalcogen⁴⁷ bond donors have been reported. These have proven to be particularly potent anion receptors,⁴⁸⁻⁵¹ as well as useful for anion binding catalysis.⁵²

Of particular interest to us was a crystal structure reported by Beer, which showed two iodo-**btp** groups arranged around a sulfate anion (Figure 1).⁴⁸ In this case, each iodo-**btp** motif belongs to a different [2]catenane molecule, but despite the conformational restrictions imposed by this, the **btp** molecules were able to arrange themselves around a sulfate anion. This gives a charge neutral assembly,⁵³ and we wondered whether the **btp** motif could be used to deliberately construct supramolecular frameworks with sulfate or other 2⁻ anions such as terephthalate (which we²⁰ and others²¹ have previously used to form hydrogen bonded frameworks). Specifically we wondered whether 2⁻ anions could be used to link ditopic **btp** receptors into 1D supramolecular chains and tetratopic **btp** receptors into 3D diamondoid networks. Herein, we describe our attempts to prepare such frameworks.

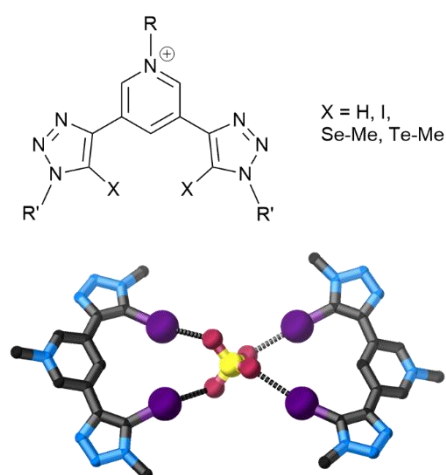


Figure 1 General structure of **btp** motif, and partial crystal structure showing two iodo-**btp** groups arranged around a sulfate anion reported by Beer⁴⁸ (CSD: 1033648).

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[†] Electronic Supplementary Information (ESI) available: details of synthesis and characterisation, synthesis of selenium containing receptors, details of X-ray crystallography. See DOI: 10.1039/x0xx00000x

Results and discussion

Synthesis of neutral hydrogen and halogen bonding motifs

The key feature in all the structures in this work is the bis(triazolyl)pyridinium (**btp**) motif with either hydrogen or iodine groups attached to the triazole rings, *i.e.* either prototriazole or iodotriazole groups. We also investigated the synthesis of a chalcogen bonding motif containing R-Se groups at the 5-position of the triazole ring. While we were able to prepare some selenium functionalised **btp** derivatives, we were unable to obtain any crystals from these and so the syntheses of these are described in the ESI.

To prepare the triazole and iodotriazole **btp** derivatives, commercially available 3,5-dibromopyridine was converted to the known molecule 3,5-diethynylpyridine in high yield through a Sonogashira coupling with TMS-acetylene followed by deprotection⁵⁴ (an optimised procedure is given in the ESI). One-pot syntheses were then used to convert either hexyl bromide or benzyl bromide to the corresponding azide and then react these with diethynylpyridine under copper-catalysed azide alkyne coupling conditions to give known hexyl substituted **btp** **1^H_{hex}**⁴⁵ and the new benzyl substituted **btp** **1^H_{Bn}** (Figure 2). We formed the known benzyl substituted iodotriazole **btp** **1^I_{Bn}** from diethynylpyridine, sodium iodide and benzyl azide using copper(II) triflate as the catalyst,⁵² with an alternative procedure using copper(II) perchlorate⁴⁸ not giving complete conversion to the product in our hands.

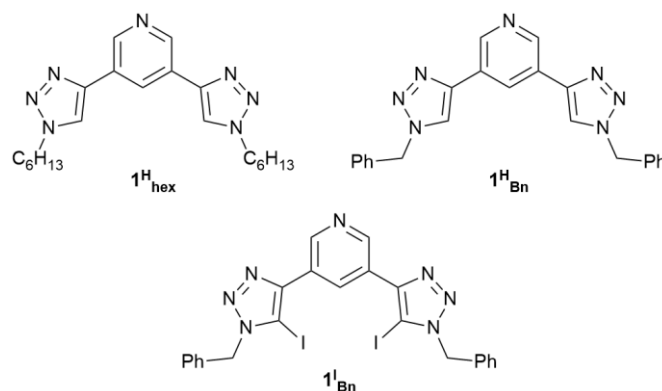


Figure 2 Btp precursors used in this work (**1^H_{Bn}** is a new compound, **1^H_{hex}**⁴⁵ and **1^I_{Bn}**⁵² have been reported previously).

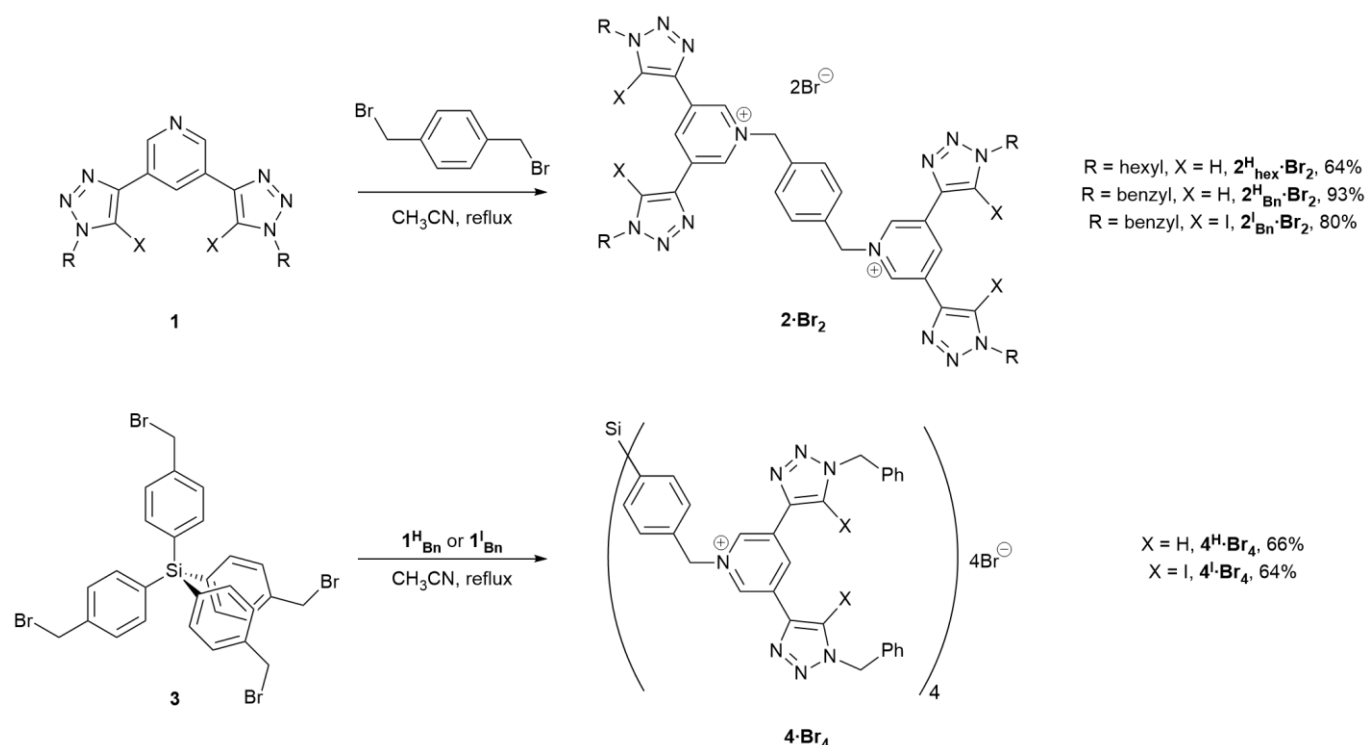
Synthesis of flexible ditopic and tetratopic btp receptors

The ditopic receptors **2^H_{hex}²⁺**, **2^H_{Bn}²⁺** and **2^I_{Bn}²⁺** were prepared by heating the appropriate neutral **btp** derivative and bis(bromomethyl)benzene to reflux in acetonitrile (Scheme 1). The bromide salts of these receptors precipitated from the reaction mixture and could be isolated in good yields (64–93%) and high purities by simple filtration. The hydrogen bonding receptors were exchanged to their PF₆[−] salts [*i.e.* **2^H_{hex}·(PF₆)₂** and **2^H_{Bn}·(PF₆)₂**] by precipitation from DMF/methanol using NH₄PF₆. When we used this procedure to prepare **2^I_{Bn}·(PF₆)₂**, we obtained a crystal structure of a compound that still contained some bromide anions suggesting that complete anion exchange was not observed (see ESI). We suggest that this may be due to the well known high affinity of iodo-substituted **btp** groups for halide anions.^{46,48} Instead, we were able to prepare **2^I_{Bn}·(BF₄)₂** using silver(I) tetrafluoroborate.

The tetratopic receptors were prepared by heating the neutral **btp** derivatives **1^H_{Bn}** and **1^I_{Bn}** and tetra bromomethyl compound **3** to reflux in acetonitrile (Scheme 1). The receptors **4^H·Br₄** and **4^I·Br₄** precipitated from the reaction mixtures and were isolated in 66 and 64% yields by simple filtration. Anion exchange reactions were conducted using NH₄PF_{6(aq)} to form **4^H·(PF₆)₄** and AgBF₄ to form **4^I_{Bn}·(BF₄)₄**.

Attempts to form 1D and 3D frameworks from flexible receptors

We attempted to crystallise the ditopic and tetratopic receptors with anions suitable to link these into either 1D or 3D networks through hydrogen/halogen bonding. Specifically, we looked at sulfate, terephthalate and the tetrahedral tetracarboxylate **5^{4−}** (Figure 3). The tetrahedral anion **5^{4−}** could theoretically give 3D frameworks with either ditopic or tetratopic receptors. Unfortunately, despite trialling numerous crystallisation solvents we were unable to obtain any crystals suitable for X-ray crystallography with either **TP^{2−}** or **5^{4−}**.



Scheme 1 Synthesis of flexible ditopic receptors $\mathbf{2^H_{hex} \cdot Br_2}$, $\mathbf{2^H_{Bn} \cdot Br_2}$ and $\mathbf{2^I_{Bn} \cdot Br_2}$, and flexible tetratopic receptors $\mathbf{4^H \cdot Br_4}$ and $\mathbf{4^I \cdot Br_4}$. All of these receptors were also anion exchanged to give the corresponding BF_4^- or PF_6^- salts.

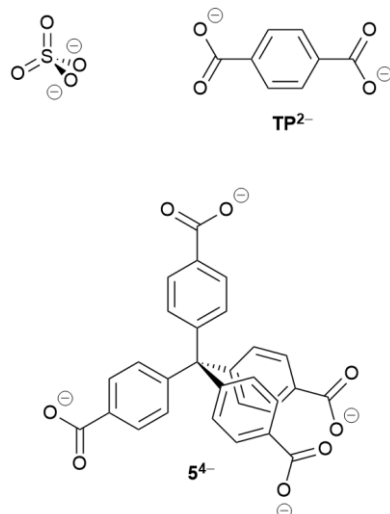


Figure 3 2- and 4- anions used in crystallisation studies.

We were able to obtain crystals by vapour diffusion techniques when we used mixtures of either $\mathbf{2^H_{hex} \cdot (PF_6)_2}$ or $\mathbf{2^I_{Bn} \cdot (BF_4)_2}$ and TBA_2SO_4 (TBA = tetrabutylammonium). Unfortunately in both cases, X-ray crystallography revealed that the crystals were of the HSO_4^- salt of the receptor (Figure 4). Testing the pH of the “ TBA_2SO_4 ” used, revealed that it was significantly acidic, suggesting the presence of significant amounts HSO_4^- ($\text{p}K_a$ of $\text{HSO}_4^- \sim 2.55$). Attempts to crystallise these receptors with a fresh batch of TBA_2SO_4 , which was not acidic, were unsuccessful.

In both the structures of $\mathbf{2^H_{hex} \cdot (HSO_4)_2}$ and $\mathbf{2^I_{Bn} \cdot (HSO_4)_2}$, the HSO_4^- anions are located in the **btp** pockets, although it is notable that the actual mode of binding to the anion is quite different in each structure. In the case of $\mathbf{2^H_{hex} \cdot (HSO_4)_2}$, one crystallographically independent triazole C–H group points into the cleft, while the other points out; this therefore means that a triazole nitrogen atom points towards the HSO_4^- anion, and forms a short hydrogen bond with the hydrogen atom of the HSO_4^- anion ($\text{H} \cdots \text{N} = 1.90 \text{ \AA}$, 66% of the sum of the van der Waals radii of these atoms,⁵⁶ Σ_{vdW}). Interestingly the triazole hydrogen atom that does point into the cleft does not form a significant hydrogen bond to the anion (> than the sum of the van der Waals radii) and instead there is a relatively long hydrogen bond from the interior pyridinium hydrogen atom to the HSO_4^- anion ($\text{H} \cdots \text{O} = 2.50 \text{ \AA}$, 92% Σ_{vdW}).

Conversely, the structure of $\mathbf{2^I_{Bn} \cdot (HSO_4)_2}$ has both crystallographically independent iodotriazole rings pointing into the binding cleft and forming short halogen bonds to the anion's oxygen atoms [$\text{I} \cdots \text{O} = 2.826(9), 2.890(7) \text{ \AA}$; 80, 82 Σ_{vdW}]. These interactions are relatively close to 180° , although not as linear as some halogen bonds [$\text{C} \cdots \text{I} \cdots \text{O}$: $171.9(2)$ and $164.8(3)^\circ$ for the shorter and longer interaction, respectively]. The anion's hydrogen atom then hydrogen bonds to a methanol solvent molecule, and the anion and solvent form a hydrogen bonded chain (Figure 4c).

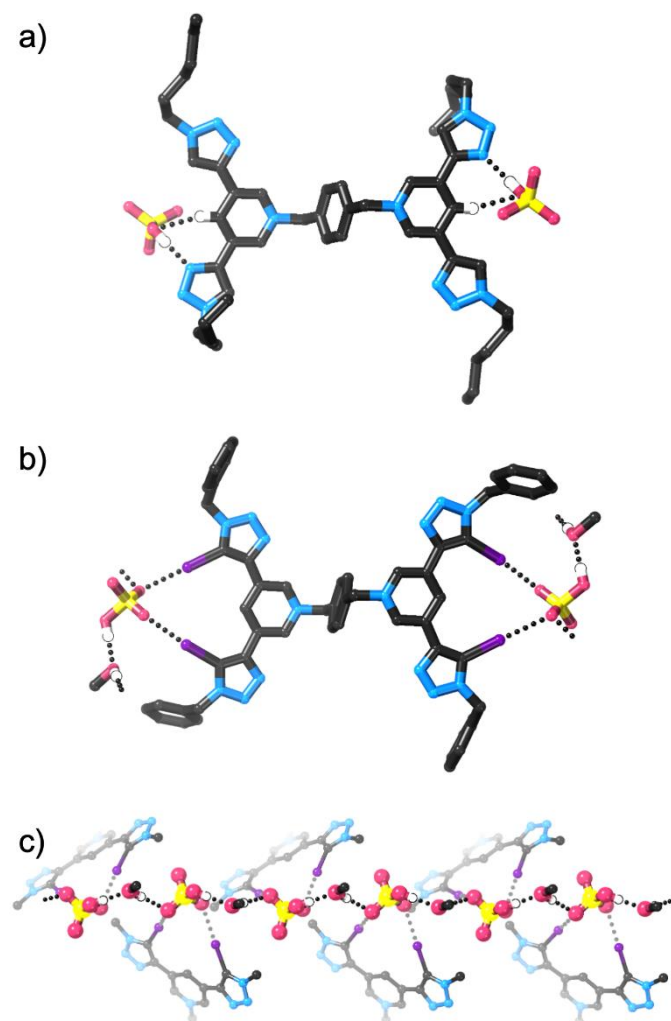


Figure 4 Structures of HSO_4^- complexes of $2^{\text{H}}_{\text{hex}}^{2+}$ and $2^{\text{I}}_{\text{Bn}}^{2+}$: a) structure of $2^{\text{H}}_{\text{hex}}^{2+}(\text{HSO}_4)_2$, b) structure of $2^{\text{I}}_{\text{Bn}}^{2+}(\text{HSO}_4)_2$, c) structure of HSO_4^- -methanol hydrogen bonded polymer in the structure of $2^{\text{I}}_{\text{Bn}}^{2+}(\text{HSO}_4)_2$. Only hydrogen atoms involved in hydrogen bonding are shown, with hydrogen bonds shown as dotted lines. PLATON-SQUEEZE⁵⁷ was used in the refinement of $2^{\text{H}}_{\text{hex}}^{2+}(\text{HSO}_4)_2$.

We also obtained crystals when we crystallised $2^{\text{I}}_{\text{Bn}}^{2+}(\text{BF}_4)_2$ in the presence of tetrabutylammonium terephthalate from a mixture of dichloromethane, acetonitrile and methanol. In this case, the crystals are of the chloride salt, $2^{\text{I}}_{\text{Bn}}^{2+}\text{Cl}_2$ (Figure 5). It is unclear where this chloride anion has come from, but we suggest it may result from breakdown of dichloromethane over the extended time period used to grow crystals. Given that strong halogen bond donors have been used as organocatalysts for halide abstraction,⁵⁸⁻⁶⁰ it is plausible that $2^{\text{I}}_{\text{Bn}}^{2+}$ can cause the breakdown of small amounts of dichloromethane over long periods of time. Attempts to grow crystals from solvent mixtures that did not contain dichloromethane were unsuccessful.

In the structure of $2^{\text{I}}_{\text{Bn}}^{2+}\text{Cl}_2$, one crystallographically independent iodotriazole group points into the **btp** binding cleft, while the other points in the opposite direction. Each iodotriazole group forms a short halogen bond to a chloride anion [$\text{I}\cdots\text{Cl} = 2.987(1), 3.053(1) \text{ \AA}$; 77, 79 % Σ_{vdW}] and these interactions are close to linear [$\angle\text{C-I}\cdots\text{Cl}^-: 172.6(1)$ and $178.8(1)^\circ$ for the shorter and longer interaction, respectively].

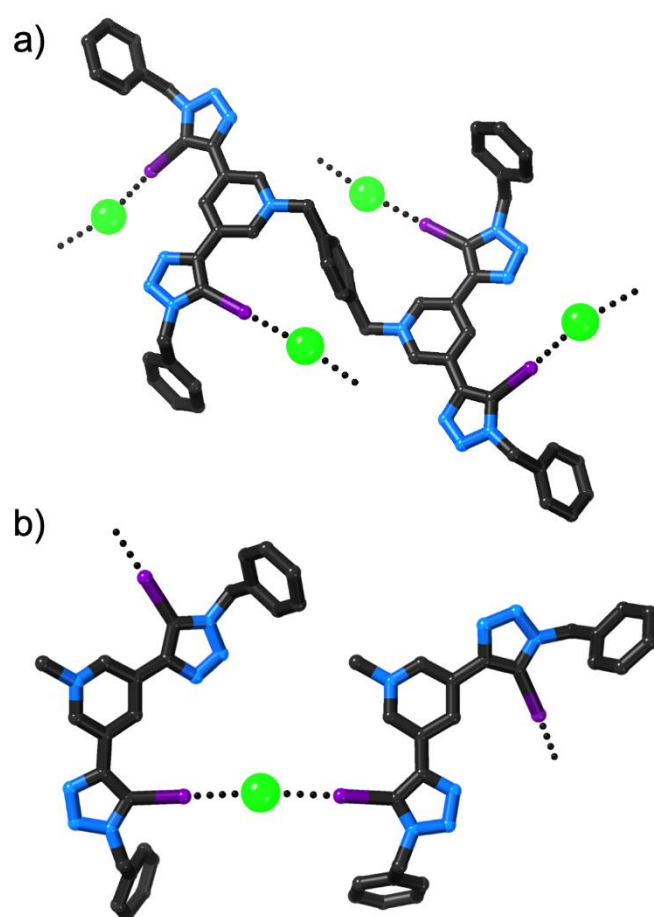


Figure 5 Two views of the structure of $2^{\text{I}}_{\text{Bn}}^{2+}\text{Cl}_2$: a) view showing a complete receptor with all positions of the anion, b) view showing two partial receptors forming linear interactions with a single anion. Halogen bonds shown as dotted lines, hydrogen atoms omitted for clarity.

These $\text{I}\cdots\text{Cl}^-$ contacts observed in the structure of $2^{\text{I}}_{\text{Bn}}^{2+}\text{Cl}$ seemed surprisingly short, and so we surveyed the Cambridge Structural Database (CSD)⁶¹ to compare these with related systems. Indeed, the 77 % Σ_{vdW} interaction is shorter than any other iodotriazole $\cdots$ halide interaction in the database (Table 1). The $\text{I}\cdots\text{O}^-$ interactions observed in the structure of $2^{\text{I}}_{\text{Bn}}^{2+}(\text{HSO}_4)_2$ are slightly shorter than the average iodotriazole $\cdots$ oxoanion contact observed in the database, although it is notable that the length of these interactions varies much more than those of iodotriazole $\cdots$ halides.

Table 1 Length (as % Σ_{vdW}) of halogen bonds in the CSD for iodotriazole groups and various anions.

	Cl^-	Br^-	I^-	Oxoanions
Minimum	78	82	82	73
Maximum	86	86	88	97
Number	16	4	9	10
Mean	81	83	85	84

To put these results into a broader context, we also compared the lengths of the short iodotriazole...Cl⁻ interactions observed in **2^I_{Bn}·Cl₂** with those of chloride and other iodine containing halogen bond donor motifs such as perfluoroiodoarenes,^{62,63} iodypyridiniums,⁶⁴⁻⁶⁹ iodotriazoliums⁷⁰ and iodoimidazoliums.^{71,72} While there are a limited number of such structures, it is notable that the I...Cl⁻ interaction in **2^I_{Bn}·Cl₂** is as short as the shortest of the 25 iodypyridinium...Cl⁻ contacts in the CSD despite the fact that the pyridinium ring in these systems is cationic while the iodotriazole group in **2^I_{Bn}·Cl₂** is neutral. Generally iodotriazole...Cl⁻ contacts seem to be similar in length to perfluoroiodoarene...Cl⁻ contacts and shorter than iodypyridinium...Cl⁻ contacts but longer than iodoimidazolium/iodotriazolium...Cl⁻ contacts (see ESI for full details).

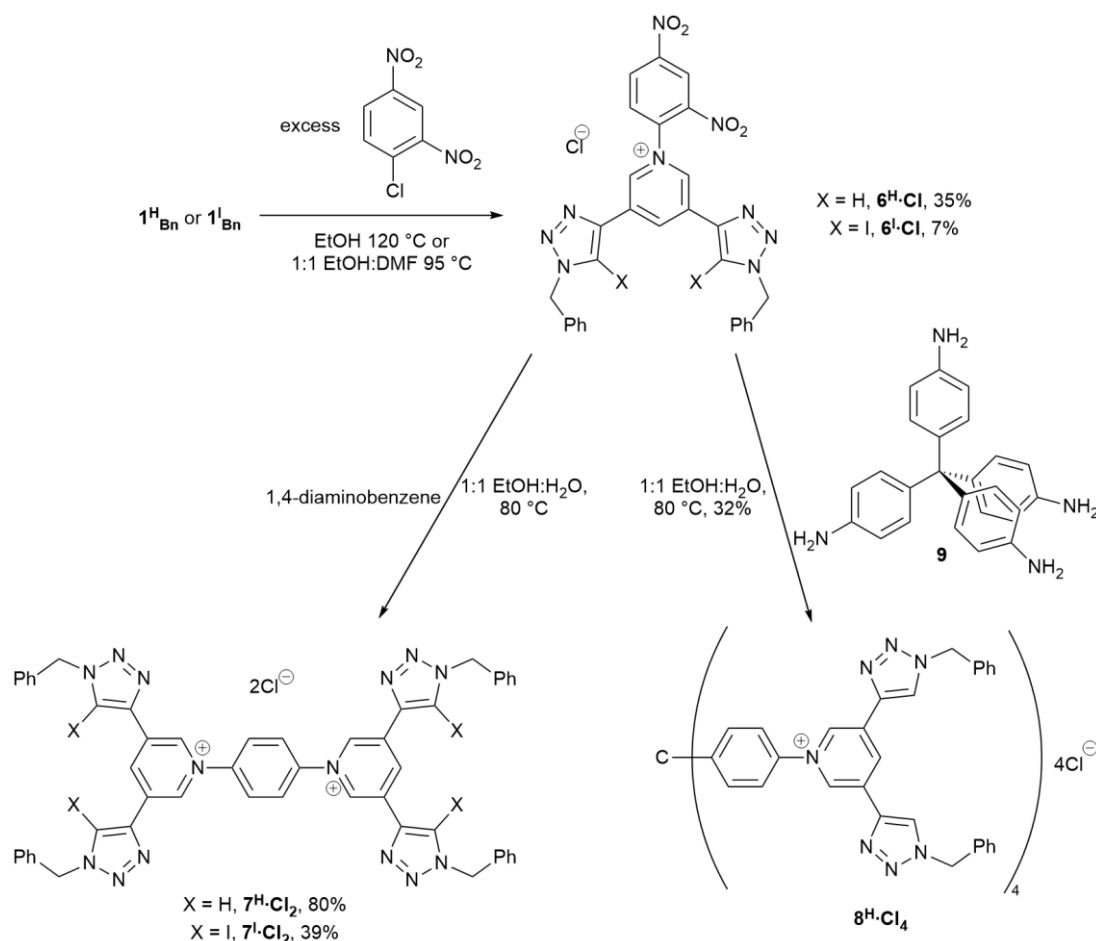
We attempted to use anions to link tetratopic receptors **4^{H4+}** and **4^{I4+}** into 3D frameworks but despite numerous attempts to crystallise these using sulfate, **TP²⁻** or **5⁴⁻**, no crystals were obtained. We hypothesised that this may be due to the flexibility imparted by the methylene groups in the receptors leading to numerous possible conformations and making crystallisation difficult, and we note that the vast majority of known hydrogen bonded frameworks include highly rigid building blocks.^{1,2} To this end, we next sought to prepare more rigid receptors without these methylene groups.

Synthesis of rigid ditopic and tetratopic btp receptors

To increase the rigidity of the systems, we sought to prepare receptors with direct aryl-pyridinium bonds, *i.e.* to remove the methylene groups present in **2²⁺** and **4⁴⁺**. This can be achieved using Zincke methodology, where the substituted pyridine group is reacted with chlorodinitrobenzene to form a “Zincke salt,” *i.e.* a substituted 2,4-dinitrophenylpyridinium compound, which then reacts with a primary aniline to give the phenylpyridinium bond. While there are well-established methodologies for forming Zincke salts containing simple substituents, there are few reports of more complex salts forming. Additionally the reaction is known to struggle when there are electron-withdrawing substituents on the pyridine ring.⁷³

Perhaps unsurprisingly, it was therefore quite difficult to form Zincke salts from **1^H_{Bn}** or **1^I_{Bn}** — however, after considerable optimisation, we were able to form **6^H·Cl** in moderate yields (Scheme 2). This required heating a large excess of chlorodinitrobenzene and **1^H_{Bn}** in ethanol at 120 °C in a sealed vial for ten days, and even under these conditions, yields were modest (35%). The modest yield is due to both incomplete reaction, and difficulties in purification – as **6^H·Cl** decomposes on silica gel. Attempts to scale up the reaction (using > 0.5 g of **1^H_{Bn}**) were difficult as the product could no longer be separated by recrystallization. The synthesis of **6^I·Cl** was even more challenging, as **1^I_{Bn}** decomposed at 120 °C and had poor solubility in ethanol. After optimisation, it was possible to achieve a 7% yield of **6^I·Cl** by reacting **1^I_{Bn}** with ten equivalents of dichloronitrobenzene in 1:1 ethanol:DMF for ten days at 95 °C. This reaction does not go to completion and large amounts of unreacted starting material were observed meaning that the product required extensive and laborious purification by precipitation and washings (**6^I·Cl** decomposes on silica gel). With routes to the two Zincke salts in-hand, we next prepared the rigid ditopic receptors **7^H·Cl₂** and **7^I·Cl₂** by simply heating an excess of the salt with 1,4-diaminobenzene in 1:1 ethanol:water (Scheme 2). This gave the rigid receptors in 80 and 39% yields, respectively, after sonicating in acetonitrile to remove excess Zincke salt. Anion exchange using NH₄PF_{6(aq)} and AgBF₄ gave **7^H·(PF₆)₂** and **7^I·(BF₄)₂**, respectively.

Due to the low yielding reaction to form **6^I·Cl**, we only isolated small amounts of this compound and so were unable to pursue the synthesis of **8^{I4+}**. We prepared the rigid tetratopic receptor **8^{H4+}** by reacting an excess of **6^H·Cl** with tetraamine **9** (Scheme 2). The reaction was sluggish, and even after heating for seven days, the yield for this compound was modest (32%). Nevertheless, it was possible to isolate clean **8^H·Cl₄** after purification by sonicating in acetonitrile and then in acetone. Anion exchange using NH₄PF_{6(aq)} gave **8^H·(PF₆)₄**.



Scheme 2. Synthesis of Zincke salts **6^H-Cl** and **6^I-Cl**, and rigid receptors **7^H-Cl₂**, **7^I-Cl₂** and **8^H-Cl₄**. The ditopic and tetratopic receptors were also anion exchanged to give the corresponding BF_4^- or PF_6^- salts.

Attempts to form 1D and 3D frameworks from rigid receptors

We attempted to crystallise **7^{H2+}** and **7^{I2+}** with sulfate, **TP²⁻** or **5⁴⁻** in order to form hydrogen bonded chains, but were not able to obtain crystals. We were able to crystallise **7^H-Cl₂** by vapour diffusion of diethyl ether into a methanol solution of the compound. As shown in Figure 6, the two chloride anions sit in the **btp** pockets with all four triazoles C–H groups pointing “outwards” to hydrogen bond to the anions. There are relatively short hydrogen bonds between the anions and triazole groups ($\text{H}\cdots\text{Cl}^-$: 2.51–2.69 Å, 83–89% Σ_{vdW}) and between the anions and the pyridinium ring’s internal C–H proton ($\text{H}\cdots\text{Cl}^-$: 2.56, 2.60 Å, 85, 86% Σ_{vdW}). The coordination sphere of each chloride anion is completed by two more hydrogen bonds: in one case from the methanol solvent and from a C–H group from the phenylene ring of a neighbouring receptor, in the other case by two C–H hydrogen bonds from phenylene rings. The hydrogen bond with methanol is quite short ($\text{H}\cdots\text{Cl}^-$: 2.33 Å, 77% Σ_{vdW}), while those with phenylene C–H groups are longer ($\text{H}\cdots\text{Cl}^-$: 2.60–2.70 Å, 86–89% Σ_{vdW}).

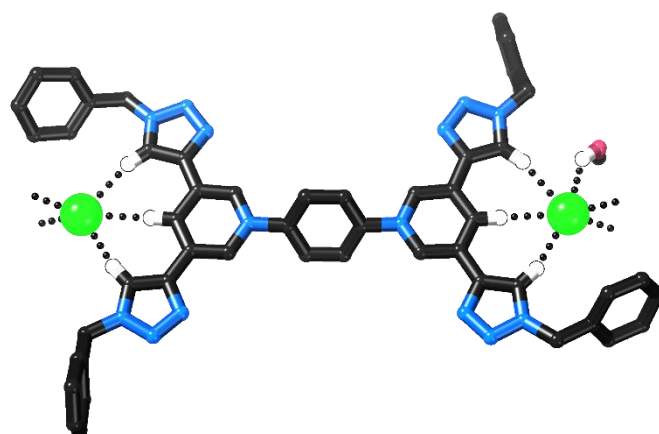


Figure 6 Structure of **7^H-Cl₂**: only hydrogen atoms involved in hydrogen bonding are shown, hydrogen bonds are shown as dotted lines. the dotted lines without a donor group represent relatively long hydrogen bonds (86–89% Σ_{vdW}) to phenylene C–H donors of an adjacent receptor.

We attempted to crystallise **8^{H4+}** with sulfate, **TP²⁻** and **5⁴⁻**. In one case, we were able to obtain crystals, of **8^H·(SO₄)₂**. The asymmetric unit contains a complete molecule of **8^{H4+}** as well as two sulfate anions (Figure 7), one of which was modelled as disordered over two positions. Areas of diffuse electron density are present, which we attribute to poorly resolved disordered

solvent molecules. This electron density was included in the model using PLATON-SQUEEZE.⁵⁷ Disappointingly, the sulfate anions are not located in the expected binding clefts: instead seven of the eight triazole groups adopt an *anti* conformation and the anions are located in “supramolecular hugs” in pockets close to the tetraphenylmethane part of the receptor.⁷⁴ Hydrogen bonds are formed between the anions and triazole C–H donors (H...O: 2.17–2.66 Å, 81–98% Σ_{vdw}) as well as “exterior” pyridinium hydrogen atoms (*i.e.* the group *ortho* to the pyridinium nitrogen atom, H...O: 2.18–2.53 Å, 81–94% Σ_{vdw}). One of the anions also participates in relatively long hydrogen bonds with phenyl groups from a phenyl–pyridinium motif (H...O: 2.46, 2.53 Å, 91, 94% Σ_{vdw}). While the targeted porous structure was not obtained due to the unexpected location of the anions, there are still moderate size voids in the structure (17% of the unit cell volume as analysed using PLATON-SQUEEZE⁵⁷), which we attribute to the inability of the large and bulky **8**^{H4+} cations to pack efficiently.

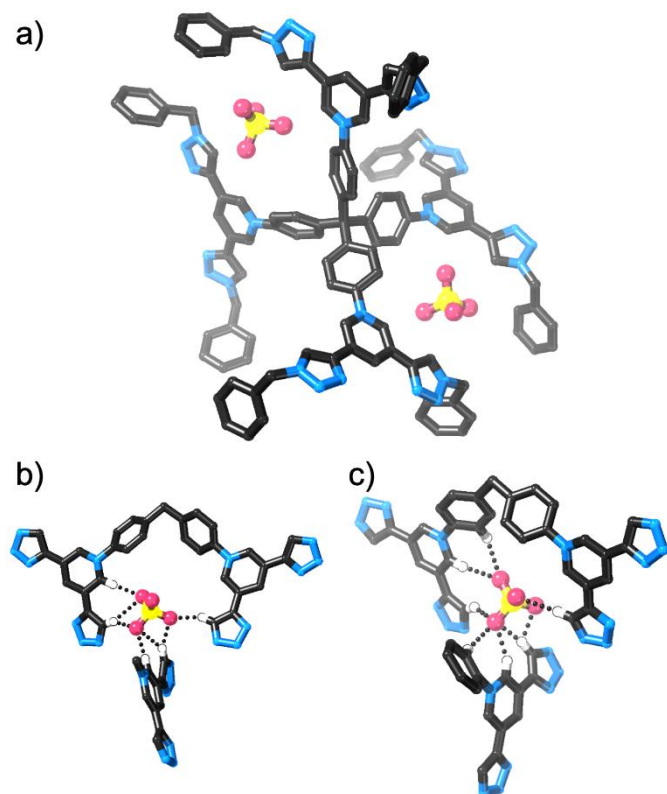


Figure 7 Structure of **8**^{H+}(SO₄)₂: a) view of the asymmetric unit cell (hydrogen atoms omitted), b and c) view of the hydrogen bonding environments around each independent SO₄²⁻ anion (only hydrogen atoms involved in hydrogen bonding shown, hydrogen bonds shown as dotted lines). PLATON-SQUEEZE⁵⁷ was used.

Conclusions

We have prepared a series of new ditopic and tetratopic hydrogen and halogen bonding receptors, including a family of rigid receptors prepared using Zincke methodology. We were not able to prepare the desired anion templated 1D and 3D networks using these, which may be due to a number of factors. Perhaps the most important appears to be the propensity of the

triazoles groups to rotate such that their C–H or C–I group does not point towards the anion binding cleft. It is conceivable that additional functionality could be added to preorganise the triazole groups to point towards the cleft,⁷⁵ although this would be synthetically challenging for the systems used in this work. We note that while the hexyl and benzyl substituents are necessary for synthetic reasons, they have some potential disadvantages in terms of framework formation. Specifically their flexible nature may interfere with crystallisation and minimise potential void space.

Crystal structures reveal that iodo-**btp** derivatives form very short halogen bonds with halide anions. The strength of these halogen bonding interactions was also apparent in difficulties achieving complete anion exchange of bromide salts of these receptors with PF₆⁻, and by the observation of a chloride salt of a receptor where the chloride anion appears to have arisen from decomposition of dichloromethane solvent.

Generally, it appears that the use of **btp** motifs to prepare 3D supramolecular frameworks may be challenging. A possible alternative strategy would be to use the 3,5-pyridinium-bis(amide) motif popularised by Beer,⁷⁶ which contains amide groups in place of triazoles. While this would be limited to hydrogen bonded materials rather than halogen/chalcogen bonds, amides are more potent hydrogen bond donors than triazoles and significantly smaller substituents (e.g. H, Me) can be installed at the amide group. It is hoped that the Zincke conditions developed in this work might prove useful for these or other systems.

Experimental

X-ray crystallography

Crystal structures of **1**^H_{Bn}, **2**^H_{hex}·(HSO₄)₂, **2**^I_{Bn}·(HSO₄)₂, **2**^I_{Bn}·(HSO₄)_{1.2}·Br_{0.8}, **2**^I_{Bn}·Cl₂, **7**^H·Cl₂ and **8**^{H+}·(SO₄)₂ were obtained. These were collected using either an Oxford Diffraction Supernova diffractometer, or beamlines MX1⁷⁷ or MX2⁷⁸ of the Australian Synchrotron. Data collected using the Supernova diffractometer were collected at 150 K and raw frame data (including data reduction, interframe scaling, unit cell refinement and absorption corrections) were processed using CrysAlis Pro.⁷⁹ Data collected using synchrotron radiation were collected at 100 K and raw frame data were processed using XDS.⁸⁰ Structures were solved using either Superflip⁸¹ or SHELXT⁸² and refined using either CRYSTALS⁸³ or OLEX2.⁸⁴ Full crystallographic data in CIF format are available from the Cambridge Structural Database (CCDC Numbers: 2130560–2130566). Refinements of individual structures are discussed in the ESI, and crystallographic data are summarized in Table S1.

Synthesis

General remarks Benzyl azide,⁸⁵ **1**^H_{hex},⁴⁵ **1**^I_{Bn},⁵² tetrakis(4-tolyl)silane (**3**),⁸⁶ tetrakis(4-aminophenyl)methane (**9**),⁸⁷ TBA₂·TP⁸⁸ and TBA₄·5⁸⁹ were prepared as previously described. THF was dried by distilling from sodium. Other chemicals were bought from commercial suppliers and used as received. An optimised procedure for the synthesis of 3,5-diethynylpyridine

is provided in the ESI, as well as details of the preparation of selenium containing receptors. Details of instrumentation and copies of spectra are provided in the ESI.

1^H_{Bn}: 3,5-Diethynylpyridine (1.00 g, 7.81 mmol, 1.0 equiv.) was dissolved in 4:1 DMF:H₂O (100 mL). Sodium azide (1.22 g, 18.8 mmol, 2.4 equiv.), sodium carbonate (0.830 g, 7.81 mmol, 1.0 equiv.), ascorbic acid (1.38 g, 7.81 mmol, 1.0 equiv.) and copper(II) sulfate pentahydrate (0.12 g, 0.49 mmol, 0.063 equiv.) were added, followed by benzyl bromide (2.1 mL, 17 mmol, 2.2 equiv.) and the solution was heated to 80 °C under a nitrogen atmosphere for 3 days. The resulting brown solution was cooled and ethyl acetate (75 mL) and an aqueous EDTA/K₂CO₃ solution (50 mL) were added. The organic layer was taken, washed with water (2 × 50 mL) and brine (2 × 50 mL) and dried (MgSO₄). It was concentrated under reduced pressure to give a yellow solid, which was purified by column chromatography (95:5 dichloromethane:methanol) to give **1^H_{Bn}** as a white powder. Yield: 2.6 g (6.5 mmol, 84%).

¹H NMR (d₆-DMSO): 9.01 (d, *J* = 2.1 Hz, 2H), 8.84 (s, 2H), 8.66 (t, *J* = 2.1 Hz, 1H), 7.33–7.43 (m, 10H), 5.69 (s, 4H) ppm. ¹³C NMR (d₆-DMSO): 145.6, 143.6, 135.8, 128.8, 128.5, 128.3, 128.0, 126.8, 122.6, 53.2 ppm. HRESI-MS (pos.): 394.1775, calc. for [C₂₃H₁₉N₇·H]⁺ = 394.1776 Da.

2^H_{hex}·Br₂: A suspension of **1^H_{hex}** (0.025 g, 0.066 mmol, 2.0 equiv.) and 1,4-bis(bromomethyl)benzene (0.0086 g, 0.033 mmol, 1.0 equiv.) in acetonitrile (2 mL) was heated at reflux under N₂ overnight. The suspension was cooled to room temperature and the resulting precipitate was isolated via filtration, washed with acetonitrile (3 × 5 mL), and air dried to give **2^H_{hex}·Br₂** as a white powder. Yield: 0.021 g (0.020 mmol, 64%).

¹H NMR (d₆-DMSO): 9.67 (s, 4H), 9.31 (br. s, 2H), 8.99 (br. s, 4H), 7.74 (s, 4H), 5.99 (s, 4H), 4.50 (t, *J* = 7.0 Hz, 8H), 1.83–1.90 (m, 8H), 1.23–1.32 (m, 24H), 0.85 (t, *J* = 6.8 Hz, 12 H) ppm. ¹³C NMR (d₆-DMSO): 140.4, 139.5, 136.0, 135.3, 131.9, 129.6, 124.7, 63.3, 50.0, 30.6, 29.5, 25.4, 21.9, 13.9 ppm. HRESI-MS (pos.): 433.2946, calc. for [C₅₀H₇₀N₁₄]²⁺ = 433.2948 Da.

2^H_{hex}·(PF₆)₂: To a solution of **2^H_{hex}·Br₂** (0.021 g, 0.020 mmol, 1.0 equiv) in DMF (7 mL) was added NH₄PF₆ (0.040 g, 0.25 mmol, 13 equiv). Methanol (3 mL) and water (1 mL) were added to give a clear solution. Water (30 mL) was then added causing the formation of a white suspension. The solid was isolated by centrifugation and dried *in vacuo* to give **2^H_{hex}·(PF₆)₂** as a white powder. Yield: 0.018 g (0.016 mmol, 78%).

¹H NMR (d₆-acetone): 9.62 (d, *J* = 1.4 Hz, 4H), 9.35 (t, *J* = 1.4 Hz, 2H), 8.85 (s, 4H), 7.92 (s, 4H), 6.27 (s, 4H), 4.56 (t, *J* = 7.1 Hz, 8H), 1.94–2.02 (m, 8H), 1.25–1.39 (m, 24H), 0.87 (t, *J* = 7.1 Hz, 12H) ppm. ¹⁹F NMR (d₆-acetone): –72.3 (d, *J* = 708 Hz) ppm. ³¹P NMR (d₆-acetone): –144.2 (hept., *J* = 708 Hz) ppm. ESI-MS (pos.): 1011.6, calc. for [(C₅₀H₇₀N₁₄)²⁺·(PF₆)[–]]⁺ = 1011.6 Da.

2^H_{Bn}·Br₂: A suspension of **1^H_{Bn}** (0.25 g, 0.64 mmol, 2.0 equiv) and 1,4-bis(bromomethyl)benzene (0.084 g, 0.32 mmol, 1.0 equiv) in acetonitrile (5 mL) was heated at reflux under N₂ overnight.

The suspension was cooled to room temperature and the resulting precipitate was collected by filtration, washed with cold acetonitrile (3 × 10 mL), and air-dried to give **2^H_{Bn}·Br₂** as a beige powder. Yield: 0.310 g (0.295 mmol, 93%).

¹H NMR (d₆-DMSO): 9.72 (br. s), 9.34 (br. s, 2H), 9.06 (s, 4H), 7.73 (s, 4H), 7.34–7.43 (m, 20H), 5.99 (s, 4H), 5.77 (s, 8H) ppm. ¹³C NMR (d₆-DMSO): 140.8, 139.7, 136.2, 135.4, 135.2, 131.6, 129.5, 128.9, 128.5, 128.1, 124.9, 63.2, 53.5 ppm. HRESI-MS (pos.) 445.2004, calc. for [C₅₄H₄₆N₁₄]²⁺ = 445.2009 Da.

2^H_{Bn}·(PF₆)₂: A suspension of **2^H_{Bn}·Br₂** (0.200 g, 0.190 mmol, 1.0 equiv.) was suspended in methanol (20 mL) and heated to 60 °C. DMF (10 mL) was added causing everything to dissolve to give a pale yellow solution. NH₄PF₆ (0.200 g, 1.23 mmol, 6.5 equiv.) in water (5 mL) was added, followed by more water until a precipitate started to form (~15 mL more). The mixture was placed in an ice bath for an hour, and the white powder was isolated by filtration, washed with water (3 × 10 mL) and then diethyl ether (3 × 10 mL) and then dried under vacuum. Yield: 0.205 g (0.174 mmol, 91%).

¹H NMR (d₆-acetone): 9.58 (s, 4H), 9.33 (s, 2H), 8.78 (s, 4H), 7.84 (s, 4H), 7.37–7.44 (m, 20H), 6.22 (s, 4H), 5.76 (s, 8H) ppm. ¹⁹F NMR (d₆-acetone): –72.3 (d, *J* = 708 Hz) ppm. ³¹P NMR (d₆-acetone): –144.2 (hept., *J* = 708 Hz) ppm. ESI-MS (pos.): 1035.6, calc. for [(C₅₄H₄₆N₁₄)²⁺·(PF₆)[–]]⁺ = 1035.4 Da.

2¹_{Bn}·Br₂: A suspension of **1¹_{Bn}** (0.200 g, 0.310 mmol, 2.0 equiv.) and 1,4-bis(bromomethyl)benzene (0.0409 g, 0.155 mmol, 1.0 equiv.) in acetonitrile (12 mL) was heated at reflux under N₂ overnight. The suspension was cooled to room temperature and the resulting cream powder isolated by filtration, washed with acetonitrile (3 × 10 mL) and diethyl ether (10 mL) and dried under vacuum. Yield: 0.192 g (0.123 mmol, 80%).

¹H NMR (d₆-DMSO): 9.74 (s, 4H), 9.69 (s, 2H), 7.77 (s, 2H), 7.31–7.40 (m, 12H), 7.25 (d, *J* = 7.0 Hz, 8H), 6.10 (s, 4H), 5.79 (s, 8H) ppm. ¹³C NMR (d₆-DMSO): 143.3, 141.2, 136.7, 135.3, 134.9, 131.3, 130.0, 128.8, 128.2, 127.4, 89.6, 63.4, 53.6 ppm. HRESI-MS (pos.): 696.9934, calc. for [C₅₄H₄₂N₁₄I₄]²⁺ = 696.9942 Da.

2¹_{Bn}·(BF₄)₂: A solution of AgBF₄ (0.0243 g, 0.124 mmol, 2.0 equiv.) was added to a solution of **2¹_{Bn}·Br₂** (0.097 g, 0.062 mmol, 1.0 equiv.) in DMF (2 mL) and stirred at room temperature under N₂ with the exclusion of light for 2 hours. The resulting suspension was filtered through a small plug of celite, washing through with more DMF (3 mL). The filtrate was concentrated under vacuum to give a dark solid. Acetone (3 mL) was added, causing the formation of a brown solid, which was removed via filtration. The yellow filtrate was concentrated under vacuum and the resulting yellow solid dissolved in acetone (5 mL) and precipitated by the addition of diethyl ether (45 mL). The flask was cooled in the freezer, and then the powder isolated by filtration and washed with diethyl ether (3 × 10 mL) and dried *in vacuo* to give **2¹_{Bn}·(BF₄)₂** as an off-white powder. Yield: 0.047 g (0.030 mmol, 48%).

¹H NMR (d₆-acetone): 9.80 (t, *J* = 1.6 Hz, 4H), 9.72 (d, *J* = 1.6 Hz, 2H), 7.97 (s, 4H), 7.32–7.41 (m, 20H), 6.37 (s, 4H), 5.83 (s, 8H) ppm. ¹⁹F NMR (d₆-acetone): –151.26 (s), –151.31 (s) ppm.

ESI-MS (pos.): 1482.1, calc. for $[(C_{54}H_{42}N_{14}I_4)^{2+} \cdot (BF_4)^-]^{+} = 1482.0$ Da.

3: This compound has been reported previously by a similar method but using CCl_4 as solvent.⁹⁰ No NMR data were provided.

A suspension of tetrakis(4-tolyl)silane (0.200 g, 0.508 mmol, 1.0 equiv.), *N*-bromosuccinimide (0.769 g, 4.47 mmol, 8.8 equiv.) and benzoyl peroxide (0.026 g, 0.10 mmol, 0.20 equiv.) in chloroform (20 mL) was heated to reflux for 64 hours. It was cooled to room temperature and then taken to dryness under reduced pressure to give an orange solid. Methanol (15 mL) was added and the suspension stirred for 30 minutes. The resulting white powder was isolated by filtration, washed with methanol (3 × 5 mL) and air-dried to give **3**. Yield: 0.108 g (0.152 mmol, 30%).

¹H NMR ($CDCl_3$): 7.51 (d, *J* = 8.1 Hz, 8H), 7.41 (d, *J* = 8.1 Hz, 8H), 4.50 (s, 8H) ppm. ¹³C NMR ($CDCl_3$): 139.6, 136.9, 134.0, 128.7, 33.3 ppm. HRESI-MS (pos.) 703.8383, calc. for $[C_{28}H_{24}SiBr_4]^+ = 703.8381$ Da.

4^H·Br₄: **1^H_{Bn}** (0.033 g, 0.085 mmol, 4.0 equiv.) and **3** (0.015 g, 0.021 mmol, 1.0 equiv.) were dissolved in acetonitrile (5 mL) and heated to reflux for 3 days under N_2 resulting in the formation of an orange precipitate. The supernatant was decanted and the resulting solid was dried under vacuum to give the pure product as a pale orange powder. Yield: 0.032 g (0.14 mmol, 66%).

¹H NMR (d_6 -DMSO): 9.69 (s, 8H), 9.34 (s, 4H), 9.03 (s, 4H), 9.02 (s, 4H), 7.61 (d, *J* = 7.0 Hz, 8H), 7.35–7.50 (m, 48H), 5.98 (s, 8H), 5.77 (s, 16H) ppm. ¹³C NMR (d_6 -DMSO): 140.8, 139.7, 136.4, 136.2, 136.1, 135.7, 135.3, 134.3, 133.6, 131.6, 128.9, 128.5, 128.2, 128.1, 124.9, 63.3, 53.5 ppm. HRESI-MS (pos.): 490.4616, calc. for $[C_{120}H_{100}N_{28}Si]^+ = 490.4614$ Da.

“Doubling” of peaks belonging to the pyridinium and triazole resonances is apparent in the ¹H NMR and ¹³C NMR spectra, which we attribute to hindered rotation.

4^H·(PF₆)₄: Separately, **4^H·Br₄** (0.030 g, 0.013 mmol, 1.0 equiv.) and NH_4PF_6 (0.017 g, 0.10 mmol, 8.0 equiv.) were dissolved in 2:1 methanol:DMF (3 mL each). The two solutions were mixed and then water (4 mL) was added causing the solution to become cloudy. The precipitate was isolated by centrifugation, and the resulting solid suspended in water, sonicated, and then isolated by centrifugation. The resulting pale yellow powder was dried *in vacuo* to give **4^H·(PF₆)₄**. Yield: 0.020 g (0.0079 mmol, 60%).

¹H NMR (d_6 -DMSO): 9.62 (s, 4H), 9.61 (s, 4H), 9.31 (s, 2H), 9.29 (s, 2H), 8.93 (s, 4H), 8.92 (s, 4H), 7.32–7.60 (m, 56 H), 5.95 (s, 8H), 5.76 (s, 16H) ppm. ¹⁹F NMR (d_6 -DMSO): –72.3 (d, *J* = 711 Hz) ppm. ³¹P NMR (d_6 -DMSO): –144.2 (hept., *J* = 711 Hz) ppm. ESI-MS (pos.): 1126.2, calc. for $[(C_{120}H_{100}N_{28}Si)^{4+} \cdot (PF_6)_2^{2-}]^{2+} = 1125.9$; 702.2, calc. for $[(C_{120}H_{100}N_{28}Si)^{4+} \cdot (PF_6)^-]^{3+} = 702.3$ Da.

“Doubling” of peaks belonging to the pyridinium and triazole resonances is apparent in the ¹H NMR spectrum, which we attribute to hindered rotation.

4^I·Br₄: **1^I_{Bn}** (0.092 g, 0.14 mmol, 4.0 equiv.) and **3** (0.025 g, 0.036 mmol, 1.0 equiv.) were suspended in acetonitrile and

heated to reflux for 3 days under N_2 . The resulting light brown precipitate was isolated by filtration, washed with acetonitrile (3 × 10 mL) and diethyl ether (10 mL) and dried *in vacuo* to give **4^I·Br₄** as a pale brown powder. Yield: 0.075 g (0.023 mmol, 64%).

¹H NMR (d_6 -DMSO): 9.75 (s, 8H), 9.68 (s, 4H), 7.66 (d, *J* = 7.6 Hz, 8H), 7.53 (d, *J* = 7.6 Hz, 8H), 7.19–7.41 (m, 40H), 6.09 (s, 8H), 5.80 (s, 16H) ppm. ¹³C NMR (d_6 -DMSO): 143.3, 141.3, 136.6, 135.8, 134.9, 131.3, 128.8, 128.6, 128.5, 128.2, 127.5, 127.4, 89.1, 63.6, 53.7 ppm. HRESI-MS (pos.): 742.0035, calc. for $[C_{120}H_{92}N_{28}SiI_8]^+ = 742.0041$ Da.

4^I·(BF₄)₄: A solution of $AgBF_4$ (0.0064 g, 0.033 mmol, 4.0 equiv.) in DMF (1 mL) was added to a solution of **4^I·Br₄** (0.027 g, 0.0083 mmol, 1.0 equiv.) in DMF (3 mL) and the mixture stirred in the dark under N_2 for 2 hours. The resulting grey suspension was filtered through a short plug of celite, and washed with further DMF (6 mL). The resulting orange solution was taken to dryness under reduced pressure and the solid was sonicated in methanol (5 mL). This solid was isolated via filtration and washed with methanol (3 × 5 mL) and diethyl ether to give a brown crystalline product. Yield: 0.018 g (0.0053 mmol, 64%).

¹H NMR (d_6 -DMSO): 9.76 (s, 4H), 9.74 (s, 4H), 9.62 (s, 4H), 7.67 (d, *J* = 7.5 Hz, 8H), 7.52 (d, *J* = 7.5 Hz, 8H), 6.07 (s, 8H), 5.81 (s, 16H) ppm. ¹⁹F NMR (d_6 -DMSO): –148.3 (s), –148.2 (s) ppm. ESI-MS (pos.): 1571.6, calc. for $[(C_{120}H_{92}N_{28}SiI_8)^{4+} \cdot (BF_4)_2^{2-}]^{2+} = 1571.5$; 1018.7, calc. for $[(C_{120}H_{92}N_{28}SiI_8)^{4+} \cdot (BF_4)^-]^{3+} = 1018.7$ Da. “Doubling” of peaks belonging to the pyridinium resonances is apparent in the ¹H NMR spectrum, which we attribute to hindered rotation.

6^H·Cl: In a heavy-walled glass vial behind a blast shield, **1^H_{Bn}** (0.500 g, 1.27 mmol, 1.0 equiv.) and 1-chloro-2,4-dinitrobenzene (1.54 g, 7.63 mmol, 6.0 equiv.) were suspended in ethanol (6 mL) and heated to 120 °C for 10 days. During this time the reaction changed from yellow to orange-red with some dark oily residue forming. The reaction was cooled to room temperature, filtered to remove the dark residue, and the filtrate was taken to dryness under reduced pressure to give an orange solid. This was dissolved in acetone (50 mL) and filtered to remove an insoluble white solid. Diethyl ether (150 mL) was added to the filtrate resulting in the precipitation of a yellow powder. The mixture was cooled in the freezer overnight and then the yellow powder was isolated via filtration, washed with diethyl ether (3 × 10 mL) and dried *in vacuo* to give **6^H·Cl**. Yield: 0.267 g (0.448 mmol, 35%).

¹H NMR (d_6 -DMSO): 9.87 (d, *J* = 1.6 Hz, 2H), 9.65 (t, *J* = 1.6 Hz, 1H), 9.15 (d, *J* = 2.5 Hz, 1H), 9.03 (s, 2H), 9.01 (dd, *J* = 8.7, 2.5 Hz, 1H), 8.48 (d, *J* = 8.7 Hz, 1H), 7.35–7.44 (m, 10H), 5.79 (s, 4H) ppm. ¹³C NMR (d_6 -DMSO): 149.4, 143.1, 141.1, 140.6, 138.7, 138.4, 135.4, 132.0, 131.3, 130.4, 129.2, 128.7, 128.4, 125.4, 121.6, 53.7 ppm. HRESI-MS (pos.): 560.1794, calc. for $[C_{29}H_{22}N_3O_4]^+ = 560.1795$ Da.

6^I·Cl: A mixture of **1^I_{Bn}** (0.528 g, 0.818 mmol, 1.0 equiv.) and 1-chloro-2,4-dinitrobenzene (1.66 g, 8.20 mmol, 10 equiv.) in 1:1 ethanol:DMF (90 mL) was heated to 95 °C in a heavy-walled vial

behind a blast shield for 10 days. The resulting yellow suspension was cooled to room temperature, filtered to remove an insoluble solid, and the filtrate taken to dryness under reduced pressure to give a yellow oil. This was suspended in acetone (100 mL), stirred for an hour and then filtered to remove an insoluble solid. The filtrate was taken to dryness under reduced pressure, methanol (50 mL) was added and the suspension again filtered to remove an insoluble solid. The filtrate was again taken to dryness under reduced pressure and then the residue dissolved in methanol (10 mL) and diethyl ether (250 mL) added resulting in the precipitation of a yellow solid. The mixture was left in a freezer overnight and then the solid isolated by filtration. This was sonicated in dichloromethane (20 mL) and the solid again isolated by filtration. Taking this solid up in methanol (2 mL) and precipitating with diethyl ether (10 mL) finally gave pure product, which was isolated by filtration, washed with diethyl ether (3 × 5 mL) and dried *in vacuo* to give **6^H-Cl**. Yield: 0.049 g (0.060 mmol, 7%).

¹H NMR (d₆-DMSO): 10.08 (t, *J* = 1.6 Hz, 1H), 9.95 (d, *J* = 1.6 Hz, 2H), 9.14 (d, *J* = 2.5 Hz, 1H), 8.99 (dd, *J* = 8.7, 2.5 Hz, 1H), 8.52 (d, *J* = 8.7 Hz, 1H), 7.26–7.43 (m, 10H), 5.83 (s, 4H) ppm. ¹³C NMR (d₆-DMSO): 149.2, 143.2, 143.1, 142.4, 138.7, 138.3, 134., 131.9, 130.9, 130.0, 128.7, 128.1, 127.3, 121.0, 90.6. 53.6 ppm. HRESI-MS (pos.): 811.9730, calc. for [C₂₉H₂₀N₉O₄l₂]⁺ = 811.9728 Da.

7^H-Cl₂: A mixture of **6^H-Cl** (0.250 g, 0.419 mmol, 4.0 equiv.) and *para*-phenylenediamine (0.011 g, 0.11 mmol, 1.0 equiv.) were dissolved in 1:1 ethanol:water (24 mL). The resulting orange solution was heated at 80 °C under N₂ for 5 days. It was then taken to dryness under reduced pressure to give a yellow solid. This was suspended in acetonitrile (10 mL) and sonicated for 10 minutes. The resulting yellow powder was isolated by filtration, washed with acetonitrile (3 × 10 mL) and then diethyl ether (10 mL) and dried *in vacuo* to give **7^H-Cl₂**. Yield: 0.078 g (0.084 mmol, 80%).

¹H NMR (d₆-DMSO): 9.70 (d, *J* = 1.4 Hz, 4H), 9.63 (t, *J* = 1.4 Hz, 2H), 9.15 (s, 4H), 8.44 (s, 4H), 7.36–7.46 (m, 20H), 5.82 (s, 8H) ppm. ¹³C NMR (d₆-DMSO): 144.3, 140.6, 140.1, 135.4, 131.5, 129.0, 128.5, 128.2, 126.9, 125.1, 99.5, 53.5 ppm. HRESI-MS (pos.) 431.1844, calc. for [C₅₃H₄₂N₁₄]²⁺ = 431.1853 Da.

7^H-(PF₆)₂: **7^H-Cl₂** (0.030 g, 0.032 mmol, 1.0 equiv.) was dissolved in methanol (3 mL) with heating. A solution of NH₄PF₆ (0.031 g, 0.19 mmol, 6.0 equiv.) in water (2 mL) was added, resulting in the formation of a pale yellow precipitate. The reaction was left to stand at room temperature for 2 hours and then the solid was isolated by filtration, washed with methanol (3 × 5 mL) and diethyl ether (5 mL) and dried *in vacuo* to give **7^H-(PF₆)₂** as a pale yellow powder. Yield: 0.027 g (0.024 mmol, 74%).

¹H NMR (CD₃CN): 9.37 (t, *J* = 1.4 Hz, 2H), 9.32 (d, *J* = 1.4 Hz, 4H), 8.55 (s, 4H), 8.18 (s, 4H), 7.39–7.47 (m, 20H), 5.71 (s, 8H) ppm. ¹⁹F NMR (CD₃CN): –72.9 (d, *J* = 707 Hz) ppm. ³¹P NMR (CD₃CN): –144.7 (hept., *J* = 707 Hz) ppm. ESI-MS (pos.): 1007.4, calc. for [(C₅₂H₄₂N₁₄)²⁺·(PF₆)[–]]⁺ = 1007.3 Da.

7^I-Cl₂: A mixture of **7^H-Cl** (30 mg, 0.036 mmol, 4.0 equiv.) and *para*-phenylenediamine (0.98 mg, 0.0091 mmol, 1.0 equiv.) were dissolved in 1:1 ethanol:water (4 mL). The resulting orange solution was heated at 80 °C under N₂ for 3 days during which time a yellow precipitate formed. This precipitate was isolated by filtration and suspended in acetonitrile (5 mL) and sonicated for 10 minutes. The resulting yellow powder was isolated by filtration, washed with acetonitrile (3 × 5 mL) and then diethyl ether (5 mL) and dried *in vacuo* to give **7^I-Cl₂**. Yield: 5.1 mg (0.0036 mmol, 39%).

¹H NMR (d₆-DMSO): 9.92 (t, *J* = 1.3 Hz, 2H), 9.72 (d, *J* = 1.3 Hz, 4H), 8.45 (s, 4H), 7.29–7.44 (m, 20H), 5.84 (s, 8H) ppm. ¹³C NMR (d₆-DMSO): 144.6, 143.4, 141.4, 138.4, 135.0, 131.1, 128.9, 128.3, 127.6, 127.1, 89.4, 53.7 ppm. HRESI-MS (pos.) 1400.9253, calc. for [(C₅₂H₃₈N₁₄l₄)²⁺·Cl[–]]⁺ = 1400.9271 Da.

7^I-(BF₄)₂: **7^I-I₂** (3.5 mg, 0.0024 mmol, 1.0 equiv.) was dissolved in DMF (1 mL), and separately AgBF₄ (0.94 mg, 0.0048 mmol, 2.0 equiv.) was dissolved in DMF (1 mL). The two solutions were mixed and stirred under N₂ in the dark for 2 hours. The resulting suspension was filtered through a celite plug, with the celite washed with more DMF (2 mL). The resulting yellow filtrate was taken to dryness under reduced pressure to give an orange-brown solid. Acetone (5 mL) was added and the suspension filtered to remove an insoluble brown solid. The filtrate was taken to dryness to give **7^I-(BF₄)₂** as a yellow powder. Yield: 2.0 mg (0.0013 mmol, 54%).

¹H NMR (d₆-acetone): 10.05 (br. s, 2H), 9.92 (d, *J* = 1.2 Hz, 4H), 8.72 (s, 4H), 7.37–7.44 (m, 20H), 5.91 (s, 8H) ppm. ¹⁹F NMR (d₆-acetone): –152.53 (s), –152.47 (s) ppm. ESI-MS (pos.): 1453.1, calc. for [(C₅₂H₃₈N₁₄l₄)²⁺·(BF₄)[–]]⁺ = 1453.0 Da.

8^H-Cl₄: A mixture of **6^H-Cl** (0.339 g, 0.569 mmol, 7.0 equiv.) and tetra-amine **9** (0.031 g, 0.081 mmol, 1.0 equiv.) were dissolved in 1:1 ethanol:water (40 mL). The resulting orange solution was heated at 80 °C for 7 days under N₂. It was then cooled to room temperature and taken to dryness under reduced pressure to give an orange-red solid. This solid was suspended in acetonitrile (10 mL), sonicated, and then the resulting solid isolated by filtration to give the crude product as an orange powder. This powder was dissolved in methanol (20 mL) and then diethyl ether (20 mL) added resulting in the formation of a precipitate, which was isolated by filtration. This solid was suspended in acetone (20 mL) and sonicated, and the resulting pale brown powder isolated by filtration, washed with acetone (3 × 5 mL) and diethyl ether (5 mL) to give **8^H-Cl₄**. Yield: 0.053 g (0.026 mmol, 32%).

¹H NMR (d₆-DMSO): 9.59–9.66 (m, 12H), 9.24 (s, 8H), 8.09–8.17 (m, 8H), 7.80 (d, *J* = 8.3 Hz, 8H), 7.34–7.44 (m, 40H), 5.80 (s, 16H) ppm. ¹³C NMR (d₆-DMSO): 148.2 141.0, 140.7, 139.8, 135.7, 135.4, 131.5, 131.4, 128.9, 128.5, 128.2, 125.3, 125.2, 64.4, 53.5 ppm. HRESI-MS (pos.): 472.1992, calc. for [C₁₁₇H₉₂N₂₈]⁴⁺ = 472.2010 Da.

8^H-(PF₆)₄: **8^H-Cl₄** (0.043 g, 0.021 mmol, 1.0 equiv.) was dissolved in methanol (5 mL) with heating, and NH₄PF₆ (0.041 g, 0.25 mmol, 12 equiv.) in water (2 mL) was added resulting in the

formation of a yellow precipitate. The mixture was left to stand for 2 hours and then the precipitate was isolated by filtration, washed with methanol (3 × 5 mL) and diethyl ether (5 mL) and dried *in vacuo* to give **8^H·(PF₆)₄**. Yield: 0.036 g (0.015 mmol, 70%).

¹H NMR (d₆-DMSO): 9.52–9.58 (m, 12H), 9.10 (s, 8H), 8.08 (d, *J* = 8.4 Hz, 8H), 7.82 (d, *J* = 8.4 Hz, 8H), 7.35–7.44 (m, 40H), 5.80 (s, 16H) ppm. ¹⁹F NMR (d₆-DMSO): –70.2 (d, *J* = 711 Hz) ppm. ³¹P NMR (d₆-DMSO): –144.2 (hept., *J* = 711 Hz) ppm. ESI-MS (pos.): 2323.9, calc. for [(C₁₁₇H₉₂N₂₈)⁴⁺·(PF₆)₃^{3–}]⁺ = 2323.9 Da; 1089.4, calc. for [(C₁₁₇H₉₂N₂₈)⁴⁺·(PF₆)₂^{2–}]²⁺ = 1089.4 Da; 677.9, calc. for [(C₁₁₇H₉₂N₂₈)⁴⁺·(PF₆)[–]]³⁺ = 678.0 Da.

Conflicts of interest

There are no conflicts to declare.

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