NH-bridged Dimeric Phosphazanes: Inorganic Molecular Switches based on Anion Responsive Bifurcated to Trifurcated Hydrogen Bond Transitions

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SUMMARY

Molecular machines and switches, supramolecular chemistry, and crystal engineering are vibrant areas of research. Organic chemists have devoted considerable efforts to develop a wide range of complex functional building blocks with enhanced properties and chemically responsive properties to advance these fields. However, the rational design of topologically versatile and chemically responsive building blocks in the main group arena has not been traditionally part of the main group chemical space. This chemical diversity – when implemented in molecular machines – could become a transformative force in the field. Here, we report a robust main group anion responsive molecular switch based on bifurcated to trifurcated hydrogen bond transitions. The herein reported molecular switch is based – for the first time – on a fully inorganic backbone. This work provides proof-of-concept toward a new strategy for designing chemically responsive molecular machines and switches based on p-block elements.

INTRODUCTION

The last three decades have seen the rise of rationally designed synthetic molecular architectures with stimuli controlled molecular-level motion. These advances have allowed mankind to build artificial structures that can control and exploit molecular-level motion, giving rise to a wide range of molecular machines and switches.²–⁷

There has been a wide range of reported examples of molecules, including catenanes and rotaxanes, where molecular motion is triggered by various stimuli (light, electrochemistry, pH, heat, solvent polarity, cation, or anion binding, etc.). Despite the extraordinary progress already made, researchers have merely scratched the surface, and further developments are required to reach the level of competence/sophistication displayed by biological systems.⁸–⁹

Future molecular machines will require a multidisciplinary approach with inputs and expertise from other fields, which necessitates the development of molecular machinery based on main group backbones (i.e., based on non-carbon-carbon bonds). Over the last few decades, the field of main group chemistry has not only contributed to chemistry at large by providing important chemical concepts, but also has uncovered a wealth of catalytic systems and energy materials. However, its implementation in the area of molecular machines is still lagging behind their organic counterparts.

Note: The text is a summary of the research on NH-bridged dimeric phosphazanes as inorganic molecular switches based on anion-responsive bifurcated to trifurcated hydrogen bond transitions. The research involves the design and synthesis of phosphazane species that respond to anions, demonstrating versatile and chemically responsive building blocks in the main group arena. The work provides proof-of-concept for a new strategy in designing chemically responsive molecular machines and switches based on p-block elements.
In contrast to carbon-based systems, where the tetravalent state dominates the chemistry, other many main group elements display multiple valencies and oxidation states with very distinctive reactivity and chemical properties (Figure 1A). Therefore, main group elements provide a wealth of unexplored backbones in the molecular machinery space, which we envision will impact the way future molecular machines are designed.

However, prior to selecting a suitable main group system, the kinetic and thermodynamic stability of the non-carbon bonds have to be taken into consideration (Figure 1B). The ideal main group frameworks are those with high bond energies (relative to carbon-carbon bonds) and display low bond polarities (Figure 1B). Within this context, among the potential main group families (i.e., P-N, Al-N, Si-N, B-N, P-O), P-N bonds fulfil both requirements displaying a comparable to carbon-based bond energies (i.e., C-C, C-O, and C-N), as well as a low polarity. In addition, P-N-based backbones are the largest family of main group compounds displaying these requirements, making them the ideal frameworks for proof-of-concept studies (Figure 1C).

Among the molecular motifs comprising P-N bonds, P,N,N cyclophosphazane building blocks are capable of forming a broad range of cyclic and acyclic frameworks. These main group systems, have shown to be excellent ligands for metal coordination and versatile modular building blocks for the construction of larger molecules for biological applications and supramolecular chemistry.

More recently, it has been demonstrated that cyclodiphosphazanes, P,N,N frameworks, are versatile HB donors that rival ureas, thioureas and squaramides, thanks to their increased bite angles. In addition, these species have been shown to effectively bind to small
molecules (e.g., acetone, DMSO and DMF), and be versatile building blocks for the engineering for high-order ternary and quaternary multicomponent cocrystals, which further broadens the scope of their applications in supramolecular applications and crystal engineering. \textsuperscript{38,45}

Common strategies for improving the HB donor ability of urea and thioureas for their use as building block in both supramolecular chemistry and molecular machines are to increase (i) the complexity (i.e., adding extra HB functionalities, electron withdrawing groups, etc.) of the substituents (\textit{Approach 1})\textsuperscript{46-49} or (ii) the number of repeating units of urea/thiourea crafted within the molecular backbone (\textit{Approach 2}).\textsuperscript{49-55} Both strategies aim to increase HB ability, translating into better binding affinities and performance versus their classical counterparts.

Similar approaches can – in theory – be applied to P\(_2\)N\(_2\) species. The influence of varying substituents has been studied for monomeric species (\textit{i.e., Approach 1}).\textsuperscript{53,34,44} However, in contrast to carbon-based frameworks, it was found that effective HB abilities are only observable after the P\(^{\text{iii}}\)N\(_2\) backbone of choice is oxidised to P\(^{\text{iv}}\)N\(_2\) (i.e., from P\(^{\text{iii}}\) to P\(^{\text{iv}}\)). Notably, the oxidation process P\(^{\text{iii}}\)N\(_2\) to P\(^{\text{iv}}\)N\(_2\) enables further fine-tuning of their HB ability (\textit{Approach 3}), since various chalcogen elements (\textit{i.e., O, S or Se}) can be readily installed into the backbone during a simple post-synthetic oxidation step. Notably, this “gain of function” feature – \textit{i.e.}, the one-step installation of chalcogen elements – is not readily available for widely used carbon-based building blocks, which limits the fine-tuning of their properties and reduces their scope through post-synthetic backbone alteration.

In terms of increasing the number of repeating units to form oligomeric P\(_2\)N\(_2\) species (\textit{i.e., Approach 2}), this approach has been traditionally impaired due to the lack of selectivity between cyclic and acyclic oligomeric P\(^{\text{iv}}\)N\(_2\) species containing NH moieties.\textsuperscript{56-58} However, novel topologically tuneable N-bridged acyclic oligo-P\(^{\text{iv}}\)N\(_2\) dimeric and trimeric species have been recently reported.\textsuperscript{59} The latter comprise different substituents (\textit{e.g., H, ’Pr, Ph, and ’Bu}) at the two backbone bridging positions, which determine their final topological conformation. This report represents the first presentation of different topological conformations using non-covalent interactions in the phosphazane P\(^{\text{iv}}\)N\(_2\) family. In addition, theoretical studies predict acyclic dimeric and trimeric P\(^{\text{iv}}\)N\(_2\) species as topologically tuneable frameworks with superior halide receptors with increased binding ability towards chlorides compared to their monomeric counterparts (\textit{i.e., squaramide and thiourea R\(_1\)(8 type building blocks)).\textsuperscript{59} Noteworthy, is that anion binding has been successfully used as a chemical stimulus in a wide range of molecular switches.\textsuperscript{50-65}

The previously demonstrated rational selection of different topological conformations in dimeric and trimeric acyclic P\(^{\text{iv}}\)N\(_2\) phosphazane species, combined with the predicted superior halide binding ability of P\(^{\text{iv}}\)N\(_2\), suggests their suitability as potential main group building blocks towards chemically responsive frameworks based on a fully inorganic backbone.

Herein, we report the synthesis of novel acyclic NH-bridged dimeric P\(^{\text{iv}}\)N\(_2\) species and demonstrate them as effective molecular switches activated by anionic species. This new family of NH-bridged P\(^{\text{iv}}\)N\(_2\) molecular switches feature both topologically responsiveness to external anion stimuli and an adaptable cavity size. We envision that these unique properties will enable oligomeric cyclophosphazane frameworks to play a crucial role in designing molecular machines, host-guest systems, and supramolecular chemistry in the future.

RESULTS

\textbf{Synthesis of acyclic dimeric-P\(^{\text{iv}}\)N\(_2\) molecular switches}

The basic building block in our studies, compound 1, can be obtained via the single step reaction of \textit{Cl}(\textit{P}(\mu-N’Bu))\textit{NH}’Bu with LiNH\(_2\) in THF at room temperature (\textit{Scheme S1}).\textsuperscript{58,66} This recently reported synthetic methodology allows for a simple and straightforward route to NH-bridged acyclic dimeric P\(^{\text{iv}}\)N\(_2\).\textsuperscript{59}

Compound 1 was then oxidised to form the NH-bridged acyclic dimeric-P\(^{\text{iv}}\)N\(_2\) counterpart to enable its HB ability (\textit{Figure 2A}). Treatment of 1 with six equivalents of H\(_2\)O\(_2\), added dropwise at 0 °C, afforded its oxygen oxidised counterpart 2 (\textit{Scheme S2}). The \textit{1H NMR} spectrum of 2 in CDCl\(_3\) exhibits three different NH signals at 3.63, 5.36 and 7.39 ppm and two different tert-butyl signals at 1.34 and 1.47 ppm for bridging and terminal positions, respectively, revealing the asymmetric nature of compound 2 (\textit{Figure S4}). This suggests that compound 2 adopts a twisted
exo,endo/endo,exo “S” conformation (i.e., 2<sup>OFF</sup>) in which both P<sup>V</sup>,N<sub>2</sub> fragments are non-equivalent. This feature was attributed to the presence of intramolecular hydrogen bonding within the dimeric backbone. Furthermore, the <sup>31</sup>P-{<sup>1</sup>H} NMR of 2 in CDCl<sub>3</sub> also shows two heavily broadened signals at -1.11 and -6.66 ppm, which further suggests the existence of intramolecular P=O···H-N HB interactions in 2<sup>OFF</sup> (Figure S5).

In a similar fashion, the overnight reaction of 1 with 4.2 equivalents of elemental sulfur in THF at room temperature furnished 3 (Scheme S3). In contrast to compound 2, the <sup>1</sup>H NMR in CDCl<sub>3</sub> for 3 reveals two NH signals at 4.12 and 5.16 ppm with a ratio of 2:1, while the two terminal tert-butyl groups are also equivalent, giving rise to only one signal at 1.44 ppm (Figure S9), suggesting an exo,exo/endo,exo “C” conformation (i.e., 3<sup>ON</sup>). However, compound 3 is expected to favour the 3<sup>OFF</sup> conformation ([3<sup>ON</sup>]/[3<sup>OFF</sup>] < 0.01%) according to DFT calculations (Figure 4 and ESI). Therefore, the observed <sup>1</sup>H NMR spectrum suggests a fluxional behaviour of the compound 3, where there is a rapid interconversion between 3<sup>ON</sup> and 3<sup>OFF</sup>. In addition, the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum shows significantly sharper signals at 34.28 and 41.93 ppm relative to compound 2 (Figure S11), supportive of much weaker HB interactions with the P=S moiety.

To confirm this hypothesis, variable temperature (VT) <sup>1</sup>H NMR of 3 was performed, and two broad singlets at δ 3.34 and 5.15 ppm in a 1:2 ratio was observed at -60 °C (cf. 4.12 and 5.16 ppm in a 2:1 ratio at RT, see Figure S12), which is indicative of a “S” topological arrangement (i.e., 3<sup>OFF</sup>). The presence of only two resonances in the NMR spectrum – instead of the three that would have been expected – combined with the observed inversion of the signal ratio, is attributed to small differences in the chemical shift, which results the coincidental overlapping of two of the three distinct NH environments in 3<sup>OFF</sup>. Determination of the energy barrier of rotation based on the VT <sup>1</sup>H NMR data (T<sub>C</sub> = -20 °C, Δν = 722 Hz) suggests a relatively low rotation barrier between the 3<sup>ON</sup> and 3<sup>OFF</sup> conformations (~11.0 kcal·mol<sup>-1</sup>). This experimental value is in good agreement with the DFT calculated rotation barrier of 12.57 kcal·mol<sup>-1</sup> (Figure 2B, see Figure S15 for details), where the 3<sup>ON</sup> conformer is calculated 4.72 kcal·mol<sup>-1</sup> above the 3<sup>OFF</sup> counterpart (Figure 4).

![Figure 2. Synthesis of dimeric-dichlocyclodiphosphazanes (P<sub>2</sub>N<sub>2</sub>) and their switch mode of action. (A) Synthetic route to phosphazane molecular switches. (B) Phosphazane switch OFF to ON (i.e., S to C) topological conformational change mode of action observed in solution for 2 and 3 – the energy barriers displayed were calculated by DFT using B3pw91/6-311g(d,p) basis set](image)

To confirm if the same ON/OFF conformational changes can be observed for compound 2, high-temperature NMR studies were performed. Upon heating to 60°C the signal displayed by compound 2 broadened substantially. However, the coalescence temperature could not be achieved in the solvent system used (b.p. CDCl<sub>3</sub> = 60.9 °C), indicating the compound has a higher ON/OFF rotational barrier than 3. The different ON/OFF behaviour between compounds 2 and 3 observed is attributed to the different HB strengths present in these species, where only the stronger P=O···H-N is sufficient at room temperature to prevent fluxionality.
To assess the effect of HB donor/acceptor solvents on 2\textsuperscript{ON}, where the OFF conformation is “locked” in place by intramolecular HB interactions, the compound was dissolved in methanol-d\textsubscript{4}, and its \textsuperscript{1}H NMR spectrum was recorded. The spectrum shows an absence of NH signals which is attributed to peak broadening due to HB interactions of the amino protons with the methanol-d\textsubscript{4}. Notably, there is only one resonance at 1.38 ppm corresponding to terminal tert-butyl groups (cf. \(\delta 1.34\) and 1.47 ppm in CDCl\textsubscript{3}), which suggest that competing HB interactions disrupt the intramolecular P=O···HN\textsubscript{Bu} HB in 2, allowing for fluxional behaviour in methanol-d\textsubscript{4} (Fig S4–S8).

Despite the successful synthesis of 2 and 3, the reaction of 1 with 4.2 equivalents of elemental selenium in THF did not result in the formation of expected selenium-oxidised acyclic dimeric-P\textsuperscript{V},N\textsubscript{1} ([(\(\mu\text{-}\text{NH})\text{PSe(\(\mu\text{-}\text{N\text{-}Bu})\text{PSe(\(\mu\text{-}\text{NH\text{-}Bu})\text{]}\text{]}\text{]} \text{(Scheme S4)}). Instead, the in situ \textsuperscript{31}P-[\textsuperscript{1}H] NMR spectrum reveals a mixture of products. Further insights on the reaction were obtained from diffraction quality crystals obtained from a concentrated THF solution, where \([\text{H}_{\text{2}}\text{N}\text{P(Se)(\(\mu\text{-}\text{N\text{-}Bu})\text{)}\text{P(Se(\(\mu\text{-}\text{NH\text{-}Bu})\text{]}\text{]}\text{]}\text{]}\text{]}\text{]} \text{was identified as one of the products (Figure S57). Notably, this compound is the first crystallographically characterised asymmetrically substituted monomeric-P\textsuperscript{V},N\textsubscript{1} containing a -NH\textsubscript{2} moiety.

An important property for the implementation of main group frameworks in molecular machinery is their overall stability under ambient conditions. Compounds 2 and 3 both display high air- and hydrolytic-stability, and can be bench-stored and handled under ambient atmospheric conditions.\textsuperscript{61–68} Hydrolytic studies of samples containing 2 and 3 each in 1:9 H\textsubscript{2}O/THF monitored via \textsuperscript{31}P-[\textsuperscript{1}H] NMR showed no signs of degradation for up to 4 weeks, showcasing their robustness as extended phosphazane scaffolds for a multitude of supramolecular chemistry applications (Figures S16–S17).\textsuperscript{61,68}

**P\textsuperscript{V},N\textsubscript{1} Switch OFF mode: R\textsuperscript{311}2(8) bifurcated HB to neutral guest molecules.**

To further confirm the structures of compounds 2 and 3 and their ON/OFF topologies, single crystals X-ray diffraction (SCXRD) studies were performed. These studies reveal both compounds adopting an OFF twisted topology in solid-state, comprising of a R\textsuperscript{311}2(8) bifurcated hydrogen interactions. (Figure 3A, S51 – S52)

Crystal of 2 obtained from a THF solution display strong intermolecular interactions leading to the formation dimeric aggregate via R\textsuperscript{311}2(8) bifurcated HB interactions between the amino protons and the P=O group of two molecules of 2 (Figure S49). In chloroform (i.e., a solvent comprising HB donor) the same bimolecular aggregate is observed, as well as exogenous P=O···H-CCl\textsubscript{4} HB interactions. In both structures, the HB bond distances observed are in the range of 2.87 to 3.19 Å, which is consistent with monomeric counterparts.\textsuperscript{24} In contrast to the formation of HB dimers, the solid-state structure of 3 reveals the formation of R\textsuperscript{3}2(8) bifurcated HB solvates (with MeCN and DMSO) (Fig. S54–S52). These types of HB interactions with neutral organic molecules, and their bond distances, are consistent with those observed in monomeric P\textsuperscript{V},N\textsubscript{1} counterparts.\textsuperscript{28}

The formation of dimers in 2 – instead of monomeric solvates as observed for compound 3 – is attributed to the preferential formation of strong bifurcated R\textsuperscript{311}2(8) HB with a P=O moiety over a molecule of THF. Overall, both compounds display an OFF conformation, where the second P\textsuperscript{V},N\textsubscript{1} unit does not engage in intermolecular HB (Figure 3A), which demonstrates a preference for intramolecular R\textsuperscript{311}2(8) HB in the presence of neutral molecules over an ON R\textsuperscript{3}2(8, 8) HB motif where all the NH groups are engaging in bonding.

To gain further insights into the different ON/OFF behaviour, density functional theory (DFT) studies at (B3PW91/6-311G(d,p)) level of theory) were performed. The binding energy for the coordination of a molecule of DMSO to 2\textsuperscript{OFF} was calculated to be 12.90 kcal·mol\textsuperscript{-1}. In contrast, the binding energy for the 2\textsuperscript{ON} topological conformation was calculated to be 8.97 kcal·mol\textsuperscript{-1} relative to the individual molecules (Figure 4A). The differences in stabilisation between the ON/OFF HB motifs (ca. 4 kcal·mol\textsuperscript{-1}) is attributed to the different strengths of the non-covalent interactions present (i.e., R\textsuperscript{311}2(8) vs P=S···H-N HB interactions, see Figure S55 for non-covalent interactions).

In the OFF conformation one R\textsuperscript{311}2(8) HB and one P=S···H-N are present, whereas its ON counterpart display a trifurcated HB interaction with two symmetric adjacent bifurcated R\textsuperscript{311}2(8) HB interactions “sharing” a HB donor to common acceptor (i.e., in the same manner adjacent angles are mathematically defined), which we define as a R\textsuperscript{3}2(8, 8) interaction. The stronger intramolecular HB interaction in compound 2 has been also computed and the energy difference between the ON/OFF conformation arise to ca. 7.6 kcal/mol (Table S6). In addition, we
performed non-covalent interaction (NCI) analyses for compounds 2 and 3 on their OFF confirmation (Figure 59). Our analyses show that 2-OFF display stronger attractive intramolecular HB interactions than 3-OFF, which further supports our hypothesis and is consistent with the experimental observations.

**A Phosphazane switch OFF mode - R²₁(8) HB**

![Image of A Phosphazane switch OFF mode - R²₁(8) HB](image)

**B Phosphazane switch ON mode – R³₁(8,8) HB**

![Image of B Phosphazane switch ON mode – R³₁(8,8) HB](image)

**Figure 3. Molecular switch binding modes to neutral and anionic guests.** (A) Dimeric-P₆ zeroes, switch OFF mode (3⁰ff) – R²₁(8). Solid state structures of "2c2" (displaying a fragment of the supramolecular dimer in the solid-state, left), 3cAcetonitrile (middle) and 3cDMSO (right), illustrating weak interactions with neutral molecules. Hydrogen atoms (except selected NH protons) and disorder were omitted for clarity. (B) Dimeric-P₆ zeroes, switch ON mode (3⁰ff) – R³₁(8,8). Solid state structures of 3cCl⁻ (left), 3cBr⁻ (middle) and 3cI⁻ (right). Hydrogen atoms (except selected NH protons), and disorder were omitted for clarity. For selected bond distances and expanded figures see ESI.

**P⁵ zeroes,N₂ Switch ON mode: R³₁(8,8) trifurcated HB to anions hosts.**

As observed, interactions of 2 and 3 with small neutral organic molecules favours OFF conformations displaying bifurcated R²₁(8) HB modes. However, the second P⁵ zeroes,N₂ unit does not engage in intermolecular HB, which is attributed the presence of the intramolecular P=E···NH HB present in compounds 2 and 3.

Past reports on monomeric cyclodiphosphazane receptors have shown that strong HB guest, such as halide anions, favour the exo,exo conformation,⁴⁵,⁴⁷ which enables these species to act as R²₁(8) HB donors.⁴⁹,⁵⁰,⁵¹ This preference for the exo,exo (over the exo,endo) in the presence of halide HB acceptors, has also been recently highlighted during the formation of high-order multicomponent cocrystals based on monomeric P⁵ zeroes,N₂ building blocks.⁴⁵

The presence of an additional P⁵ zeroes,N₂ provide 2 and 3 with an additional degree of freedom (i.e., OFF vs ON conformations), and could potentially provide a superior performance towards anion binding and sensing if selectively switched ON. Moreover, rationally controlling rotatory motion around a single bond has commonly used in molecular machines and switches using a wide range of organic (i.e., triptycyl, quinoline, and naphthyl moieties, etc.) and organometallic molecular architectures triggered by various chemical stimuli (e.g., protonation, anions, and cations, inter alia).¹,²,⁴³

We postulate that, in contrast to what was observed for neutral molecules (i.e., MeCN and DMSO) where only the OFF conformation is observed, the second unit would switch ON in the presence of anionic hosts via the formations of higher-order trifurcated R³₁(8,8) HB interactions, and hence, fulfilling the conformational changes required to be classified as a molecular switch.⁷² Moreover, excluding macrocycles, this type of adjacent and symmetrical HB interactions are rare⁷²,⁷³ and have only been previously described for C₆ zeroes tripodal type of frameworks – never for linear molecule – making the herein reported molecular switch unique. Hence, we proceeded to
study the ON/OFF host-guest properties of 3 towards anions. Compound 3 was selected over 2 due to its lower rotation barrier and its better expected performance than 2 in anion binding based on previous reports on monomeric P\text{V},N\text{N} species.

Indeed, cocrystals of 3 obtained with various halides (i.e., Cl, Br and I) display an ON topological conformation with a fully engaged bis-P\text{V},N\text{N} backbone effectively utilising all three NH moieties in HB interaction with the negatively charged halide (Figure 3B). This is, to the best of our knowledge, the first example of trifurcated R\text{1},(8,8) HB in cyclodiphosphazane species. In addition, the ON/OFF molecular switch ability of the phosphazane host to selectively enable different HB modes to adapt to specific guests has never been reported for inorganic frameworks.

Remarkably, 3\textsuperscript{ON} also exhibits the ability to vary its cavity size by pivoting around the central NH moiety. This enables compound to readily accommodate group 17 anions of different sizes, with little distortion to its framework (vide infra). In contrast, such topological flexibility was not observed in its cyclic counterparts due to its rigid nature, limiting its supramolecular interactions to smaller guests. Hence, dimeric P\text{V},N\text{N} species represent a promising framework with properties that are unique and complimentary to existing currently reported organic-based anion receptors and molecular switches.

**P\text{V},N\text{N} Switch ON mode: R\text{1},(8,8) Trifurcated HB anion binding abilities**

The ability of 3 to switch ON the R\text{1},(8,8) trifurcated HB mode in response to anions showcases the potential of these species to act as high anion affinity molecular switches in supramolecular and chemically responsive architectures. Therefore, we proceed to investigate sensitivity and anion binding abilities of compound 3, with respect to anions of different sizes and chemical nature. The gradual addition of tetrabutylammonium chloride (TBACl) to a solution of 3 in CDCl\textsubscript{3} displayed new resonances corresponding to host-guest adduct 3\textsuperscript{ON}Cl\textsubscript{2}, indicating negligible exchange of chloride ions between host molecules, with full conversion into 3\textsuperscript{ON}Cl\textsubscript{2} occurring at approximately two equivalents of TBACl. Due to these slow exchanges, NH resonances of 3\textsuperscript{ON} with Cl\textsuperscript{−} the binding constant (K\text{A}) was estimated using a concentration-weighted average of free host and host-guest complex.\textsuperscript{13} Using this method, the binding constant was estimated to be K\text{A} = 192.92 ± 81.89 M\textsuperscript{-1} (Figure S23).

When larger halides or more complex anions were used, namely I\textsuperscript{−}, HSO\textsubscript{4}\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} (i.e., TBAI, TBAHSO\textsubscript{4}, and TBANO\textsubscript{3}, respectively), the addition of increasing amounts of these species displayed a gradual downfield shift of NH resonances. This downfield shift is representative of anion binding to the NH sites present in 3\textsuperscript{ON}, and indicative of a rapid anion exchange between molecules of 3. The data obtained throughout the NMR titrations for each of these species were fitted into a 1:1 binding isotherm model.\textsuperscript{75,95} The binding constants obtained were 5.17 ± 0.13 (TBAI), 9.48 ± 0.25 (TBAHSO\textsubscript{4}) and 20.39 ± 1.17 M\textsuperscript{-1} (TBANO\textsubscript{3}) – see Table 1.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Binding constants K\text{A} [M\textsuperscript{-1}]</th>
<th>Binding Energy (kcal-mol\textsuperscript{-1})\textsuperscript{[a]}</th>
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<tr>
<td>Cl\textsuperscript{−}</td>
<td>192.92 ± 81.89\textsuperscript{[b]}</td>
<td>69.04</td>
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<tr>
<td>Br\textsuperscript{−}</td>
<td>N.D.</td>
<td>43.91</td>
</tr>
<tr>
<td>I\textsuperscript{−}</td>
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<td>38.19</td>
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<tr>
<td>HSO\textsubscript{4}\textsuperscript{−}</td>
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<td>44.26</td>
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<tr>
<td>NO\textsubscript{3}\textsuperscript{−}</td>
<td>20.39 ± 1.17</td>
<td>50.51</td>
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\textsuperscript{[a]} Calculated by DFT using B3pw91/6-311g(d,p) basis set
\textsuperscript{[b]} Estimated based on concentration-weighted average of [H\textsubscript{N}] and [HG]\textsuperscript{+}; N.D. = not determined.

Unfortunately, NMR titrations of 3 with Br\textsuperscript{−} displayed extensive broadening of the NH resonances of the 3\textsuperscript{ON}Br\textsuperscript{−} adduct at lower concentrations, which was attributed to a guest exchange rate within NMR timescales. To corroborate this assumption, NMR spectroscopy of 3\textsuperscript{ON} with 0.5 equivalents of TBABr was conducted in CDCl\textsubscript{3} at -50°C. The low temperature 1H NMR spectrum shows clear NH signals at 5.87 and 8.62 ppm, resulting from a lower exchange rate at -50°C, which further supports our hypothesis (Fig S14-S15). As a result, the data collected is unsuitable to be fitted either in the isotherm binding model or estimated via the concentration-weighted average of free host and host-guest complex – thus, the binding affinity of 3\textsuperscript{ON} to Br\textsuperscript{−}
was not determined. Overall, our results suggest that the halide exchange rates follow the trend Cl<Br<I.

The distinct interaction of 3ON with different halides is also observed in the solid state. The solid-state structures of 3ON⊂Cl, 3ON⊂Br and 3ON⊂I displays an increasing N···X distance with increased halide size, illustrating a cavity capable of adapting to different sized hosts while still displaying good guest binding affinities. Notably, in contrast to previously reported monomeric species, compound 3 also exhibits higher binding affinities to all anions studied (See Table S1). This is attributed to both the increased number of HB donors and larger cavity present in 3—which can accommodate different larger anions (i.e., I−, HSO4− and NO3−). The cavity displays a steady increase of the terminal N···N distance on descending the group: 3ON⊂Cl (6.272 Å) < 3ON⊂Br (6.410 Å) < 3ON⊂I (6.611 Å). Such a feature is also reminiscent of the macrocyclic pentamer [P(µ-NttBu)]4(NH)5, distorting its planar structure to host larger halides. However, in contrast to 3, this macrocycle is not known to accommodate larger complex anions (i.e., HSO4− or NO3−) likely due to the sterically encumbered and rigid nature of its cavity.

The binding energies for 3ON⊂Cl, 3ON⊂Br, 3ON⊂I, 3ON⊂NO3 and 3ON⊂HSO4 were calculated by DFT. To simplify the computation, the cations were not included in calculations. The theoretical binding energy obtained are 69.04, 43.91, 38.19, 50.51 and 44.26 kcal·mol−1 for Cl−, Br−, I−, NO3− and HSO4− respectively. Although the binding energies are overestimated due to the absence of counterions, the trend shows a good correlation with the experimentally obtained binding constants.

Figure 4. Theoretical studies for molecular switch 3 and calculated binding constants. (A) Calculated binding energies for the 3OFF and 3ON solvates with DMSO. (B) Calculated structures and binding energies for 3ON⊂Anion host-guest adducts. (C) Energy profile of the topological conformational change 3OFF/3ON

P2,N2 Switch ON/OFF Reversibility: R2(8) bifurcated ↔ R3(8,8) trifurcated transitions.

Given the OFF/ON modes observed, we hypothesise that these systems are topological responsive, and can regain its original topology once the chemical stimulus is withdrawn. This would thus provide the first example of a fully reversible molecular switch in the main group arena. Due to the distinct differences between 2OFF and 2ON observed throughout our studies, the reversibility of bifurcated and trifurcated transitions was probed using 2 as a model.
However, a full reversibility can only be fully demonstrated when the host is able to return to its initial topological state upon removal of the chemical stimulus. For this purpose, an excess of five equivalents of TBACl were added to a solution of $\text{2}^{\text{ON}}$ in CDCl$_3$. As expected, the original NH resonances transform into two signals at 5.29 and 8.38 ppm, indicating a halide induced OFF to ON topological transformation (see ESI). To prove reversibility the halide anion guest was removed from the $\text{2}^{\text{ON}}$ host. Addition of five equivalents of NaPF$_6$ to this solution resulted in an anion exchange, which is accompanied by the precipitation of non-soluble NaCl as byproduct and the return to the $\text{2}^{\text{OFF}}$ topological conformation. The OFF topology was confirmed by in situ $^1$H NMR of the mixture, which illustrated by the presence of the three characteristic -NH signals at approximately the same chemical shifts (Figure 5B). Further addition of five equivalents of TBACl results in $\text{2}^{\text{ON}}$ topology again, thus demonstrating the reversibility of the main group molecular switch.

**Figure 5.** Molecular switch reversibility studies. (A) Characteristic signals corresponding to $\text{2}^{\text{ON}}$ and $\text{2}^{\text{OFF}}$. (B) Partial $^1$H NMR spectra displaying two cycles of the reversible ON/OFF switch modes.

**CONCLUSIONS**

A novel molecular chemically responsive switch based on a fully inorganic backbone has been demonstrated for the first time. The reported NH-bridged acyclic dimeric cyclodiphosphazane molecular switch, $[(\mu-\text{NH})\text{PE}(\mu-\text{NTBu})_2\text{PE}(\text{NH}^\text{tBu})_2]_2$ (E= O and S) switch display an anion responsive bimodal bifurcated $R^2_{1,8}(8)$ and trifurcated $R^3_{1,8}(8,8)$ hydrogen bonding transition.

In contrast to conventional organic frameworks where carbon atoms display fixed valency and oxidation states, the reported parent P$^\text{III}$N backbone readily gives rise to two different P$^\text{V}$N species with distinct switching energy barriers (i.e., O vs S derivatives) via a single synthetic backbone modification step, which is possible due to the variable oxidation states available to the rest of the p-block elements.

In addition, the reported species display a higher affinity anion species than their monomeric counterparts (see ESI) – previously described in the literature as excellent alternatives to squaramides and thioureas – with a topologically responsive and adaptable cavity size.

Finally, our work serves as a proof-of-concept to highlight main group frameworks as powerful chemically responsive switches, which we envision will play a key role in designing molecular machines, host-guest systems, and supramolecular chemistry in the future.

**EXPERIMENTAL PROCEDURES**

**Resource availability**

**Lead contact**

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Felipe Garcia (fgarcia@ntu.edu.sg).

**Materials availability**

All materials generated in this study are available from the lead contact upon request.
Crystalllographic data for the structures in this Article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC XXX. Copies of data can be obtained free of charge from www.ccdc.cam.ac.uk/structures. Additional synthetic methods, nuclear magnetic resonance spectra, single crystal X-ray diffraction data, and computational details are available in the Supplementary Information.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.chempr.XXXX.

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AUTHOR CONTRIBUTIONS
G. H., I. S. J. P. performed the experimental work. S. Q.-Y. X. J. K., and C. L. assisted on the experimental work throughout the project. O. H. C. and Y. L. collected and analysed the X-ray data. O. H. C. and C. L. helped data curation. F. L. and J. D. performed and curated the theoretical studies. M. C. S. and F. G. supervised and conceptualised the work. All authors contributed to the writing, reviewing, and editing of the final manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

REFERENCES
Receptors: Metal−Organic Anion Bond  


NH-bridged Dimeric Phosphazanes: Inorganic Molecular Switches based on Anion Responsive Bifurcated to Trifurcated Hydrogen Bond Transitions

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Table of Contents
1. Experimental Section
2. NMR Spectra
3. Variable Temperature and Topological Rearrangement Experiments
4. Binding Studies
5. X-ray analyses
6. Theoretical studies
7. Author Contributions
8. References
1. Experimental Section

Compounds 1, 2, 3, 3m, 4, 4m were prepared under dry, O₂-free Ar atmosphere on a double manifold (argon/vacuum) line. All solvents (toluene, THF, n-hexane, diethyl ether, n-pentane) were freshly distilled over appropriate drying agents (sodium/benzophenone) under nitrogen atmosphere, degassed and stored under molecular sieves. Starting materials were either synthesised as described below or obtained commercially from Strem, Sigma-Aldrich, Alfa-Aesar and used without further purification unless otherwise stated. Et₃N was distilled from calcium hydride before use and stored under argon and molecular sieves. Starting material Cl[P(μ-NTBu)₂]₂NH₄₄₄₄ (1) and 4m (3) where synthesized according to reported procedures. Compounds 1, 2, 3, 3m, 4m were isolated and characterised with the aid of an Ar-filled Innovative Technology glove box. ¹H, ¹³C and ³¹P{¹H} NMR spectra were recorded on Bruker BBFO 400 MHz spectrometer in the appropriate deuterated solvent (using the solvents resonances as the internal standard for ¹H and ¹³C NMR and 85% H₃PO₄ – D₂O as the external standard for ³¹P NMR). In situ ³¹P{¹H} NMR spectroscopic studies on reaction mixtures in non-deuterated solvents were recorded using an internal acetone-d₆ capillary to obtain a lock. Single crystal x-ray diffraction studies were carried out with Bruker X8 CCD diffractometer.

1.1 Synthesis of [(μ-NH){P(μ-NTBu)₂P(NH₄₄₄₄Bu)}₂] (1)

\[
\text{Scheme S1}
\]

A suspension of Cl[P(μ-NTBu)₂]₂NH₄₄₄₄ (5.00 g, 16.0 mmol) and LiNH₂ (0.39 g, 17.0 mmol) in dry THF (60 mL) was stirred at room temperature for 3 hours. The solvent was removed under vacuum and the white residue obtained was extracted with dry hexanes (20 mL) and filtered through celite (P3). The residue was washed with hexanes (3 x 5 mL) and the solvent is removed under vacuum. The obtained crude product was dissolved in minimal amounts of hot toluene and storage at -20°C for 12 hours yielded colourless crystals. The crystals were isolated after washing with cold n-pentane (1.5 mL). Isolated Yield: 1.02 g, 1.80 mmol (22%).

³¹P{¹H} NMR (C₆D₆, 101 MHz): δ 104.62 (s), 100.90 (s); HRMS (ESI) m/z for C₂₄H₅₈N₄P₄[M+H]⁺; Calculated: 568.3704 Found: 568.3694.

1.2 Synthesis of [(μ-NH)(P(μ-NTBu)₂P(NH₄₄₄₄Bu))₂] (2)

\[
\text{Scheme S2}
\]

H₂O₂ (248 µL, 3.17 mmol) was added dropwise to a solution of [(μ-NH)(P(μ-NTBu)₂P(NH₄₄₄₄Bu))₂] (300 mg, 0.528 mmol) in dry THF (15 mL) at 0°C and stirred for 1 hour. The reaction mixture was allowed to warm up to room temperature and stirred for 24 hours. The reaction mixture was then dried over MgSO₄ and filtered. The solvent was removed under vacuum and the white solid was recrystallised in minimal amounts of THF to yield colourless crystals. Isolated Yield:
102 mg, 0.161 mmol (30%). X-ray quality crystals were grown from slow evaporation of a saturated chloroform or THF solution.

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.39 (s, 1H), 5.36 (s, 1H), 3.63 (d, J = 10.2 Hz, 1H), 1.55 (s, 36H), 1.47 (s, 9H), 1.34 (s, 9H); $^1$H NMR (CD$_2$OD, 400 MHz): δ 1.55 (s, 36H), 1.38 (s, 18H); $^{13}$C($^1$H) NMR (CDCl$_3$, 101 MHz): δ 57.36 (s), 53.89 (s), 32.29 (d, J = 4.8 Hz), 31.27 (t, J = 4.6 Hz); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz): δ -1.11 (br), -6.66 (br); $^{31}$P($^1$H) NMR (CD$_2$OD, 162 MHz): δ -0.68 (d, J = 57.3 Hz), -5.76 (d, J = 56.9 Hz); HRMS (ESI) m/z for $C_{24}H_{58}N_7O_4P_4$ [M+H]$^+$, Calculated: 632.3501 Found: 632.3497

1.3 Synthesis of [(μ-NH){PS(μ-N$^t$Bu)$_2$PS(NH$^t$Bu)$_2$}] (3)

A suspension of [(μ-NH){P(μ-N$^t$Bu)$_2$P(NH$^t$Bu)$_2$}] (300 mg, 0.528 mmol) and elemental sulfur (71.2 mg, 2.22 mmol) dissolved in dry THF (12 mL) was stirred at room temperature for 12 hours. The reaction mixture was filtered, and the solvent was removed under vacuum. Methanol was added to the crude product and the solution was filtered to remove the unreacted elemental sulfur. The solvent was removed under vacuum and the pale-yellow solid was recrystallised in minimal amounts of methanol to yield colourless crystals. Isolated Yield: 118 mg, 0.170 mmol (32%).

Co-crystals and solvates of 3.

3 ⊂ Acetonitrile: X-ray quality crystals were grown from slow evaporation of a saturated acetonitrile solution.
3 ⊂ DMSO: X-ray quality crystals were grown from slow evaporation of a saturated dichloromethane solution with a few drops of DMSO.
3 ⊂ Cl$: X$-ray quality crystals were grown from slow evaporation of a 1:1 3/TBACl in chloroform solution.
3 ⊂ Br$: X$-ray quality crystals were grown from a 1:1 3/TBABr in chloroform solution layered with pentane.
3 ⊂ I$: X-ray quality crystals were grown from a 1:1 3/TBAI in chloroform solution layered with pentane.
3 ⊂ NO$_3$: X-ray quality crystals were grown from a 1:1 3/TBANO$_3$ in chloroform solution layered with pentane.

$^1$H NMR (CDCl$_3$, 400 MHz): δ 5.16 (br, 1H), 4.12 (br, 2H), 1.72 (s, 36H), 1.44 (s, 18H); $^{13}$C($^1$H) NMR (CDCl$_3$, 101 MHz): δ 58.61 (s), 55.23 (d, J = 4.1 Hz), 31.58 (d, J = 4.5 Hz), 30.06 (dt, J = 4.6, 2.3 Hz); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz): δ 41.93 (d, J = 29.8 Hz), 34.28 (s); HRMS (ESI) m/z for $C_{24}H_{58}N_7P_4S_4$ [M+H]$^+$, Calculated: 696.2587 Found: 696.2588
1.4 Oxidation of \([(\mu\cdot\text{NH})_2P(\mu\cdot\text{N}^t\text{Bu})_2P(\text{N}^t\text{Bu})_2)]^2\) employing elemental selenium

A mixture of \([(\mu\cdot\text{NH})_2P(\mu\cdot\text{N}^t\text{Bu})_2P(\text{N}^t\text{Bu})_2)]^2\) (300 mg, 0.528 mmol) and elemental selenium (175 mg, 2.22 mmol) dissolved in dry THF (12 mL) was stirred at room temperature for 48 hours. The reaction mixture was filtered and solvent was removed under vacuum. The crude product was dissolved in minimum amounts of toluene and slow evaporation of this saturated solution yielded x-ray diffraction quality crystals. However, \(^{31}\text{P}\{^1\text{H}\}\text{NMR}\) of these crystals shows multiple signals similar to that of the crude mixture, suggestive that the crystals are a mixture of species, therefore, the product was only characterised by single crystal x-ray diffraction.
2. NMR Spectra

Figure S1: $^1$H NMR spectrum of \([\mu\text{-NH}]\{P(\mu\text{-N}^\text{tBu})_2P(N\text{H}^\text{tBu})\}_2\) (1) in C$_6$D$_6$.

Figure S2: $^{13}$C\{$^1$H\} NMR spectrum of \([\mu\text{-NH}]\{P(\mu\text{-N}^\text{tBu})_2P(N\text{H}^\text{tBu})\}_2\) (1) in C$_6$D$_6$. 
Figure S3: $^{31}\text{P}$($^1\text{H}$) NMR spectrum of [(μ-NH)(P(μ-NBu):P(NHtBu))$_2$] (1) in C$_6$D$_6$.

Figure S4: $^1\text{H}$ NMR spectrum of [(μ-NH)(PO(μ-NBu):PO(NHtBu))$_2$] (2) in CDCl$_3$. 
Figure S5: $^{31}$P{^1}H NMR spectrum of $[\mu$-$\text{NH}]{\text{PO}(\mu$-$\text{N}t\text{Bu})_2\text{PO(NH}t\text{Bu})}_2]$ (2) in CDCl$_3$.

Figure S6: $^1$H NMR spectrum of $[\mu$-$\text{NH}]{\text{PO}(\mu$-$\text{N}t\text{Bu})_2\text{PO(NH}t\text{Bu})}_2]$ (2) in CD$_3$OD.
Figure S7: $^1$C($^1$H) NMR spectrum of $[(\mu\cdot\text{NH})(\text{PO(\mu-N^\text{tBu})}_2\text{PO(NH^\text{tBu}})]_2$ (2) in CD$_3$OD.

Figure S8: $^{31}$P($^1$H) NMR spectrum of $[(\mu\cdot\text{NH})(\text{PO(\mu-N^\text{tBu})}_2\text{PO(NH^\text{tBu}})]_2$ (2) in CD$_3$OD.
Figure S9: $^1$H NMR spectrum of $[\mu$-NH$\{\mu$-$\textbf{N}^\text{Bu}\}_2\text{PS}(\text{NH}^\text{Bu})_2]\{3\}$ in CDCl$_3$.

Figure S10: $^{13}$C($^1$H) NMR spectrum of $[\mu$-NH$\{\mu$-$\textbf{N}^\text{Bu}\}_2\text{PS}(\text{NH}^\text{Bu})_2]\{3\}$ in CDCl$_3$. 
Figure S11: $^{31}P(^1\text{H})$ NMR spectrum of $\left[\mu\text{-NH}\right]\left\{\mu\text{-N}^t\text{Bu}\right\}_2\text{PSN}_2\text{PSN} \right\}_2$ (3) in CDCl$_3$. 
3. Variable Temperature and Topological Rearrangement Experiments

**Figure S12:** Overlaid $^1\text{H}$ NMR of 2 in CDCl$_3$ at room temperature (bottom) and 313 K (top).

**Figure S13:** Variable temperature $^1\text{H}$ NMR of 2 in CDCl$_3$ at different temperatures.
Figure S14: Overlaid $^1$H NMR of 3 in CDCl$_3$ at room temperature (bottom) and 213 K (top).

Figure S15: Variable temperature $^1$H NMR of 3 in CDCl$_3$ at different temperatures.
Using the data obtained from the variable temperature $^1$H NMR spectroscopy experiments, the rotational energy barrier for the topological rearrangement for compound 3 between C and S conformation was estimated using the following equations.

At coalescence temperature (253 K):

$$k_{Tc} = \frac{\pi \Delta\nu}{\sqrt{2}} = \frac{\pi}{722}$$

$k_{Tc} = 1604 \text{ s}^{-1}$

Therefore, the free Gibbs activation energy for the topological rearrangement can be calculated:

$$\Delta G = 4.574 \times 10^{-3} \times T_c \times (\log \frac{T_c}{k_{Tc}} + 10.318)$$

$$= 4.574 \times 10^{-3} \times 253 \times (\log \frac{253}{1604} + 10.318)$$

$\Delta G = 11.0 \text{ kcal/mol}$
Figure S16: Overlaid $^{31}$P{$^{1}$H} NMR spectrum of 2 in 1:9 H$_2$O/THF at different time points.

Figure S17: Overlaid $^{31}$P{$^{1}$H} NMR spectrum of 3 in 1:9 H$_2$O/THF at different time points.
Figure S1: Overlaid $^1$H NMR of 10 mM of 3 with 0.5 equivalents of TBABr in CDCl$_3$ at room temperature (top) and -50ºC (bottom).

Figure S19: Overlaid $^1$H NMR spectrum of (i) 2 in CDCl$_3$, (ii) 2 in CDCl$_3$ in the presence of 5 equivalents of TBACl, (iii) 2 in CDCl$_3$ in the presence of 5 equivalents of TBACl followed by addition of 5 equivalents of NaPF$_6$ (stirred overnight) and (iv) 2 in CDCl$_3$ in the presence of 5 equivalents of TBACl followed by addition of 5 equivalents of NaPF$_6$ (stirred overnight) followed by an additional 5 equivalent of TBACl.
4. Binding Studies

Anion binding abilities of 3ON was benchmarked against monomeric P\textsubscript{V}\textsubscript{2}N\textsubscript{2} species. An analogous study was performed for monomeric [\textsuperscript{1}BuHNPE(\textgreek{m}-N\textgreek{Bu})\textsubscript{2} (E = S and Se for 3\textsuperscript{m} and 4\textsuperscript{m}, respectively) in CDCl\textsubscript{3} (Table S1). Compound 4\textsuperscript{m}, previously reported as the best monomeric counterpart, exhibits increased affinity for Cl\textsuperscript{-} over 3\textsuperscript{m} which is in line with previous reports.\cite{4} Notably, among 3\textsuperscript{m} and 4\textsuperscript{m}, binding strengths decrease as the size of anions increases, with decreasing binding strength differences for larger anions, such as Br\textsuperscript{-}, I\textsuperscript{-}, HSO\textsubscript{4}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}, along with low affinities for HSO\textsubscript{4}\textsuperscript{-}. This is attributed to both the reduced number of NH HB donors as well as the smaller cavity size within the monomeric P\textsubscript{V}\textsubscript{2}N\textsubscript{2}, which results in lower binding affinities across all anions studied - except for Br\textsuperscript{-}, vide supra.

Table S1: Comparison of binding constants of 3 vs 3\textsuperscript{m} and 4\textsuperscript{m}.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Binding constants, K\textsubscript{A} [M\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>192.92 ± 81.89\textsuperscript{[a]}</td>
</tr>
<tr>
<td>Br\textsuperscript{-}</td>
<td>N.D.</td>
</tr>
<tr>
<td>I\textsuperscript{-}</td>
<td>5.17 ± 0.13</td>
</tr>
<tr>
<td>HSO\textsubscript{4}\textsuperscript{-}</td>
<td>9.48 ± 0.25</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>20.39 ± 1.17</td>
</tr>
</tbody>
</table>

[a] Estimated based on concentration-weighted average of [H\textsubscript{0}] and [HG]\textsuperscript{[5]}; N.D. = not determined.

4.1 Dimeric S (3)

Figure S20: \textsuperscript{1}H NMR titration (25 \textdegree C, CDCl\textsubscript{3}, 400 MHz) of 3 with increasing amounts of TBACL.
Due to the negligible exchange of chloride ions between host molecules at room temperature, the chemical shifts of the NH protons due to fast equilibirum was estimated using a concentration-weighted average of free host and host-guest complex,

\[ \Delta \delta = \delta_{\text{HG}} \left( \frac{[HG]}{[H_0]} \right) \]

**Table S2:** Estimated values of NH protons chemical shifts based on concentration-weighted average of free host and host-guest complex of 3 and chloride.

<table>
<thead>
<tr>
<th>Guest:Host (equiv)</th>
<th>( \delta_{\text{HG}} ) (ppm)</th>
<th>([HG]/[H_0]) (ppm)</th>
<th>( \Delta \delta ) (ppm)</th>
<th>( \delta_{\text{HG}} ) (ppm)</th>
<th>([HG]/[H_0]) (ppm)</th>
<th>( \Delta \delta ) (ppm)</th>
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<tbody>
<tr>
<td>0.00</td>
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<td>2.14</td>
<td>4.14</td>
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<td>4.14</td>
</tr>
</tbody>
</table>

**Figure S21:** Binding isotherm (1:1 system) fitted to the \(^1\)H NMR chemical shift of the NH protons in 3 with increasing amounts of TBACl after estimation using the concentration-weighted average of free host and host-guest complex.\(^5\) Due to this approximation based on integrals of the amino peaks, the error is approximately 40% despite multiple titration runs. Despite that, these values serves as an illustration that binding affinity of 3 to chloride is much higher than those compared to other anions studied, even after accounting for the large error.
Figure S22: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3 with increasing amounts of TBABr.

Figure S23: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3 with increasing amounts of TBAI.
Figure S24: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3 with increasing amounts of TBAI.\[9\]

Figure S25: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3 with increasing amounts of TBAHSO$_4$. 
Figure S26: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3 with increasing amounts of TBAHSO$_4$.[F]

Figure S27: $^1$H NMR titration (25°C, CDCl$_3$, 400 MHz) of 3 with increasing amounts of TBANO$_3$. 

Figure S28: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3 with increasing amounts of TBANO$_3$.[5]
4.2 Monomeric S (3m)

Figure S29: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3m with increasing amounts of TBACl.

Figure S30: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3m with increasing amounts of TBACl.
Figure S31: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3m with increasing amounts of TBABr.

Figure S32: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3m with increasing amounts of TBABr.
Figure S33: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of $3^m$ with increasing amounts of TBAI.

Figure S34: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in $3^m$ with increasing amounts of TBAI. [5]
Figure S35: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3$m$ with increasing amounts of TBAHSO$_4$.

Figure S36: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3$m$ with increasing amounts of TBAHSO$_4$.\(^5\)
Figure S37: $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 3$^m$ with increasing amounts of TBANO$_3$.

Figure S38: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 3$^m$ with increasing amounts of TBANO$_3$.\textsuperscript{[5]}
4.3 Monomeric Se (4m)

Figure S39: H NMR titration (25 °C, CDCl₃, 400 MHz) of 4m with increasing amounts of TBACl.

Figure S40: Binding isotherm (1:1 system) fitted to the ¹H NMR chemical shift of the NH protons in 4m with increasing amounts of TBACl. [9]
Figure S41: \( ^1\text{H} \) NMR titration (25 °C, CDCl\(_3\), 400 MHz) of 4 with increasing amounts of TBABr.

Figure S42: Binding isotherm (1:1 system) fitted to the \( ^1\text{H} \) NMR chemical shift of the NH protons in 4 with increasing amounts of TBABr.
**Figure S43:** $^1$H NMR titration (25 °C, CDCl$_3$, 400 MHz) of 4m with increasing amounts of TBAI.

**Figure S44:** Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 4m with increasing amounts of TBAI.\[5\]
Figure S45: ¹H NMR titration (25 °C, CDCl₃, 400 MHz) of 4m with increasing amounts of TBAHSO₄.

Figure S46: Binding isotherm (1:1 system) fitted to the ¹H NMR chemical shift of the NH protons in 4m with increasing amounts of TBAHSO₄.
Figure S47: $^1$H NMR titration (25 °C, CDCl₃, 400 MHz) of 4m with increasing amounts of TBANO₃.

Figure S48: Binding isotherm (1:1 system) fitted to the $^1$H NMR chemical shift of the NH protons in 4m with increasing amounts of TBANO₃.\(^{(5)}\)
5. X-ray analyses

Crystallographic Analyses. Diffraction-quality crystals were obtained via methods presented in the experimental section. Diffraction intensity data were measured at 100 K with a Bruker Kappa diffractometer equipped with a CCD detector, employing either Mo Kα (λ = 0.71073 Å) radiation, with the SMART suite of programs. Data were processed with SAINT and SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs. In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Structures 3⊂I- and 3⊂NO3 displayed less that ideal diffraction properties with broad reflections and a significant amount of diffuse scatter. The structures are both 50 % disordered around a special position. Accordingly both the cation and the tertiary butyl groups were only modelled isotropically and a number of bond length restraints were required. Despite these limitations the connectivity is unambiguous.
Table S3: X-ray data of compounds 2, 2-Chloroform, 3-4Acetonitrile, 3-DMSO and 3-Cl.

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<th>Chemical formula</th>
<th>2-Chloroform</th>
<th>3-4Acetonitrile</th>
<th>3-DMSO</th>
<th>3-Cl</th>
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<td>C₂H₅NO₂P₂S₄</td>
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<td>monoclinic</td>
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<td>P 1 21/n 1</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>c/Å</td>
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<td>γ/°</td>
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<td>0.71073</td>
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<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
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Table S4: X-ray data of compounds 3-Br, 3-Cl, 3-NO₃, 4a and 4-cDMSO.

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<td>8410 (0.0923)</td>
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<td>99.5%</td>
<td>99.2%</td>
<td>99.9%</td>
<td>98.9%</td>
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<td><strong>Refinement Method</strong></td>
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<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
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<td>100(2)</td>
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Figure S49. Solid-state structures of 2. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for 2: N1-P1 1.633(2), N2-P2 1.671(2), N2-P1 1.685(2), N4-P2 1.659(2), N3-P1 1.668(2), N4-P2 1.670(2), O1-P1 1.468(2), O2-P2 1.464(2), O1-P1-N1 112.13(12), O1-P1-N2 118.83(12), N1-P1-N2 110.44(12), N1-P1-N3 109.01(12), N2-P1-N3 118.50(12), O1-P1-N3 119.81(12), N1-P1-N3 112.54(12), O1-P1-N2 120.88(11), N3-P2-N2 84.68(11), N4-P2-N2 108.51(11).

Figure S50. Solid-state structures of 2Chloroform. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for 2Chloroform, P1-O1 1.469(2), P1-N1 1.611(2), P1-N2 1.690(2), P1-N3 1.700(2), P2-O2 1.4813(19), P2-N2 1.661(2), P2-N3 1.672(2), P2-N4 1.674(2), O1-P1-N1 113.37(12), O1-P1-N2 119.21(12), N1-P1-N2 108.76(12), O1-P1-N3 116.57(11), N1-P1-N3 111.81(12), N2-P1-N3 83.73(11), O2-P2-N2 120.47(12), O2-P2-N3 118.05(11), N2-P2-N3 85.48(11), O2-P2-N4 106.27(11), N2-P2-N4 112.64(11), N3-P2-N4 113.16(12).
Figure S51. Solid-state structures of 3⊂Acetonitrile. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for 3⊂ Acetonitrile: S3-P3 1.9290(5), S4-P4 1.9280(6), P3-N4 1.6793(13), P3-N5 1.6824(13), P3-N6 1.6876(13), P3-P4 2.5190(5), P4-N7 1.6277(13), P4-N5 1.6996(12), P4-N6 1.7089(13), N2-P2-N4 112.17(6), N3-P2-S2 112.09(6), N2-P2-S2 120.63(5), N3-P2-S2 120.23(5), N4-P2-S2 107.32(5), N4-P3-N5 103.36(6), N4-P3-N6 112.42(6), N5-P3-N6 84.17(6), N4-P3-S3 112.77(5), N5-P3-S3 118.16(5), N7-P4-N5 107.50(7), N7-P4-N6 109.67(7), N5-P4-N6 83.01(6), N7-P4-S4 114.52(5), N5-P4-S4 119.31(5), N6-P4-S4 118.62(5).

Figure S52. Solid-state structures of 3⊂DMSO. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for 3⊂ DMSO: S1-P1 1.9283(14), S2-P2 1.9352(14), P1-N2 1.703(3), P1-N3 1.711(3), P1-P2 2.5056(14), P2-N2 1.668(3), P2-N3 1.685(3), P2-N4 1.686(3), N1-P1-N2 105.09(16), N1-P1-N3 111.07(15), N2-P1-N3 114.63(12), N2-P1-S1 120.44(11), N3-P1-S1 118.00(12), N2-P2-N3 85.28(15), N2-P2-N4 112.57(16), N3-P2-N4 110.11(14), N2-P2-S2 119.97(11), N3-P2-S2 120.23(12), N4-P2-S2 108.18(12).
**Figure S53.** Solid-state structures of $3 \subset \text{Cl}$. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $3 \subset \text{Cl}$: P1-N1 1.627(18), P1-N2 1.691(18), P1-N3 1.692(18), P2-N4 1.655(17), P2-N2 1.6811(18), N1-P1-N2 109.02(9), N2-P1-N3 110.38(9), N1-P1-N3 83.12(8), N1-P1-S1 114.32(7), N2-P1-S1 118.88(7), N3-P1-S1 117.19(7), N4-P2-N2 106.09(9), N4-P2-N3 110.15(9), N2-P2-N3 83.80(9), N4-P2-S1 113.59(7), N2-P2-S2 120.45(7), N3-P2-S2 118.93(7).

**Figure S54.** Solid-state structures of $3 \subset \text{Br}$. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and disorder are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $3 \subset \text{Br}$: P1-N7 1.658(16), P1-N2 1.671(15), P1-N1 1.681(19), P1-S2 1.928(7), P1-P2 2.492(14), P2-N5 1.60(3), P2-N2 1.685(14), P2-N1 1.71(2), P2-S1 1.93(7), N7-P1-N2 101.9(7), N7-P1-N1 111.0(9), N2-P1-N1 85.2(8), N7-P1-S2 113.8(5), N2-P1-S2 122.7(6), N1-P1-S2 118.3(8), N5-P2-N2 104.8(11), N5-P2-N1 109.3(9), N2-P2-N1 83.9(10), N5-P2-S1 115.5(10), N2-P2-S1 120.8(6), N1-P2-S1 118.0(12), N5-P2-P1 116.3(6).
**Figure S55.** Solid-state structures of $3$-$\text{I}$. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and disorder are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $3$-$\text{I}$: P1-N2 1.679(10), P1-N7 1.684(18), P1-N1 1.690(12), P2-N5 1.630(2), P2-N1 1.674(12), P2-N2 1.700(10), P2-S1 1.942(7), N2-P1-N7 103.0(6), N2-P1-N1 111.8(8), N2-P1-S2 122.1(5), N7-P1-S2 114.1(5), N5-P2-N1 111.8(9), N5-P2-N2 116.8(9), N1-P2-N7 83.4(7), N5-P2-S1 113.8(6), N1-P2-S1 117.7(9), N2-P2-S1 119.6(6).

**Figure S56.** Solid-state structures of $3$-$\text{NO}_3$. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and disorder are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $3$-$\text{NO}_3$: P1-S1 1.934(6), P2-S2 1.916(5), P3-S3 1.928(6), P4-S4 1.926(6), N1-P1 1.670(3), N1-P2 1.668(15), N2-P2 1.689(11), N2-P1 1.694(11), N3-P2 1.657(14), N8-P1 1.64(11), O1-N7 1.229(14), O2-N7 1.239(14), O3-N7 1.239(14), P1-N1-P2 96.4(8), P2-N2-P1 94.6(10), N8-P1-N2 106.2(13), N1-P1-N2 84.4(11), N8-P1-S1 114.7(14), N1-P1-S1 119.6(16), N2-P1-S1 122.0(10), O3-N7-01 122.0(10), O3-N7-02 119.7(10), O1-N7-02 118.4(10).

**Figure S57.** Solid-state structures of $4\text{a}$. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $4\text{a}$: N2-P2 1.686(2), N2-P1 1.695(2), N3-P2 1.691(2), N3-P1 1.696(2), N4-P2 1.623(2), P1-Se1 2.0944(7), P2-Se2 2.1076(7), N1-P1-N2 111.63(12), N1-P1-N3 111.51(12), N2-P1-N3 83.17(11), N1-P1-Se1 108.28(8), N2-P1-Se1 120.26(8), N3-P1-Se1 120.16(8), N4-P2-N2 114.44(12), N4-P2-N3 113.95(12), N2-P2-N3 83.59(11), N4-P2-Se2 106.83(8), N2-P2-Se2 118.52(8), N3-P2-Se2 118.53(8).
Figure S58. Solid-state structures of $4^m\subset$ DMSO. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for $4^m\subset$ DMSO: S1-P1 1.9347(9), S2-P2 1.9316(10), P1-N1 1.628(2), P1-N2 1.689(2), P1-N3 1.690(2), P1-P2 2.5256(9), P2-N4 1.631(2), P2-N3 1.686(2), P2-N2 1.689(2), N1-P1-N2 110.24(12), N1-P1-N3 108.49(11), N2-P1-N3 83.06(10), N1-P1-S1 114.45(9), N2-P1-S1 117.97(8), N3-P1-S1 118.58(9).
6. Theoretical Studies

Calculations were performed with Gaussian 16 package (DFT),\textsuperscript{[9]} using the Becke Three-Parameter functional with the non-local correlation by Perdew and Wang (B3PW91)\textsuperscript{[10]} and the D3 version of Grimme’s dispersion with Becke-Johnson damping (GD3BJ).\textsuperscript{[11]} H, C, P, N, O, S atoms were represented with the 6-311G(d,p)\textsuperscript{[12]} basis set as implemented in Gaussian 16, while Cl, I, and Br atoms were represented with sdd pseudopotential. Frequency calculations were performed at the same level of theory to characterize the stationary points as minima (no imaginary frequencies) or transition states (one imaginary frequency), as well as to calculate free energy (G) corrections. The two minima connected by a given transition state were confirmed by manually freezing the coordinates at both sides of the imaginary frequency and further optimization at the theory level stated above. The matrix coordinates of all reactants, products and TSs computed are given as xyz files in a compressed folder.

| Table S5: Energies free anion, host and adducts of P(V) species. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| E (a.u.) | zpe | H (a.u.) | S (cal/kmol) | G (a.u.) |
|---------|---------|---------|---------|---------|---------|
Table S6: Energy differences of the different conformations of 2 and 3 as well as their adducts.

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<th>2</th>
<th>3</th>
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<td><strong>S versus C</strong></td>
<td>6.72</td>
<td>4.72</td>
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<tr>
<td>C + Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>-65.47</td>
<td>-69.04</td>
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<tr>
<td>C + Br&lt;sup&gt;-&lt;/sup&gt;</td>
<td>-41.41</td>
<td>-43.91</td>
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<tr>
<td>C + I&lt;sup&gt;-&lt;/sup&gt;</td>
<td>-36.78</td>
<td>-38.19</td>
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<tr>
<td>C + HSO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>-43.19</td>
<td>-44.26</td>
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<tr>
<td>C + NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>-47.61</td>
<td>-50.51</td>
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<tr>
<td>C + DMSO</td>
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<tr>
<td><strong>S + DMSO</strong></td>
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Table S7: Relative energies differences of the computed ON/OFF switching for 3.

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<td><strong>TS</strong></td>
<td>12.57</td>
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A
**Figure S59.** Non-Covalent Interaction (NCI) computed at B3PW91/6-311G(d,p). The weak interactions revealed by the NCI analysis are color coded from blue, for the strongest attractive weak interactions (like hydrogen bonds), to red for repulsive ones, for weaks van der Waals interactions NCI interaction appears in green. NCI surfaces correspond to $\sigma = 0.5$ au and a colour scale of $-2 < \rho < 2$ au.
7. Author Contributions

G. H., I. S. J. P. performed the experimental work. S. Q. Y. X. J. K., and C. L. assisted on the experimental work throughout the project. O. H. C., Y. L. and J. K. Clegg collected and analysed the X-ray data. O. H. C. and C. L. helped data curation. F. L. and J. D. performed and curated the theoretical studies. M. C. S. and F. G. supervised and conceptualised the work. All authors contributed to the writing, reviewing, and editing of the final manuscript.

8. References