Article

Superphanes: Old Yet New Binding–Agents for Highly Selective Recognition of Fluoride by Size–Sieving Effect

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Abstract: Superphanes, namely percyclophanes, have been widely investigated, *inter alia*, by organic chemists for the sake of their aesthetically pleasing structures with high symmetry, intriguing physical and chemical properties and synthetic challenges. Nonetheless, the host–guest chemistry of superphanes remains to be an unmet challenge. Herein, we delineate the design, preparation, characterization, and host–guest chemistry of an unprecedented superphane–based receptor **15**, which was evidenced by mass spectroscopy, NMR spectroscopy, X–ray crystallography, and DFT calculations. Superphane **15** features six bridges to the top and bottom, up to 18 Csp–**H** hydrogen–bonding donors (for binding anions) well–distributed around the near–closed inner cavity in three dimensions. This allows receptor **15** to exhibit exclusive selectivity towards F^- against Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} and $HP_2O_7^{3-}$ probably attributed to the size–sieving effect. This contribution opens up new opportunities for design and synthesis of most complex supramolecular hosts for anions of interest with high selectivity for purpose of anion recognition, sensing, elimination and recycling, *etc.*

Keywords: Superphanes; cyclophanes; anion receptors; host–guest chemistry; selectivity

1. Introduction

Particular interest in anions has risen on account of the complexity and rich diversity in structures of anions, as well as their importance in biology, chemistry, energy, resource management, and the environment.[1] Over the past roughly 30 years, considerable advances in anion recognition chemistry have been achieved.[2-6] This benefits from the rising occurrence of functionalized anionic receptors, apart from the emergence of a range of weak force interactions.[7-11] Notably, intensive and extensive investigations have been focused on the macrocycles and cages due to the pronounced macrocyclic effect or so–called cage effect.[3, 7, 12-14] For examples, Sessler, Ballester, Gale and coworkers have been dedicated to developing calix[4]pyrrole–based receptors, *e.g.* strapped calix[4]pyrroles and bis–calix[4]pyrroles, for anions and ion pairs.[15-17] Those host–dominated binding affinity and selectivity led to their wide uses for anion (ion pair) recognition, sensing, transmembrane transport, extraction, crystal engineering, self–assembly, and catalysis.[15-22] Due to the fact that cages normally have more variations, such as binding site distribution in the three–dimensional space and well–defined size of the cavity, to control the binding affinity and selectivity, Nitschke and coworkers alike have established a plethora of cage–based architectures via metal induced self–assembly for anion recognition and application.[23, 24] Amazingly, Flood et al. have demonstrated that a well–designed cage was able to capture chloride anion with extremely high affinity (binding constant (K_1) in wet CH_2Cl_2: up to 10^{17} M^{-1}) and selectivity ($Cl^- > Br^- > NO_3^- > I^-$).[25] Quest for new receptors for anions, *inter alia* fluoride with large hydration energy, with tight binding and high selectivity has been a challenging topic and perpetual task for the supramolecular chemistry community.

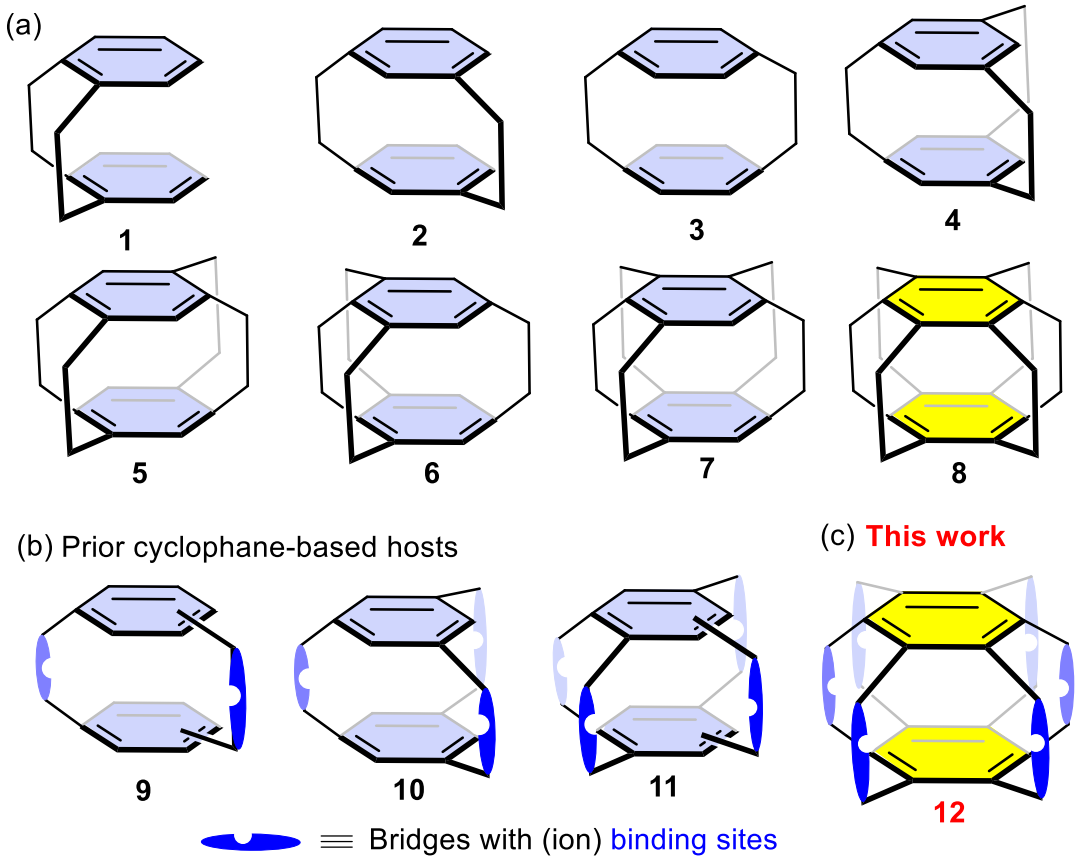


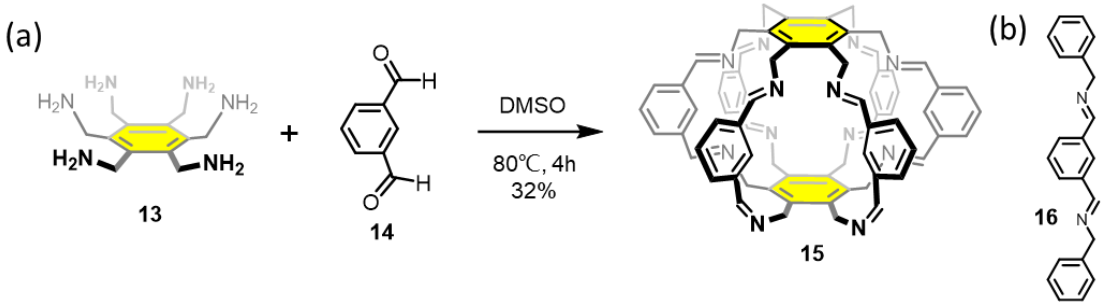
Figure 1. (a) Representative examples of cyclophanes **1**–**7** and superphane **8**; (b) The reported cyclophane–based supramolecular hosts **9**–**11** derived from respective cyclophanes by introducing appropriate binding sites to the bridges; (c) New superphane **12** as supramolecular hosts reported here.

Cyclophanes refer to a vast range of bridged aromatic compounds with at least one aliphatic n–membered bridge with n ≥ 0.[26] As a special subclass of cyclophanes, the [2$_2$]phanes consist of two benzene rings and two ethylenic bridges in different positions at the benzene rings, *viz* [2$_2$]*ortho*cyclophane **1**, [2$_2$]*meta*cyclophane **2**, and [2$_2$]*para*cyclophane **3** (Figure 1).[27-29] From this premise, the star supramolecular hosts including calixarenes, resorcarenes, cyclotriveratrylenes, and pillarenes are formally members of the cyclophane family since they can be deemed as derivatives **9** of [2$_2$]phanes by incorporating functional groups (binding sites) into the bridges of **1**–**3**.[30-34] Likewise, when a variety of functional groups are introduced into the bridge units of cyclophanes with multiple bridges (e.g., **4**–**7**), fascinating cage–type cyclophanes (**9**–**10**) have been reported to be elegant synthetic supramolecular receptors in molecular recognition, especially anion recognition.[35-41] Of particular interest is a sub–group of cyclophanes with all hydrogen atoms of the two face–to–face cyclic conjugated rings tethered by bridges (**8**), which were termed *superphanes* by Hopf.[27] Chemists have extensively investigated the synthesis, structures, properties, and unusual reactions of superphanes in order to elucidate the through–space interactions between the aromatic subunits.[26, 28, 29, 42-45] Nevertheless, using functionalized superphanes as supramolecular hosts for molecular recognition remains challenging and unexplored.

2. Results and Discussions

Superphane **8** features one "closed" or "near–closed" cavity surrounded by two benzene rings and six bridges. However, the inner cavity of **8** is too small to complement guests. We envision that, in analogy to the functionalization of **1**–**3** to **9**, **4** to **10**, and **5**–**6** to **11**, superphane **8** could be also functionalized into novel supramolecular host **12** by simply integrating appropriate functional groups, such as anion binding sites or cation coordination sites, onto the bridges, generating a unique

cavity for entrapping guest species. In principle, the inner cavity sizes, binding affinity and selectivity of superphane **12** towards guest species of interest can be well defined and finely tuned by adjusting the length and functional groups of the tethered bridges. In addition, due to the ostensibly "closed" feature, superphane **12** could be also used as molecular prisons for locking small gas molecules and ionic species for the purpose of active substance protection, new phase investigation, mass transport, cluster entrapment and critical material fabrication, *etc*. While seemingly straightforward, the design and preparation of such complex superphanes for molecular recognition is not necessarily simple. One way to overcome this barrier is to introduce highly efficient and selective chemical reactions. In this regard, dynamic covalent reactions are appealing due, in major part, to the fact that such highly efficient, thermodynamically controlled reactions have been widely utilized to construct covalently linked complex 2–D and 3–D molecular architectures, *i.e.* macrocycles, cages, catenanes, rotaxanes, molecular knots, and molecular machines, through judicious selection of building blocks.[46-49]



Scheme 1. (a) Synthetic route to superphane **15**; (b) Molecular structure of control compound **16**.

With such a predictive postulate in mind, we carefully designed an unprecedented superphane–based supramolecular host, *viz.* superphanes **15** (Scheme 1). To prepare the desired product **15**, a key precursor, namely hexakisbenzene–amine **13**, was synthesized according to the reported literature.[50, 51] Upon mixing **13** and *m*–phthalaldehyde **14** in deuterated dimethyl sulfoxide (DMSO–d_6) at room temperature, a library of intractable oligomeric or polymeric byproducts were seen as inferred from the ill–defined ^{1}H NMR spectral signals (Figure 2). However, much to our surprise, a new set of sharp and well–recognized resonances appeared in the ^{1}H NMR spectrum after heating the mixture solution at 80 °C for 4 h with the disappearance of both starting materials **13** and **14**. The resonance peaks at 8.11, 7.39, 7.31, and 6.96 ppm could be assigned to the corresponding protons of the imine moieties and the disubstituted benzyl groups of **15** while that at 4.99 ppm was recognized as the CH_2 groups tethered to the hexasubstituted benzene rings as denoted in Figure 2. Meanwhile, precipitates that were not soluble in commonly used solvents occurred. Further heating at 80 °C for additional 2 hours failed to give better results. Then the reaction was scaled up in the flask at 80 °C for 4 h. After filtration, the filtrate was diluted with $CHCl_3$ and washed with large excess of water. The organic phase was separated, dried and concentrated to give crude superphane **15** as yellowish powders in 32% yield. The product could be further purified by crystallization in $CHCl_3$. The structure of superphane **15** was tentatively characterized by ^{1}H NMR spectrometry (Fig. S1 and S2, supporting information) and mass spectrometric analysis (Fig. S3 and S4). For instance, prominent peaks corresponding to $[M + H]^+$ and $[M + 2H^+]^{2+}$ were clearly seen in the high–resolution mass spectrum, indicating the condensation of **13** and **14** occurred in a [2 + 6] manner.

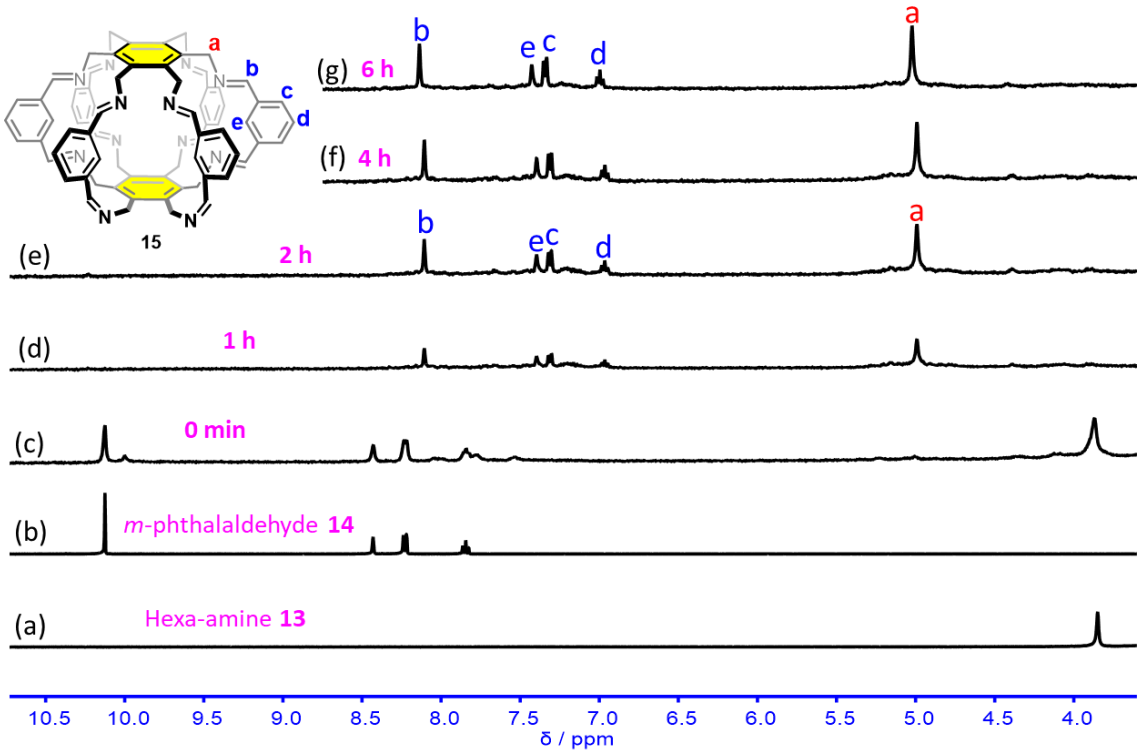


Figure 2. Partial ^{1}H NMR spectra (400 MHz, DMSO–d_6, 298 K) of the 2 : 6 mixture of **13** (0.40 mg, 3.0 μmol) and **14** (0.25 mg, 1.0 μmol) in DMSO–d_6 (0.5 mL) after the system was heated at 80 ℃ for (c) 0 h, (d) 1 h, (e) 2 h, (f) 4 h, and (e) 6 h. The ^{1}H NMR spectra of **13** and **14** were recorded in (a) and (b), respectively. Inset: the structure of superphane **15** with proton assignment.

Further evidences for the formation of superphane **15** came from an X–ray diffraction analysis of single crystals obtained by allowing diethyl ether to undergo slow diffusion into a $CHCl_3$ solution of **15**. The resulting crystal structure revealed that superphane **15** was formed exactly in a [2 + 6] manner as expected. The whole molecule attains a lantern–like or pumpkin–shaped conformation with face–to–face arrangement of two benzene rings and near–uniform distribution of six bridges (Figure 3a and 3b). The height of **15** is measured to be ~ 9.0 Å and the diameter is estimated to be 6.8 Å, suggesting a relatively large void for hosting guest species (Figure 3c). A closer inspection at the crystal structure of **15** revealed that its internal cavity is occupied by two disordered water molecules. The orientation of the hydrogen atoms of the water molecules could be deduced from the fact that on each half of the complex, two out of six lone pairs of the imine groups point to the oxygen atoms of the corresponding water, indicating the existence of hydrogen between N and O (Fig. S5). Additionally, all C–**H** protons at 2–positions of disubstituted benzyl groups point inside of the cavity to interact with oxygen atoms of water guests via C–**H**···O hydrogen bonding. More supports for the inclusion of two water molecules were from matrix–assisted laser desorption/ionization–time of flight mass spectrometry, where two peaks corresponding to [**15** + $2H_2O$ + Na^+]$^+$ and [**15** + $2H_2O$ + K^+]$^+$, respectively, were observed in the spectrum (Fig. S6). Interestingly, apart from water molecules included within the cavities of **15**, no other solvent molecules are found in the unit cell. Each $(H_2O)_2$⊂**15** complex as a whole is stabilized in the lattice via multiple edge–to–face π···π interactions in cooperative manners (Figure 3d).[52]

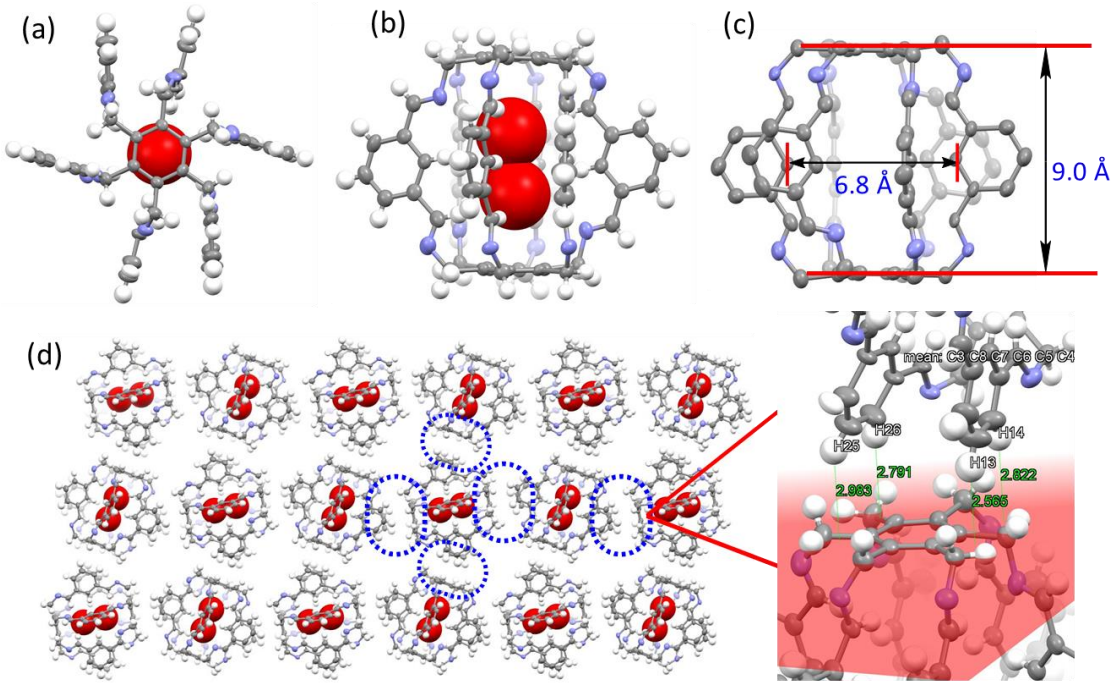


Figure 3. Single crystal structures of the $(H_2O)_2$⊂**15** complex: (a) Top view; (b) front view; (c) side view of **15** with hydrogen atoms and water molecules omitted for clarity; (d) The coordination network in this complex. Insert: multiple edge–to–face π···π interactions between each hexasubstitued benzene ring and its adjacent disubstituted benzyl groups on the periphery of **15**. The contacts of H13, H14, H25, H26 and the plane defined by the hexasubstitued benzene ring were estimated to be 2.57, 2.82, 2.98, 2.79 Å, respectively. Superphane **15** was shown in ellipsoid model with 50% probability while the oxygen atoms of two disordered water molecules were presented in space–filling model.

With such a new super cage in hand, we carefully examined its potential conformation. According to the ^{1}H NMR and ^{13}C spectrum in $CDCl_3$, a very simple and symmetrical set of resonance signals were seen (Fig. S1 and S2), suggesting a relatively flexible system that is in conformational equilibrium. Basically, each imino unit could freely rotate around the connecting carbon–carbon single bonds, generating a library of conformers. Amongst them, of particular interest are three representative conformers, *viz.* **15**$_{in–in}$, **15**$_{out–out}$, and **15**$_{in–out}$, where *in–in*: all imino C–**H**s orient to the inner cavity; *out–out*: all imino C–**H**s point outside or opposite to the cavity; *in–out*: all six imino C–**H**s tethered to one hexasubstituted benzene ring point inside while all six imino C–**H**s connected to the other hexasubstituted benzene ring orient opposite to the cavity. Based on these three conformers, density functional theory (DFT) calculations were carried out to map the electrostatic potential surfaces (EPS) (Figures 4a, 4b and Fig. S7). In the case of the conformer **15**$_{in–in}$, since all 12 imino C–**H**s and six 2–Ar–**H**s point to the interior of **15**, a relatively small void is surrounded by 18 slightly positively polarized C–**H**s. This allows us to suggest that superphane **15**$_{in–in}$ might serve as a new anion receptor for selectively binding small anions, *e.g.* fluoride. As to conformer **15**$_{out–out}$, due to the fact that all 12 imino C–**H**s orient outside of the cavity, which allows all lone pairs of the imino groups distribute around the cavity, **15**$_{out–out}$ might be working as a cation receptor. With regard to conformer **15**$_{in–out}$, it is straightforward to imagine that this conformer would work as a potential ion pair receptor on the account of heteroditopic nature of the interior cavity. Since the binding pocket of **15** is well defined by two parallel benzene rings and six C–type bridges, superphane **15** might be selective to species with small sizes, such as F^-.

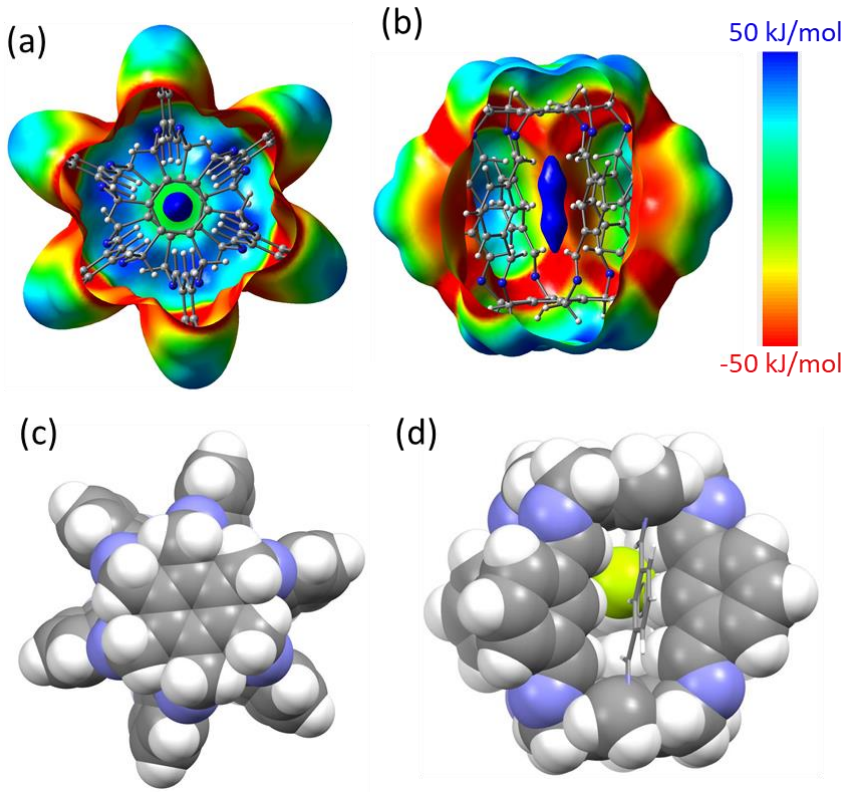


Figure 4. (a) Top view and (b) front view of molecular structure and electrostatic potential surfaces (EPS) (at X3LYP/6–31+g* level) of **15**$_{in–in}$. For all surfaces shown in this work, the potential energy values range from −50 kJ mol^{-1} (red) to 50 kJ mol^{-1} (blue). Red color represents a value equal to or greater than the maximum in negative potential, and blue corresponds to a value equal to or greater than the maximum in positive potential. (c) Top view and (d) side view of DFT–optimized structure of F$^-$⊂**15** complex in space–filling model. For a clear view of fluoride embedded, one of the bridge unit was shown in capped sticks model.

To test the hypothesis that superphane **15** is capable of complexing fluoride anion, prior to any experimental studies, DFT calculations were carried out in the gas phase at the X3LYP/6–31g* level. An energetically stable F$^-$⊂**15** complex with –70.89 kcal/mol complexation energy was obtained (Figure 4c and 4d). Interestingly, the fluoride anion was observed to be thoroughly wrapped by the six bridges and two benzene rings in three dimensions, which is reminiscent of an anion–in–prison system. Six imino C–**H**s and six 2–Ar–**H**s point to fluoride anion in a cooperative manner, where the averaged imino C···F$^-$ and 2–Ar–C···F$^-$ distances were estimated to be 3.45 Å and 3.60 Å, respectively, suggesting the occurrence of a favorable binding of F$^-$.

To ascertain the putative encapsulation of fluoride by superphane **15** experimentally, initial screening studies were carried out in $CDCl_3$ using ^{1}H NMR spectroscopy. It was found that when 20 equiv of TBAF was added into a 1.0 mM solution of **15** in $CDCl_3$, two singlets ascribed to the imino C–**H** signals at 8.12 ppm and 2–Ar–**H**s signals at 7.37 ppm (designated as *b* and *e*, respectively, in Figure 2) in free **15** downshifted to 8.15 ppm and 7.38 ppm, respectively. Although these changes are not quite significant, the conclusion that fluoride anion is being bound effectively by **15** could be drawn from the fact that the addition of 20 equiv of TBAF to the control compound **16** under identical experimental conditions didn't cause any slight chemical shifts at all (Fig. S8). To gain insights in greater details into the binding of fluoride by **15**, ^{1}H NMR spectroscopic titrations were carried out in CD_3Cl using TBAF as the fluoride anion source (Fig. S9). Under the conditions of the titration, it was found that upon incremental addition of TBAF, the signals corresponding to the free imino C–**H** protons at δ = 8.12 ppm and 2–Ar–**H**s at δ = 7.37 moved to the downfield at δ = 8.15 and 7.38, respectively. The resulting binding isotherm could be fitted to a 1:1 binding model, allowing a

binding constant of (5.2 ± 0.2) × 10^2 M^{-1} to be determined (Fig. S9 and S10). The 1:1 binding of F^- and **15** was supported by the ESI high–resolution mass spectrum (Fig. S11).

Fascinatingly, adding 20 equiv of larger anions (than F^-), *i.e.*, Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} or $HP_2O_7^{3-}$, respectively, as their TBA salts to solutions of superphane **15** in $CDCl_3$ failed to produce any noticeable changes in the proton signals of **15** (Figure 5). This is consistent with the absence of any appreciable interaction between **15** and any of these anionic species in question. These findings lead us to conclude that receptor **15** is capable of binding F^- exclusively in the presence of not only larger spherical Cl^- and Br^- but also the more structurally complex N_3^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} or $HP_2O_7^{3-}$ anions.[53] Given the near–closed feature of superphane 15, such exclusive selectivity could be accounted for the "gate" effect or size–sieving effect dominated by the multiple bridges.

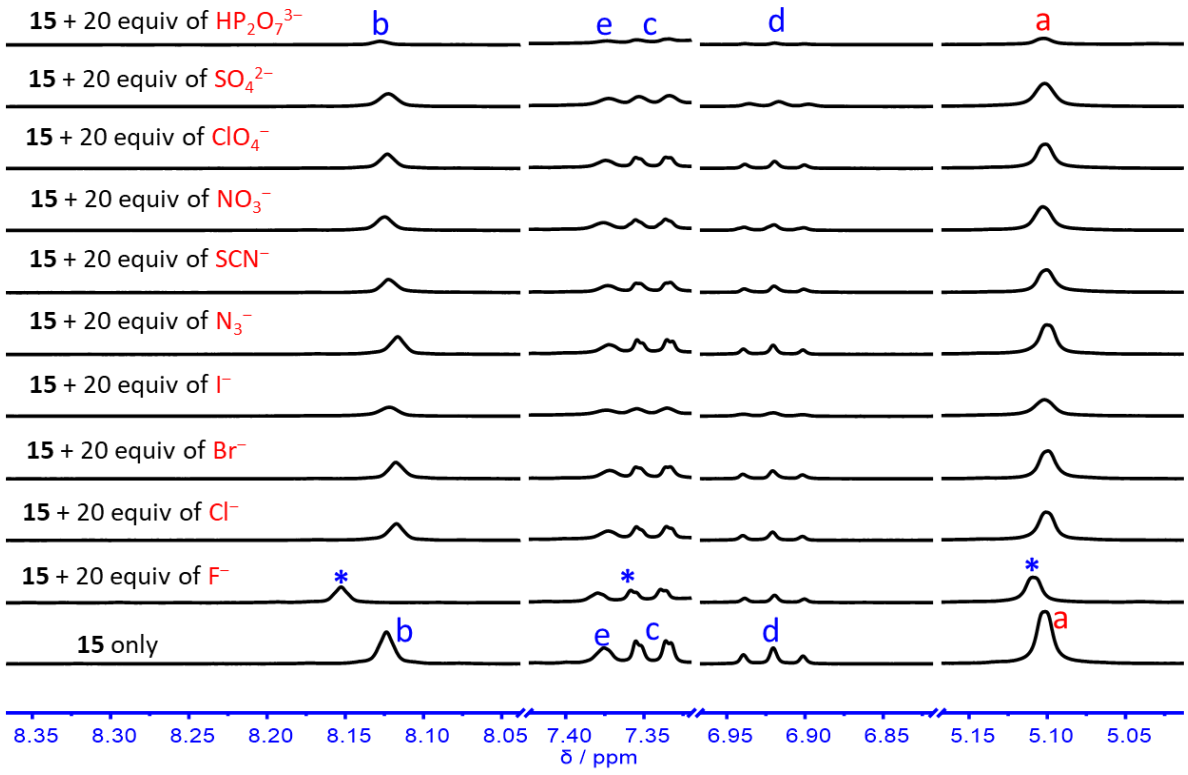


Figure 5. Selected regions of the ^1H NMR spectra ($CDCl_3$, 298 K) of solutions of **15** recorded in the absence or presence of 20 equiv of F^-, Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} or $HP_2O_7^{3-}$, respectively, as their TBA salts. The proton assignment could refer to Figure 2. A new set of ^1H NMR signals (indicated by an asterisk) was also seen only in the presence of F^-.

3. Conclusions

In summary, we established the first covalent superphane–based anion receptor **15** by integrating the structurally "complex" and synthetically challenging superphane with uncommon imino C–**H**s and Ar–**H**s as hydrogen–bonding donors. Superphane **15** was synthesized in "one pot" via reversible dynamic covalent reaction of a hexakis–amine **13** and *m*–phthalaldehyde **14** in a [2 + 6] manner. **15** features a near–closed or –isolated inferior space surrounded by two benzene rings on the top and bottom, respective, and six C–shaped bridges as the "walls" with anion binding sites, inferred from the ESI high–resolution mass spectroscopy, X–ray diffraction analysis and theoretical calculations. Superphane **15** was found capable of binding the smallest anion except for hydride (H^-), namely F^-, with exclusive selectivity against larger anions, *i.e.*, Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-} or $HP_2O_7^{3-}$, as supported by ^1H NMR spectroscopic analyses and DFT calculations. Therefore, we believe that the old–yet–new superphanes will enlarge host–guest chemistry and should be used as

new hosts. More works on preparing all kinds of functional superphanes and their uses in host–guest chemistry and critical materials, *etc*., are ongoing and will published in due course.

Conflicts of Interest

The authors declare no conflict of interest.

Acknowledgment

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