Superphanes: Facile and Efficient Preparation, Functionalization and Unique Properties

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ABSTRACT: Superphanes, compounds in which the two benzene rings clamped parallel on top of each other by six bridges, have garnered considerable interest due to their aesthetically pleasing structures and unique chemical physical properties. However, until now progress in the research of superphane chemistry and beyond has been seriously hampered by their poor availability. Herein, we report the facile and scalable synthesis of a collection of superphanes with structural diversity and their unique photophysical properties, as well as their unusual host–guest behavior. Initially, a set of dodecaimino–containing superphanes 7a–7e are obtained via dynamic self–assembly of a hexakis–amine and a series of readily derived aromatic dialdehyde in one pot. The resulting superphanes are found capable of being reduced with NaBH₄ to their corresponding secondary–amine versions 3a–3e. Subsequently, superphane 3c bearing 12 amine–NHs was further subject to post–functionalization with various functional groups, e.g., ethyl, allyl, propargyl and but–2–yn–1–yl. Unprecedentedly, the secondary amine–based superphanes 3a–3e were observed to exhibit genuine fluorescence both in solution and in the solid state while the imine–based superphanes 7a–7e were found to highly emissive only in solid state with fluorescent quantum yields of 3.5 ~ 17.1. Finally, fully protonated 3a was exemplified to encapsulate a 2Cl⁻·H₂O cluster both in the solid state and in solution. With the easy and versatile synthesis, modification, as well as unique photophysical and host–guest properties, we believe that this study will break the bottleneck in superphane chemistry and open the door to a novel class of supramolecular hosts and advanced functional materials on the basis of superphanes.

Introduction

Since the pioneering work of Cram in the early 1950s,1 cyclophane chemistry has blossomed into an active research area and the cyclophane–based systems have spurred considerable interest in the fields of supramolecular chemistry, natural products, organometallic chemistry, asymmetric synthesis, functional π systems, polymer chemistry, and materials science.2–8 However, as stated by Vögtle in 1972 “the ultimate achievement of work in the cyclophane field would be the synthesis of the fully bridged [2.2.2.2.2.2][1,2,3,4,5,6]cyclophane (1)” that was trivially termed as superphane initially proposed by Boekelheide and Hopf in 1979.9–10 Later, the terminology superphanes were extended and, inter alia, designate compounds in which the two benzene rings clamped parallel on top of each other by six bridges (e.g., 1, Figure 1a).11 As a tour de force in man–made organic molecules, superphanes, featuring aesthetically pleasing structures with high symmetry (D₆h), were initially designed as a highly strained synthetic goal for the discovery of new preparative procedures, and attractive physicochemical properties such as chemical bond, ring strain, and unusual π–electron interactions.11 In theory, superphanes could be rendered to be unique yet useful supramolecular hosts for specific guest species via well–designed extension and decoration of the toroidal bridges to furnish suitable binding cavities. Nevertheless, most, if not all, of these possibilities have been limited by their availability over the past 40 years or so.10,12–13 Therefore, developing facile, efficient, scalable and robust synthetic protocols for superphanes is key to the flourish of superphane chemistry and beyond. Compared with the conventional supramolecular hosts such as macrocyclic receptors and cages,14–18 superphane–based supramolecular hosts are expected to have many advantages and unique characteristics. Firstly, the exceptionally high structural symmetry (D₆h or C₆v) may simplify its synthesis; Secondly, the highly dense binding sites (6n, where n is the number of binding site(s) on each bridge) may allow for tight guest binding, that is of significance to biomolecular recognition, ion extraction, and cluster stabilization;19–22 Thirdly, the uniform three–dimensional distribution of the six connecting bridges around the near–closed internal cavity may prevent the embedded species from solvation or attack by the external substrates. Given the complexity and symmetry of superphanes per se, we envisioned that highly efficient and selective dynamic covalent reactions are beneficial to access such a class of complicated superstructures.23–26 Amongst them, imine dynamic chemistry proved to be particularly appealing.27–30 For example, in 2020, our group successfully introduced the imine dynamic chemistry to construct the first–ever superphane (2)
as a supramolecular receptor for hosting either small anions or neutral species, e.g., a water dimer, via self-assembly of two simple substrates in a 2:6 ratio in one pot (Figure 1a). Almost simultaneously and independently, Badić group reported a so-called hexapodal capsule for the recognition of anions, where the capsule was prepared through a dynamic reaction of a hexa-amine and a readily premade hexa-podal aldehyde precursor in a 1:1 fashion, coincidently, using a similar strategy. These two examples provided some interesting results for superphane chemistry. However, both systems 1) consist of multiple unstable and reversible amine bonds; 2) didn’t show structural diversity and modification; 3) prepared in milligram scale. Thus, the best is still yet to come.

(a) Previously reported superphanes

(b) Pre- and post-modified superphanes (this work)

Figure 1. (a) Chemical structures of the previously reported superphanes 1 and 2. (b) Representative chemical structures of superphanes with large cavities via pre-modification (for 3) and post-modification (for 4) strategies reported in this work.

On the basis of our previously reported imine dynamic strategy, herein, we describe a general synthetic route accessible to a series of highly stable superphanes (3, Figure 1b) with irreversible covalent bonds via in-situ reduction of the corresponding imino–based superphanes using NaBH₄ as the reductive reagent. The easy accessibility and high efficiency were exemplified with successful gram-scale preparation of the secondary–amine–based superphane 3c, which was successfully post-functionalized with ethyl iodide, allyl bromide, propargyl bromide or 1-bromobut-2-yne bromide, giving the peraza-substituted superphanes 4 (Figure 1b). Notably, the synthesis of all superphanes under current study was chromatography free. More importantly, unprecedented solid-state and solution-state fluorescent properties were also discussed. Finally, protonated superphane 3a proves capable of binding a labile trimeric chloride hydrate cluster (2Cl⁻·H₂O). To the best of our knowledge, this is the first report on the facile and gram-scale synthesis of superphanes that feature liquid and solid fluorescence, as well as effective encapsulation of a 2Cl⁻·H₂O cluster.

Results and Discussion

One-pot, gram-scale synthesis and pre-modification

According to our previously reported work, the imino-containing superphane 7a could be accessible via dynamic self-assembly of hexakis-amine (5) and m-phthalaldehyde (6a) in a 2:6 ratio in one pot. Inspired by the fact that macrobicyclic azacryptands and sandwich-like azacyclophanes could be easily prepared through reversible and thermodynamically driven imine condensation, followed with a reduction step, we next sought to transform imine superphane 7a into its stable amine form. To our delight, treatment of 7a with NaBH₄ in a mixture of CH₂Cl₂ and CH₃OH (1:1, v/v) at room temperature over 5 h led to the formation of amine superphane 3a in 81% yield (Scheme 1). Similarly, self-assembly of 5 with 5-bromoisophthalaldehyde 6b gave imine-based superphane 7b in 39% yield. After reduction with NaBH₄, 7b was transformed into 3b in a yield of 74% (Schemes S1 and S2). Satisfyingly, we managed to further simplify the synthesis of 3a and 3b via in-situ reduction of 7a or 7b after the completion of self-assembly process in one pot with decent yields (69% for 3a and 59% for 3b, respectively).

To confirm the versatility of this approach to amine-based superphanes of interest, different variants of m-phthalaldehyde, viz., 2,6-pyridinedicarboxaldehyde (6c), 2,5-furandicarboxaldehyde (6d) and larger 4,4’-oxydibenzoaldehyde (6e), were utilized to replace 6a. Expectedly, using a similar imine condensation strategy, compounds 3b–3e were successfully obtained by the simple one-pot self-assembly of hexakis-amine 5 with 6c, 6d and 6e, respectively, followed by in-situ reduction reactions in the presence of NaBH₄ (Scheme S3). Of particular note is that, during the course of synthesis, no chromatography was needed for the purification of either 7a–7e or 3a–3e. All imine-based superphanes 7b–7e and amine-bearing superphanes 3a–3e have been well characterized by ¹H NMR, ¹³C NMR spectroscopy, and electrospray ionization high-resolution mass spectrometry (ESI–HRMS) (see supporting information).

Subsequently, the availability of this facile and concise synthetic approach to a wide range of amine-based superphanes was further examined by the demonstrative gram-scale synthesis of superphane 3c in one pot. Concretely, the synthesis started from 2,6-pyridinedicarboxaldehyde 6c (1.27 g), which was subject to imine condensation with hexakis-amine 5 (2.36 g) in methanol at 65°C for 12 h. Then, the resulting mixtures with a substantial number of precipitates were in-situ treated with excess NaBH₄ for a further 12 h at RT, where the precipitates disappeared gradually thereafter. After solvent removal, the resulting residuals were dispersed in water and repeatedly extracted with chloroform. The organic phases were combined, dried, and evaporated to yield crude product, which was washed with excessive acetonitrile to offer 1.32 g of desired superphane 3c as a light yellow powders in 47% overall yield.
Post–functionalization

Generally, post–synthetic functionalization of the core macrocycles or molecular cages has been ascertained to be a most effective synthetic route to access new analogues without a need to rework the synthesis of the core structures. However, the binding properties of the core systems in question could be modulated with greater fidelity. With this in mind, we next sought to explore the post–functionalization of superphane 3c, for example, containing 12 NHs with alkyl halides. Initially, ethyl iodide (8a) was subject to reaction with 3c pretreated with NaH in DMF. As expected, the per–substituted product 4a was obtained in yield of 8% (Schemes 2 and S4). Given the fact that allyl and propargyl groups are two of the most commonly used functionalizable moieties for fabrication of functional molecules and materials via olefin metathesis, alkyne metathesis or click reactions, then commercially available allyl bromide (8b), propargyl bromide (8c) and 1–bromobut–2–yne bromide (8d) were utilized for direct modification of 3c. Specifically, treatment of 3c with excess allyl bromide in the presence of NaOH (in DMF) at 65 °C for 20h led to the expected peraza substituted product 4b in 21% yield. Similarly, triple bond–containing groups proved capable of being incorporated into 3c via the electrophilic addition of 3c with excess propargyl bromide or 1–bromobut–2–yne bromide in the assistance of NaH (in DMF) at room temperature, offering 4c and 4d in yields of 11% and 5%, respectively. Superphanes 4a–4d bearing 12 allyl substituents have been well characterized by 1H NMR, 13C NMR spectroscopy, and electrospray ionization high–resolution mass spectrometry (ESI–HRMS) (see supporting information). Interestingly, based on the 1H NMR spectrum of 4a–4d in CDCl3 or DMSO–d6 at 298 K, all three sets of methylene proton signals were found split, respectively, indicating that these methylene protons were distinguishable even at room temperature probably due to the restriction of intramolecular rotation of methylene units in question (Figures S1–S4).

**Scheme 1.** Facile synthesis of dodecamino–containing superphanes 7a–7e, and the reduction of 7a–7e to prepare their corresponding dodecazasuperphanes 3a–3e containing secondary amines.

**Scheme 2.** Representative post–functionalization of superphane 3c with ethyl bromide (8a), allyl bromide (8b), propargyl bromide (8c), and 1–bromobut–2–yne (8d) and the chemical structures of 4a–4d.

**Solid–state structures**

To obtain detailed insight into the structure, conformation, and potential binding properties of superphanes 3a–3e, substantial trials have been dedicated to growing their single crystals in either neutral form or protonated fashion. In the case of superphane 3c, many efforts have been made to grow single crystals of either 3c or its protonated form in the presence of strong acids, e.g. HCl, HBr, TsOH (4–methylbenzenesulfonic acid) and CF3COOH, but to no avail. Much to our surprise, upon slowly diffusing acetone vapor into a solution of 3c in a mixture of chloroform and methanol in the presence of excess CF3COOLi, colorless block–like single crystals suitable for X–ray single crystal structure analyses were obtained. Unexpectedly, the yielding crystal structure revealed a 2CH3OH@3c·2H+ complex, instead of an expected CF3COOLi inclusion complex of 3c. Although the exact locations of protons are usually not able to be identified by X–ray scattering, the diprotonated 3c could be deduced by the occurrence of two CF3COO– anions in each asymmetric unit (Figure S5). In the solid state, the framework of 3c·2H+ displayed D2h symmetry and a tunnel right through the center of the cage (Figure 2a). Unambiguously, one methanol molecule was observed to be entrapped within the center of 3c and the other one was clamped by two out of six pyridyl–containing bridges (Figures 2b and S6).
To elucidate the structure of the post modified superphane 4b with 12 allyl groups, suitable single crystals were obtained by slow diffusion of ethyl ether vapor into a solution of 4b in a mixture of CH$_3$OH, CHCl$_3$ and Et$_2$O at low temperature (0~5 °C). The resulting crystal structure gave an expected super cage with exceptionally high symmetry (near D$_{4h}$) (Figures 3a and 3b). Due to steric congestion, all allyl groups are oriented opposite to the core of superphane 4b to form two identical bowl-shaped outer cavities with the depth of 3.83 Å (Figure S7). Meanwhile, the two face-to-face benzene rings are somewhat extruded to generate a close benzene--benzene contact of 4.57 Å, indicating the occurrence of weak π···π interactions and the disappearance of internal void of 4b. In this case, no solvent molecules were found within the internal cavity of superphane 4b. Instead, an ethyl ether molecule was observed in each outer cavity formed by six allyl moieties as the fences (Figure S8). Each pyridinyl group at the periphery of 4b was aligned nearly perpendicular to the corresponding bridge plane and almost parallel to the other one at its opposite site. Interestingly, each 4b cage was found surrounded tightly by other six 4b molecules at the same plane via multiple cooperative C$_{sp2}$--H···π, offset π···π, and C$_{sp3}$--H···π interactions, giving rise to a regular hexagon with the side length of 14.23 Å (Figures 3c and S9).

**Photophysical Properties**

Fluorescence is a property of matter that is critical for many research fields, such as chemistry, biology, material science and the like. The marriage of macrocycles or cages and fluorescence has garnered growing interest of the chemists in recent years. Interestingly, although no specific fluorophores were integrated, genuine blue–green fluorescent emissions were observed when chloroform solutions of 3c, 3d and 3e were exposed to 365–nm UV light (Figure 5a, inset). Upon excitation of 3c, 3d, and 3e in chloroform at 340, 373, and 367 nm, respectively, they showed similar emission bands of 400–600 nm with an emission maxima at 452, 449, and 439 nm, respectively (Figures S14–S16). Due to the poor solubility of 3a and 3b in commonly used solvents, they were subject to protonation with HCl and the resulting salts were found soluble in DMSO. Upon excitation of the protonated 3a, 3b in DMSO at 365 and 376...
nm, respectively, emission bands of 400~600 nm with corresponding emission maxima at 443 and 442 nm were seen (Figures S17 and S18). Notably, all of these superphanes in solution displayed poor fluorescence quantum yields (Φ < 0.01). In contrast, both imino–based superphanes 7a–7c, 7e and tertiary amine–based superphanes 4a–4d in solutions proved nearly fluorescence–silent. These findings indicated that the observed weak emission of 3a–3e in solution might be attributed to an intramolecular proton transfer mechanism.

Interestingly, as opposed to the weak/non–fluorescent features in solution, relatively strong solid–state fluorescent emission of the imino–based compounds 7a–7c, and 7e was observed (Figure 5b). Specifically, when exited with light at 433, 446, 497 and 446 nm for 7a, 7b, 7c, and 7e, respectively, their solid samples emitted strong visible fluorescent light with the corresponding emission maxima at 505, 517, 551 and 527 nm (Figures S19–S22). Similarly, the secondary amine–based superphanes 3a–3e in solid state also exhibited relatively strong fluorescence with the emission maxima ranging from 439 nm to 549 nm (Figure S23–S27). Structurally, compounds 7a–7e, inter alia the former four, are quite similar. Nevertheless, their solid-state emitting color differs from one another significantly ranging from chartreuse to near white with fluorescence quantum yields (Φ) of 7.1, 5.8, 3.5 and 14.0 for 7a, 7b, 7c and 7e, respectively (Figure 5c). Likewise, cages 3a–3e as powders emit near white, blue/green, yellowish, near–white, and white fluorescence, respectively, with the corresponding fluorescent quantum yields of 5.2, 9.0, 10.0, 17.1 and 4.0. Taken together, based on the framework of superphane, a series of emissive fluorescent super cages were easily obtained via incorporating various substituents into the bridges between the top and bottom benzene rings. The acquired fluorescence could be finely designed and tuned by modifying the bridges with specific units or by reducing the imine bonds of the superphanes. To the best of our knowledge, this is the first report on superphane systems featuring tunable fluorescent emission. Given the weak solution–state emission and strong solid–state fluorescence, these findings might be somewhat rationalized by aggregation induced emission (AIE) effect.48 However, more experimental and theoretical studies are needed to shed light on the detailed mechanism, inter alia, involving the unusual (near–) white emission.

Host–guest properties

Cryptands and aza–cryptands have been well–established to work as versatile anionic receptors for negatively charged guest species, inter alia, in their protonated form.49 Inspired by those findings in the literature, a selected example, 3a containing 12 NH units, was subject to protonation with strong acids, e.g. hydrochloric acid and H₂SO₄. Specifically, superphane 3a proves not soluble in commonly used solvents, but it becomes soluble in either DMSO or a mixture of DMSO and water (5:1, v/v) and only one set of resonances were observed upon treatment of 3a with excess HCl or H₂SO₄ (Figures S28 and S29). These findings allow us to suggest that 3a was capable of being fully protonated with HCl or H₂SO₄ in relatively flexible conformation at 298 K.

We next sought to explore whether NH–bearing superphanes 3a in its protonated manners could serve as a receptor for binding anions, such as Cl⁻. Initial evidence for anion encapsulation of protonated 3a came from the single crystal X–ray structure of its hydrochloric complex. Specifically, suitable crystals were obtained by allowing a solution of HCl–protonated 3a in water to evaporate slowly at room temperature. The resulting crystal structure revealed a protonated complex in the solid state (Figure 6a). Due to the limitations of crystallography and the disorder of the solvent molecules and the counter chloride outside the cavity, the degree of protonation of 3a was not able to be exactly determined. In terms of the structure of protonated 3a, the two face–to–face benzene rings are clamped parallel on top of each other by six bridges bearing m–xylendediamine moieties and the six toroidal bridges are almost uniformly distributed around the internal cavity, generating a lantern–like superstructure (Figures S30 and S31). Notably, each bridge of superphane 3a has at least two NHs and one Ar–H as the binding sites, pointing to the inside cavity. These enable protonated 3a to feature a unique supramolecular receptor for binding specific guests with up to 18 hydrogen bonding donors. Interestingly, a closer inspection at this crystal structure revealed that a trimeric cluster consisting of two Cl⁻ anions and one H₂O molecule were found embedded right within the cavity of 3a, wherein the Cl⁻···Cl⁻ and averaged Cl⁻···O(water) distances were measured to be 4.15 and 3.19 Å, respectively (Figures 6b and S32). Each hydrogen atom of the water molecule points to one chloride anion, leading to a Cl⁻···H–O···H···Cl⁻ complex, which as a whole was stabilized by multiple hydrogen bonds.

![Figure 5](image-url)
The ability of protonated 3a to bind chloride in solution was further probed via $^1$H NMR spectroscopy using a mixture of DMSO–$d_6$ and D$_2$O (5:1, v/v) as the solvent. As discussed above, spectroscopic analysis of the H$_2$SO$_4$–protonated 3a revealed only one set of resonance signals in the complex, indicating that the dominant species is 3a·H$_2$SO$_4$, with all secondary amino groups protonated (Figure 5c). Of particular note is that the aromatic C$_{sp2}$–H resonances in protonated 3a was observed to be located at 6.55 ppm, a relatively upfield region, presumably suggesting that no counter sulfate anion was captured within the central cavity of 3a (Figure S33). However, upon addition of excess Cl$^-$ (as its TBA salt) to a 1.0 mM solution of H$_2$SO$_4$–protonated 3a, the broad singlet associated with the C$_{sp2}$–H protons seen at 6.55 ppm (e) underwent a pronounced downshift to 7.01 ppm. Meanwhile, the aromatic C$_{sp2}$–H protons at 7.02 (c) and 6.93 (d) suffered a shift to 6.91 and 6.76 ppm, respectively, and the methylene protons showed chemical shift changes from 4.43 (a) and 4.04 ppm (b) to 4.51 and 4.23 ppm, respectively (Figure S33). These findings led us to suggest that protonated superphane 3a binds effectively the Cl$^-$ anion well in solution.

Figure 6. X-ray single-crystal structures of (a) 3a in its protonated form; (b) 2Cl$^-$·H$_2$O@3a (protonated). The superphane frameworks are presented in ellipsoid model while the entrapped guest species, e.g. Cl$^-$ and H$_2$O, are shown in space-filling form. All solvent molecules and other counter anions were omitted for clarity.

Figure 7. (a) selected regions of $^1$H NMR spectra (DMSO–$d_6$/D$_2$O, 5:1, v/v, 298 K) acquired during the titration of H$_2$SO$_4$–protonated 3a with increasing quantities of TBACl: (bottom to top) 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75, 3.0, 3.25, 3.5, 3.75, 4.0, 4.25, 4.5, 4.75, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0, 23.0, 27.0, 31.0, and 35.0 equiv; (b) A schematic view of the chloride binding by 3a·H$_2$SO$_4$.

To obtain greater insights into the binding of chloride by protonated 3a, $^1$H NMR spectroscopic titrations were carried out in a mixture of DMSO–$d_6$ and D$_2$O (5:1, v/v) using TBACl as the chloride anion source (Figure 7a). Specifically, upon incremental addition of 0–4 equivalents of Cl$^-$, all proton signals ascribable to protonated 3a were observed to gradually decrease while a new set of resonances progressively increase, reflecting the first chloride binding event in slow exchange on the NMR time scale. Interestingly, apart from the increase, the new set of signals (e.g. e) corresponding to the chloride complex simultaneously underwent either downfield or upfield shifts regardless of the first saturation point achieved, presumably indicating the second chloride binding event in fast exchange on the NMR time scale. Consequently, the binding constants of $K_{11} = (1.8 \pm 0.3) \times 10^3$ and $K_{12} = (1.1 \pm 0.1) \times 10^3$ M$^{-1}$ can be estimated by fitting the $^1$H NMR data corresponding to the C$_{sp2}$–H, C$_{sp2}$–H, and C$_{sp2}$–H proton resonances to a 1:2 binding model (Figure S34). These findings allowed us to conclude that the fully protonated 3a was probably capable of encapsulating two chloride anions, as reflected in the single crystal structure mentioned above.

A careful inspection of the $^1$H NMR spectrum of HCl–protonated 3a in DMSO–$d_6$ at room temperature revealed the occurrence of a broad singlet around 8.47 ppm, which was able to be deuterated with D$_2$O within 30 min, reflecting the active role of protons in question (Figure S35). In contrast, no such active protons were seen in the case of H$_2$SO$_4$–protonated 3a in a mixture of DMSO–$d_6$ and H$_2$O (5:1, v/v). However, upon addition of excess TBACl to the beforementioned solution, a broad singlet at 8.50 ppm occurred (Figure S36). These observations led us to suggest that water molecules might get involved in the binding of the chloride dimer, resulting a possible complexation of a Cl$^-$···H–O···H–Cl$^-$ cluster in solution as observed in the single crystal structure.

Conclusion

In summary, a series of dodecaazasuperphanes, featuring exceptionally high ($D_{18h}$) symmetry and multiple (up to 18) binding sites, have been firstly established via a facile and efficient in–situ reductive amination strategy. The structural diversity could be achieved by the pre–modification of the dialdehydes. To the best of our knowledge, this is the first paper to describe the concise, easy–to–operate and gram–scale synthesis of superphanes, which opens the door to superphane chemistry. Furthermore, the feasible post–modification of secondary amine–based superphanes was exemplified by furnishing superphane 3e with various functional groups, viz. ethyl, allyl, propargyl and but–2–yn–1–yl. Importantly, compounds 7a–7e and 3a–3e under study were found to exhibit solid-state fluorescence with various emission colors ranging from bluish to near white. Meanwhile, 3a–3e proved emissive in solution as well.
These represent the first fluorescence emissive superphane systems. Last but not least, with suitable internal apertures and appropriate binding sites as demonstrated by crystallography, and $^1$H NMR spectroscopy, superphane 3a in its protonated manner proved able to capture a $\text{2Cl-H}_2\text{O}$ cluster both in the solid state and in solution. This work establishes a facile and efficient synthetic approach to emissive superphanes that could be broadly utilized a new class of advanced emissive materials or as a new generation of supramolecular hosts for neutral species, anions, cations, ion pairs, as well as labile ionic solvate clusters. Further studies are ongoing in our lab to advance our understanding of superphane chemistry and will be published in due course.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental procedures, NMR spectroscopic studies, HRMS results, fluorescent spectroscopic details, and X-ray crystallographic data for 3c-TFA, 4b, 4c, and 2Cl-$\text{H}_2\text{O}$@3a complex (PDF)

X-ray crystallographic data for 3c-TFA (CIF)

X-ray crystallographic data for 4b (CIF)

X-ray crystallographic data for 4c (CIF)

X-ray crystallographic data for 2Cl-$\text{H}_2\text{O}$@3a complexes (CIF)

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Declaration of Interests

Hunan University has applied for a patent on this work.

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- Facile synthesis
- Gram-scale preparation
- Pre-modification
- Post-functionalization
- Chromatography free
- Structural diversity
- High symmetry
- Liquid fluorescence
- Solid-state fluorescence
- Up to 18 binding sites
- Near-closed 3D cavity
- Unique host-guest binding