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A New Hexaaza Bicyclic Cyclophane with Dual Binding Sites

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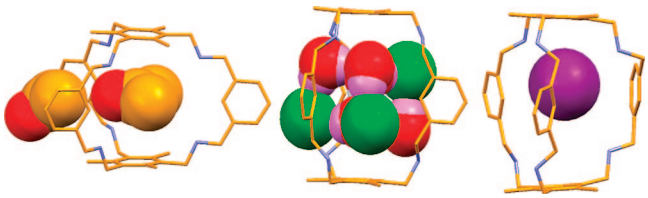

A new C_3-symmetric drum-shaped homoditopic haxaamino bicyclic cyclophane and its hexachloride and hexaiodide complexes have been synthesized and characterized and dual recognition of guests has been demonstrated. Single-crystal X-ray analysis illustrates that bicyclic cyclophane has a cavity and side pockets for acetone molecules. The hexaprotonated state of this bicycle shows encapsulation of an iodide inside its cavity, and in hexachloride complex, chloride is recognized as $Cl^- \cdots H_2O$ in each of the three side pockets which are in extensive hydrogen bonding interactions with the water and chlorides. ^{1}H NMR experiments have also been carried out on hexatosylated cyclophane with the halides to study solution state binding.

One of the major interests in molecular recognition is the design and synthesis of receptors for selective recognition of anions[1] and it is a rapidly expanding area of research because anions have a great relevance from a biological point of view. In biology over 70% of all cofactors and substrates are of anionic nature. Further anions are essential for the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation.[2] In the biochemical world, for example, ion channels have been of considerable interest and it has been shown that the presence of arenes close to the binding site also influences the chloride binding in the ion channel. Protonated azamacrobicycles have been established as good hosts for anions.[1] Especially, hexaprotonated tris(2-aminoethyl)amine, tren-capped homoditopic macrobicyclic cryptands with an arene spacer (*p*-xylyl and *m*-xylyl), have shown encapsulation of halides[3] and oxyanions[4] inside the receptor cavity. A higher degree of protonation of these receptors has also shown halide encapsulation inside the cavity.[5] Further, tren-capped homoditopic macrobicyclic cryptands with ethylene spacer also shown halide encapsulation inside the cavity upon hexaprotonation.[6]

The 1,3,5-trialkylbenzene-capped macrobicyclic azacryptand has shown solution state anion binding properties upon protonation.[7] Later on, the spatially segregated benzene derivatives have attracted much attention as efficient building blocks for functional molecules such as molecular receptors in the field of molecular recognition and supramolecular chemistry. Arene platform based tripodal[8] and macrobicyclic neutral receptors[9] have been utilized as the receptors for various guests. For example, among the cage compounds, Anslyn et al. have used 1,3,5-substituted phenyl caps to synthesize amide-based bicyclic cyclophane with pyridine spacer for nitrate selectivity[9i] whereas pyrrole-spaced bicyclic amine cyclophane has been explored for its carbohydrate recognition.[9a] The cleft binding mode of the macrobicyclic hosts is rather limited compared to the cavity binding.[3] It has been shown by solution state studies that cryptand-like calixpyrrole host can bind with halide via side pocket binding.[10b] Setsune et al. have reported the allosteric carboxylic acid binding via clefts of the cryptand-like porphy-

(1) (a) Special Issue: Anion Coordination Chemistry II. *Coord. Chem. Rev.* **2006**, *250*. (b) Sessler, J. L.; Gale, P.; Cho, W.-S. *Anion Receptor Chemistry*; RSC: London, UK, 2006. (c) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671. (d) Special Issue: 35 Years of Synthetic Receptor Chemistry. *Coord. Chem. Rev.* **2003**, *240*. (e) Vilar, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1460. (f) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (g) Lehn, J.-M. In *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.

(2) Dutzler, R.; Campbell, E. B.; Cadene, M.; Chait, B. T.; MacKinnon, R. *Nature* **2002**, *415*, 287.

(3) (a) Lakshminarayanan, P. S.; Kumar, D. K.; Ghosh, P. *Inorg. Chem.* **2005**, *44*, 7540. (b) Hossain, M. A.; Morehouse, P.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2005**, *44*, 2143. (c) Hossain, M. A.; Llinares, J. M.; Mason, S.; Morehouse, P.; Powell, D.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 2335. (d) Mason, S.; Llinares, J. M.; Morton, M.; Clifford, T.; Bowman-James, K. *J. Am. Chem. Soc.* **2000**, *122*, 1814.

(4) (a) Kang, S. O.; Hossain, M. A.; Powell, D.; Bowman-James, K. *Chem. Commun.* **2005**, 328. (b) Nelson, J.; Nieuwenhuyzen, M.; Pál, I.; Town, R. M. *Chem. Commun.* **2002**, 2266. (c) Maubert, B. M.; Nelson, J.; McKee, V.; Town, R. M.; Pál, I. *J. Chem. Soc., Dalton Trans.* **2001**, 1395. (d) Clifford, T.; Danby, A.; Llinares, J. M.; Mason, S.; Alcock, N. W.; Powell, D.; Aguilar, J. A.; García-España, E.; Bowman-James, K. *Inorg. Chem.* **2001**, *40*, 4710. (e) Mason, S.; Clifford, T.; Seib, L.; Kuczera, K.; Bowman-James, K. *J. Am. Chem. Soc.* **1998**, *120*, 8899. (f) Morgan, G.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun* **1995**, 1649. (g) Menif, R.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 3446.

(5) Lakshminarayanan, P. S.; Suresh, E.; Ghosh, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3807.

(6) (a) Arunachalam, M.; Suresh, E.; Ghosh, P. *Tetrahedron.* **2007**, *63*, 11371. (b) Hossain, M. A.; Llinares, J. M.; Miller, C. A.; Seib, L.; Bowman-James, K. *Chem. Commun.* **2000**, 2269.

(7) Heyer, D.; Lehn, J.-M. *Tetrahedron Lett.* **1986**, *27*, 5869.

(8) (a) Nativi, C.; Cacciarini, M.; Francesconi, O.; Vacca, A.; Moneti, G.; Lenco, A.; Roelens, S. *J. Am. Chem. Soc.* **2007**, *129*, 4377. (b) Hisaki, I.; Sasaki, S.-I.; Hirose, K.; Tobe, Y. *Eur. J. Org. Chem.* **2007**, 607. (c) Vacca, A.; Nativi, C.; Cacciarini, M.; Pergoli, R.; Roelens, S. *J. Am. Chem. Soc.* **2004**, *126*, 16456. (d) Wallace, K. J.; Belcher, W. C.; Turner, D. R.; Syed, K. F.; Steed, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 9699. (e) Yun, S.; Ihm, H.; Kim, H. G.; Lee, C.-W.; Indrajit, B.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, *68*, 2467.

(9) (a) Francesconi, O.; Lenco, A.; Moneti, G.; Nativi, C.; Roelens, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 6693. (b) Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L.; Douton, M.-J. R.; Ugozzoli, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 6920. (c) Ilioudis, C. A.; Bearpark, M, J.; Steed, J. W. *New J. Chem.* **2005**, *29*, 64. (d) Zhong, Z.; Postnikova, B. J.; Hanes, R. E.; Lynch, V. M.; Anslyn, E. V. *Chem. Eur. J.* **2005**, *11*, 2385. (e) Ilioudis, C. A.; Tocher, D. A.; Steed, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 12395. (f) Hennrich, G.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2218. (g) Jon, S. Y.; Kim, J.; Kim, M.; Park, S.-H.; Jeon, W. S.; Heo, J.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2116. (h) Niikura, K.; Bisson, A. P.; Anslyn, E. V. *Perkin Trans. 2* **1999**, 1111. (i) Bisson, A. P.; Lynch, V. M.; Monahan, M.-K. C.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1997**, *36*, 2340. (j) Kiggen, W.; Vögtle, F. *Angew. Chem., Int. Ed.* **1984**, *23*, 714.

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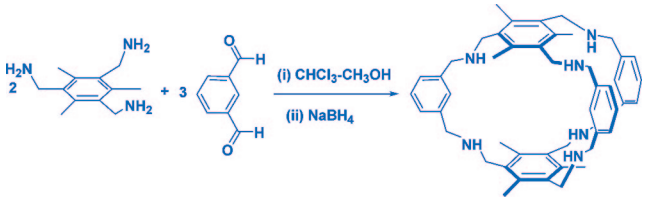
SCHEME 1. Synthesis of Macrobicyclic Cyclophane Cage, L



rinoid with dipyrrylpyridine chains.[10a] Very recently, Bowman-James and co-workers have used 1,3,5-substituted phenyl caps to synthesize amide cyclophane for anion binding at the side pockets.[11] Herein we report the synthesis of a new hexaamino bicyclic cyclophane with spatially substituted phenyl caps and a *m*-xylyl spacer and its cavity as well as cleft binding mode of this receptor toward halides upon protonation. Further we show that the synthesized cyclophane also recognizes the acetone molecule both inside the cavity and at the cleft in its native form. These results show that the newly synthesized bicyclic cyclophane possesses dual recognition sites for different guests.

The cryptand was synthesized by the reaction of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene with 1.5 equiv of isophthalaldehyde in chloroform−methanol binary solvent mixture followed by sodium borohydride reduction (Scheme 1). The resulting crude cryptand obtained after chloroform workup is recrystallized in moist acetone to obtain crystals of cyclophane cage suitable for X-ray crystallography. Further crystalline **L** is treated with 37% HCl and 57% HI to form chloride and iodide complexes. Crystallographic results are obtained for the chloride and iodide complexes which are further studied to elucidate the nature of halide binding to this cyclophane in its protonated state.

The cyclophane cage **L** crystallizes with two acetone molecules. Among them one acetone molecule resides perfectly at the center of the cavity and another acetone at the cleft (Figure 1a). No water molecule located either in the cavity or at the clefts of **L** indicates the less hydrophilic nature of the cavity and clefts. The encapsulated acetone is bound to the receptor via C−H···N interaction with the secondary nitrogen center of **L**. The apical benzene rings are 7.584 Å apart and the middle point connecting both the centroids of the apical benzene rings falls exactly on the carbonyl carbon of the encapsulated acetone (Figure 1a).

The space-filling model shows complete encapsulation of the acetone inside the cage (Figure 1c). The distances between the centroids of the apical benzene rings of **L** and the carbonyl carbon of the encapsulated acetone molecule are 3.803 and 3.787 Å. This indicates that the acetone molecule resides exactly at the center of the cavity. It is important to notice that one of the side pockets of **L** holds another acetone as a guest.

All three arms of **L** are not equally disposed and the solid state crystal structure shows that the two side arms of the cyclophane cage converge together to hold the acetone molecule in the cleft. This is evident from the distances between the centroids of the benzene rings of the adjacent arms, i.e., 11.161, 11.277, and 9.315 Å. The cleft bound acetone is in an intermolecular C−H···O interaction with the other cyclophane unit. Two of the three side arms of the cyclophane **L** form a

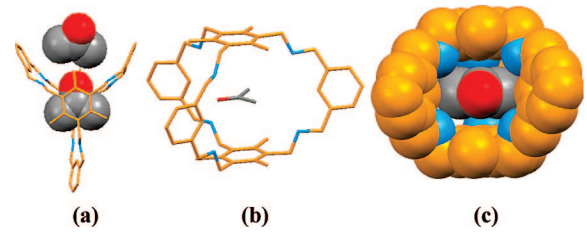


FIGURE 1. Views of encapsulated acetone inside the cage: (a) dual recognition of acetone in **L**; (b) view showing the cavity encapsulated acetone; and (c) space-filling view parallel to the arene caps showing complete encapsulation of an acetone inside the cavity.

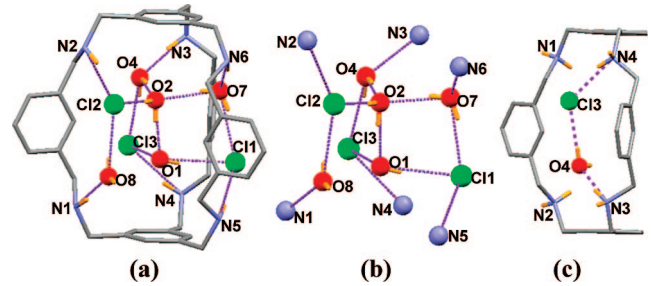


FIGURE 2. (a) View showing the hydrogen bonding interactions of $Cl_3(H_2O)_5$ moiety with the receptor unit, $[H_6\mathbf{L}]^{6+}$ (methyl of arene caps and all nonbonding hydrogen atoms of **L** are omitted for clarity); (b) clear view of the hydrogen bonding interactions of $Cl_3(H_2O)_5$ moiety with the nitrogen centers of $[H_6\mathbf{L}]^{6+}$; and (c) partial view showing the interactions of the cleft bound water−chloride with the receptor.

cavity similar to the 1,3-alternate calix[4]arene. The cleft bound acetone molecule is held weakly compared to the cavity bound acetone.

Thermogravimetric analysis (TGA) of **L** shows that onset of acetone loss starts at about 75 °C and complete loss of acetone takes place within 230.4 °C (Figure S4, Supporting Information). Total weight loss in this temperature range is 11.66%, corresponding to 1.7 molecules of acetone. The wide range of acetone loss supports the crystallographic results of one weakly interacting at the cleft and the other relatively strongly interacting acetone at the cavity.

Upon protonation with hydrochloric acid and hydroiodic acid in acetone/water and methanol/water binary systems respectively the cyclophane forms the chloride complex **1**, $[H_6\mathbf{L}][Cl]_6\cdot 9H_2O$, and the iodide complex **2**, $[H_6\mathbf{L}][I]_6\cdot 3H_2O$. The complex **1** crystallizes as a monoclinic system with $P2_1/n$ space group (Table S1, Supporting Information). All six nitrogen atoms are protonated and **1** shows binding of the water−chloride network in the cavity and at the cleft of the $[H_6\mathbf{L}]^{6+}$ moiety, which is composed of three chlorides and five water molecules, $Cl_3(H_2O)_5$ (Figure 2a,b). The distance between the apical benzene caps increased upon hexaprotonation from 7.582 to 9.336 Å. The details of the hydrogen bonding interactions of the $Cl_3(H_2O)_5$ unit are given in Table S2 of the Supporting Information. Two water molecules of the $Cl_3(H_2O)_5$ moiety are encapsulated inside the cage of $[H_6\mathbf{L}]^{6+}$ with an O1···O2 distance of 2.654 Å whereas three clefts of $[H_6\mathbf{L}]^{6+}$ recognize one chloride and a water molecule which are in hydrogen bonding interaction with the encapsulated water molecules (except O8) at the center (Figure 2a). In fact cleft binding of $Cl^-\cdots H_2O$ at the pockets of the $[H_6\mathbf{L}]^{6+}$ receptor could be represented as binding of these guests in a tetraprotonated 1,3 alternate azacalix-like cage as shown in Figure 2c. The chloride and water guests are in hydrogen bonding interactions with the receptor via N−H···Cl^-

(10) (a) Setsune, J.-I.; Watanabe, K. *J. Am. Chem. Soc.* **2008**, *130*, 2404. (b) Bucher, C.; Zimmerman, R. S.; Lynch, V.; Sessler, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 9716.

(11) Kang, S. O.; Day, V. W.; Bowman-James, K. *Org. Lett.* **2008**, *10*, 2677.

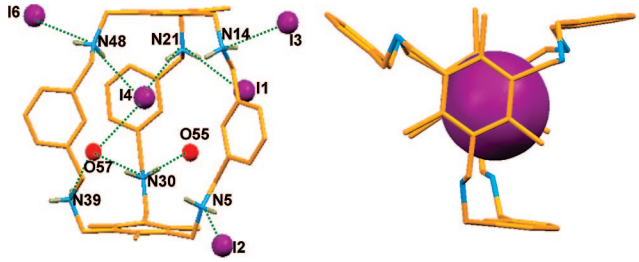


FIGURE 3. (a) View showing the hydrogen bonding interactions of the iodide ions with the receptor unit and (b) view along the apical benzene ring of complex **2**.

and N−H···O interactions, respectively (Table S2, Supporting Information). It is worth mentioning that the $[H_6\mathbf{L}]^{6+}$ bound chloride−water moieties are in extensive hydrogen bonding interaction with the rest of the lattice water and chloride ions (Figure S15, Supporting Information). In fact, packing of the chloride complex shows that receptor moieties are interlocked into the extensive three-dimensional network of the chloride−water structure.

Thermal analysis of complex **1** shows that onset of water loss starts at about 52 °C and complete loss of water takes place within 222.42 °C. Total weight loss in this temperature range is 14.83%, corresponding to nine water molecules (Figure S8, Supporting Information), which supports the crystallographic findings.

The complex **2** crystallizes as a monoclinic system with $P2_1/n$ space group. All six nitrogen atoms are protonated and **2** shows encapsulation of an iodide inside the cavity (Figure 3a) and a water molecule in each cleft. Among the cleft bound water molecules, two of the water molecules are disordered in two positions which are not shown in Figure 3. The distance between the apical benzene caps increased upon hexaprotonation from 7.582 to 9.357 Å. It is almost comparable with the hexaprotonated chloride complex **1**. Interestingly, in the case of complex **2**, $[H_6\mathbf{L}]^{6+}$ receptor encapsulates an iodide inside the cavity, which shows a different binding site preference as observed in the case of chloride complex **1** (Figure 3a). The encapsulated iodide is hydrogen bonded to one disordered water molecule located at the one of the clefts of the $[H_6\mathbf{L}]^{6+}$ receptor unit. The encapsulated iodide is inclined toward one of the apical benzene rings showing two N−H···I^- interactions and the rest of the cavity remains empty. This may be due to the large size of the iodide ion. Further $[H_6\mathbf{L}]^{6+}$ is hydrogen bonded to four lattice iodides via N−H···I^- interactions. The H···I^- distances for all the above N−H···I^- interactions range from 2.56 to 2.78 Å.

In complexes **1** and **2**, all six secondary nitrogen centers are protonated, and therefore there is maximum repulsion among the ammonium centers of the receptor, which largely modifies the size and shape of the receptor cage compared to the native cyclophane, which is evident from the $C_{Ar(cap)}$−C−N−C torsion angles of **L**, **1**, and **2** (Table S3, Supporting Information). Because of maximum protonation of **L**, the cavity of $[H_6\mathbf{L}]^{6+}$ is indeed electrophilic in nature and one would expect competition between water molecules and haildes for encapsulation. In the case of iodide complex **2**, the preference of iodide recognition over water molecules might be explained due to high electrostatic attraction.

Solution State Studies. Crystal structure analysis shows that in complexes **1** and **2**, all six secondary nitrogen centers of **L** are protonated. To understand the solution binding of halides

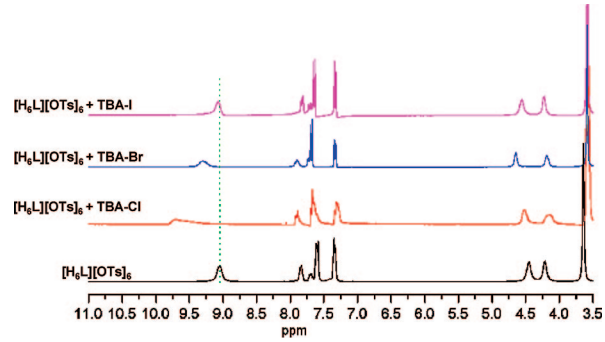


FIGURE 4. ^{1}H NMR (300 MHz) of complex **3** in DMSO-d_6 with n-$Bu_4N^+X^-$ at 25 °C.

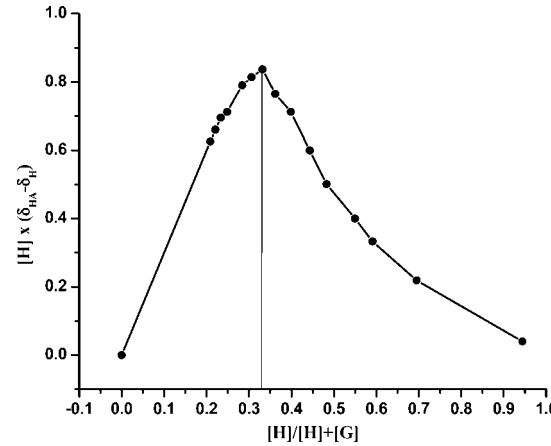


FIGURE 5. Plot of change in chemical shift of the $-NH_2^+$ protons of **3** with incerasing amounts of [n-$Bu_4N^+Cl^-$] in DMSO-d_6 at 298 K.

we have undertaken ^{1}H NMR solution studies in DMSO-d_6 with the hexatosylated cryptand $[H_6\mathbf{L}][OTs]_6$, **3**, and tetrabutylammonium salts of halides. We have protonated **L** with p-toluene sulfonic acid to obtain $[H_6\mathbf{L}][OTs]_6$, **3**, which is characterized by ^{1}H and ^{13}C NMR and MS-ESI. Figure 4 shows ^{1}H NMR spectra of **3** and **3** in the presence of tetrabutylammonium salts of Cl^-, Br^-, and I^-. Precipitation of the fluoride complex occurs from the DMSO-d_6 solution upon addition of tetrabutylammonium fluoride ions to the complex **3**. The $-NH_2^+$ resonances are selected for NMR monitoring for the halide binding. ^{1}H NMR studies revealed that addition of tetrabutylammonium chloride to $[H_6\mathbf{L}][OTs]_6$ in DMSO-d_6 showed a significant downfield shift of the $-NH_2^+$ resonances $\Delta\delta = 0.587$ ppm, which indicates the participation of the receptor in anion binding via hydrogen bonding interactions of $-NH_2^+$ protons of **3**. There is a slight shift (0.258 ppm) in $-NH_2^+$ resonances upon addition of Br^- but no change in $-NH_2^+$ resonances is observed upon addition of I^- as their tetrabutylammonium salts to the $[H_6\mathbf{L}][OTs]_6$ in DMSO-d_6 at 25 °C. But the solid state X-ray crystal structure showed encapsulation of iodide inside the $[H_6\mathbf{L}]^{6+}$ when **L** is treated with HI. The reason for not observing any shift of $-NH_2^+$ resonance of **3** in the solution state ^{1}H NMR study upon addition of iodide could be due to the lowest charge-to-radius ratio compared to other halides. Since $-NH_2^+$ resonance shift is negligible in the case of bromide we carried out ^{1}H NMR titration with the tetrabutylammonium chloride to investigate the mode of binding of **3** with chloride ions in the solution state. The titration curve (Figure 5) gives the best fit for the 1:2 binding model for host to guest, in agreement with Job's plots indicating a maximum $\Delta\delta$ at 0.33 = [**3**]/([**3**] +

[Cl^-]). Our attempt to calculate the binding constants of halides with protonated **L** by potentiometric titration experiments was unsuccessful as the receptor started precipitation at pH 4.5 though the **L** is soluble in water at lower pH (2.0 to 4.0).

Experimental Section

Compound L. Isophthalaldehyde (0.550 g, 4.1 mmol) in 300 mL of methanol was added to the 300 mL of 2:1 $CHCl_3$:MeOH solvent containing 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene[8c] (0.565 mg, 2.73 mmol) dropwise at the rate of 2−3 drops/min with vigorous stirring at room temperature. After complete addition of the dialdehyde, the reaction mixture was allowed to stir overnight. Then an excess of solid sodium borohydride was added portionwise to the above solution. An evolution of hydrogen and dissolution of the suspension was noted during the addition of $NaBH_4$. The solution was stirred at room temperature for 4 h. Then the solvent was evaporated under reduced pressure and the white crystalline solid was obtained after the usual $CHCl_3$ workup. Crystalline solid was dissolved in acetone and recrystallized at room temperature. A colorless crystal suitable for single-crystal X-ray analysis was obtained within a day. Yield of **L**: 62%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (br, 6H), 2.34 (s, 18H), 3.78 (s, 12H), 3.88 (s, 12H), 7.00−7.31 (m, 12H); ^{13}C NMR (75 MHz) δ 15.7, 49.5, 54.6, 123.6, 125.9, 127.7, 135.0, 135.9, 140.9. HRMS (ESI) calcd for [H**L**]$^+$ 721.4958, found *m*/*z* 721.6814. Anal. Calcd for $C_{54}H_{72}N_6O_2$: C, 77.47; H, 8.67; N, 10.04; O, 3.82. Found: C, 77.42; H, 8.79; N, 10.17.

Complex 1. Complex **1** was obtained by dissolving **L** (72 mg, 100 μmol) in acetone (10 mL) and adding 0.5 mL of 37% HCl. A few drops of water was added to make the solution clear, then the solution was filtered in hot condition and single crystals suitable for X-ray crystallography were obtained upon slow evaporation at room temperature as colorless crystals. Yield of **1**: 70−75%. ^{1}H NMR (D_2O, 300 MHz) δ 2.33 (s, 18H), 4.26 (s, 12H), 4.47 (s, 12H), 7.36−7.50 (m, 12H); ^{13}C NMR (75 MHz) δ 17.2, 46.1, 51.0, 128.2, 130.3, 131.0, 131.4, 132.2, 141.2. HRMS (ESI) calcd for [H**L**]$^+$ 721.4958, found *m*/*z* 721.6669 [H**L**]$^+$. Anal. Calcd. for $C_{48}H_{80}Cl_6N_6O_9$: C, 52.51; H, 7.34; N, 7.65. Found: C, 52.10; H, 7.82; N, 7.29.

Complex 2. Complex **2** was obtained by dissolving **L** (72 mg, 100 μmol) in methanol (10 mL) and adding 0.25 mL of 57% HI. A few drops of water was added to the turbid solution, which become clear upon addition of water and then was filtered in hot condition. Single crystals suitable for X-ray crystallography were obtained upon slow evaporation at room temperature as brown crystals (few) along with brown solid precipitate. Crystals were separated out for NMR measurements. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.42 (s, 18H), 4.07 (s, 12H), 4.44 (s, 12H), 7.56−7.76 (m, 12H), 8.81 (b, 12H); ^{13}C NMR (75 MHz) δ 18.6, 46.1, 49.1, 128.2, 129.7, 130.8, 132.6, 142.0. HRMS (ESI) calcd for [H**L**]$^+$ 721.4958, found *m*/*z* 721.5659 [H**L**]$^+$; calcd for [H_2**L**$^{2+}$ + I^-] 849.4081, found *m*/*z* 849.4752; calcd for [H_3**L**$^{3+}$ + I^-] 850.4159, found *m*/*z* 850.4927; calcd for [H_3**L**$^{3+}$ + 2I^-] 977.3204, found *m*/*z* 977.3867; calcd for [H_3**L**$^{3+}$ + 3I^- + Na] 1127.2146, found 1127.1985. Anal. Calcd for $C_{48}H_{80}Cl_6N_6O_9$: C, 52.51; H, 7.34; N, 7.65. Found: C, 52.10; H, 7.82; N, 7.29.

Complex 3. Complex **3** was obtained by dissolving **L** (720 mg, 1 mmol) in methanol (100 mL) and adding 1.52 g (8 mmol) of *p*-toluene sulfonic acid. The solution was stirred for 4 h then 100 mL of diethyl ether was added to the solution. White solid precipitated out from the solution, which was filtered and washed with diethyl ether to obtain analytically pure complex **3**. Yield of **3**: 67−70%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.15 (s, 18H), 2.29 (s, 18H), 4.01 (s, 12H), 4.25 (s, 12H), 7.13 (d, 12H), 7.39 (d, 12H), 7.48−7.64 (m, 12H), 8.85 (b, 12H); ^{13}C NMR (75 MHz) δ 17.2, 20.7, 44.5, 49.4, 125.4, 125.5, 125.7, 128.0, 128.3, 131.1, 131.5, 138.5, 140.9, 144.0. HRMS (ESI) calcd for [H_3**L**][OTs]$_3$ 1236.5462, found *m*/*z* 1236.5591; calcd for [H_2**L**][OTs]$_2$ 1064.5268, found *m*/*z* 1064.8330; calcd for [H**L**$^+$]][OTs] 892.5074, found *m*/*z* 892.9888.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR spectra, ^{1}H NMR titration curve, TGA analysis data, and crystallographic information files for **L**, **1**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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