The Designed Self-Assembly of Multicomponent and Multicompartmental Cylindrical Nanoarchitectures

Paul N. W. Baxter,[a] Jean-Marie Lehn,*[a] Boris O. Kneisel,[b] Gerhard Baum,[b] and Dieter Fenske[b]

Abstract: The polytopic linear **4** and circular **5** ligands undergo self-assembly with copper(I) and silver(I) ions to generate the large inorganic entities **2** and **3** containing, two and three internal cavities, respectively. The process amounts to the spontaneous assembly of a total of 15 and 19 particles to yield multicompartmental architectures. The crystal structures of two such complexes have been determined. They confirm the nature of the entities formed and show that in addition several substrate species (anions and solvent molecules) are contained in the cavities. The generation of architectures **2** and **3** presents several important features: it represents a multicomponent mixed-ligand self-assembly process involving self-compartmentalisation with simultaneous inclusion (and selection) of multiple substrate species. Such features are of interest for both the analogies with biological processes and the potential applications in nanoscience. They also amount to a further step in the design of systems of increasing structural and functional complexity.

Keywords: inorganic architectures · metal complexes · nanostructures · self-assembly · supramolecular chemistry

Introduction

The design and construction of molecular architectures lying within the nanostructural domain gives access to more and more complex entities presenting a range of novel structural and functional properties. The controlled use of intermolecular forces provides an efficient method for creating large, organised supramolecular systems through self-assembly, unimpeded by the problems associated with stepwise covalent synthetic methodology.[1–4] We present herein the spontaneous generation of multicompartmental nanoarchitectures exhibiting multiple guest encapsulation, by self-organisation from multiple components by metal ion coordination. Such a high level of structural complexity is attained through the correct association of up to twenty-five particles. The formation of these supermolecular entities represents an abiological analogue of numerous biological processes mediated by collective interactions and recognition events between large molecules. In particular, it amounts to a *self-compartmentalisation* process presenting analogies with that displayed by multicompartmental proteases.[5] Also, potential applications exist, for example, in materials science and nanotechnology, where the establishment of pathways for the controlled access to nanosized chemical entities is of paramount interest.

Mixtures of correctly instructed components represent programmed chemical systems undergoing self-assembly to give a single equilibrium supramolecular entity or eventually a collection of such species.[1] A range of structural types have been generated in this way; they include aggregates maintained through hydrogen bonding[1–6] or donor–acceptor interactions[4] as well as metal-ion-assembled structures such as cages,[7–10] helicates[1, 11, 12] and grids.[13, 14] The inorganic systems which incorporate metal ions as assembling and organising centres are particularly interesting in that they may potentially confer a variety of novel optical, redox, magnetic or catalytic properties.

Earlier work demonstrated that it was possible to utilise metal-ion-mediated self-assembly to produce the hexanuclear cage complex **1**[7a] from a mixture of five ligand components of two different types (three ligands **4** with $n = 0$ and 2 ligands **5a**) and six copper(I) ions, that is by the correct recognition and positioning of eleven particles in one stroke. An increase in size of the internal cavity was achieved by elongation of the linear pillar ligand **4**, leading to cylindrical complexes of up to 31 Å that is nanometric in height.[7b] These results raised the question as to whether this process could give access to *multicellular* inorganic architectures that would present

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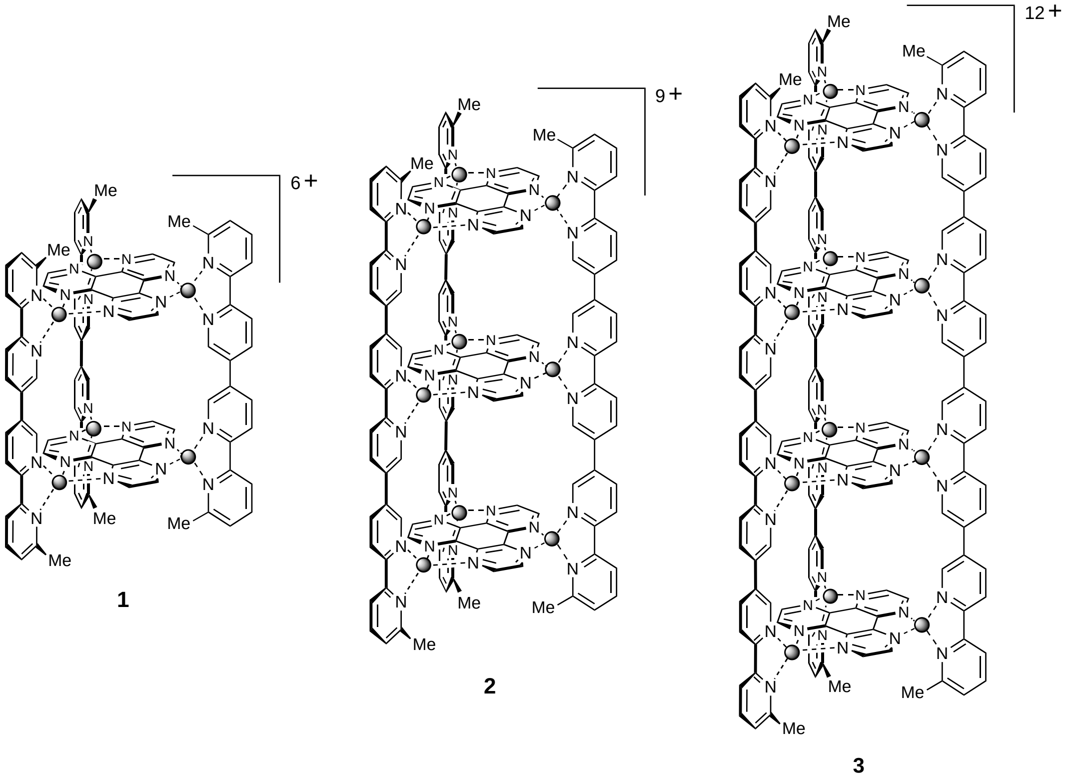


1 **2** **3**

Figure 1. Schematic representations of the structures of the cylindrical inorganic architectures **1**, **2** and **3** containing one, two and three internal cavities, respectively; their heights are 18, 26 and 35 Å, respectively, including the Van der Waals surfaces (phenyl rings of **5** omitted for clarity); ● = Cu^+ or Ag^+.

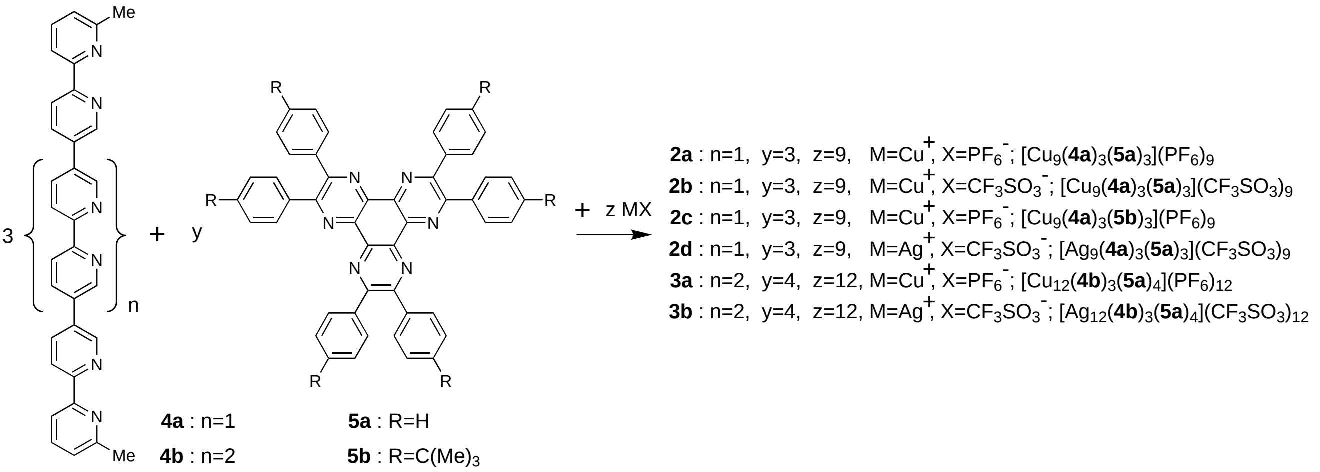
several internal cavities and might in addition incorporate selected substrates in the course of the assembly. We herein report that this is indeed the case. Thus, the bicompartmental **2** and tricompartmental **3** complex cations (Figure 1) containing anions in their cavities (see Figures 4 and 5) are generated in a single operation by self-assembly from the corresponding stoichiometric mixtures of ligand components of two different types and metal ions (see Scheme 1).

Abstract in French: *Les ligands polytopiques linéraires **4** et circulaires **5** génèrent par auto-assemblage avec des ions cuivre(I) et argent(I) les entités inorganiques de grande taille **2** et **3** contenant respectivement deux et trois cavités internes. Ce processus représente l'assemblage spontané d'un total de 15 et de 19 composants pour former des architectures à compartiments multiples. Les structures cristallines de deux complexes ont été déterminées. Elles confirment la nature des espèces formées et montrent qu'en plus des substrats (anions et molécules de solvant) sont contenus dans les cavités. la génération des architectures **2** et **3** présente plusieurs importantes caractéristiques: il s'agit d'un processus d'auto-assemblage multicomposant à partir de différents ligands avec auto-compartimentalisation et inclusion simultanée de substrats multiples. Ces propriétés sont intéressantes à la fois par leur rapport avec des processus biologiques et pour les applications potentielles en nanoscience. Par ailleurs, elles constituent aussi une étape dans le développement progressif de systèmes sièges de phénomènes de complexification spontanée.*

Results and Discussion

Self-assembly of the multicompartmental architectures 2 and 3: Mixing the linear tritopic trisbipyridine, (or sexipyridine, spy) **4a**,[15] and hexaphenylhexaazatriphenylene (hat) **5a**[16] ligands with $[Cu(CH_3CN)_4]X$ ($X = PF_6^-$, $CF_3SO_3^-$) in (2:1) nitromethane/acetonitrile solution in a 1:1:3 stoichiometric ratio resulted in slow dissolution of the sparingly soluble **4a** and a concomitant colour change from brown to deep purple (Scheme 1). After stirring at ambient temperature for five days and subsequent workup, the dark-purple organic solvent soluble complexes **2a** and **2b** were isolated in 88% and 93% yields, respectively. Complex **2c** (78%) was generated in a similar way upon reaction between **4a**, **5b** and $[Cu(CH_3CN)_4]PF_6$. Combination of **4a**, **5a** and $AgCF_3SO_3$ in nitromethane in a 1:1:3 ratio yielded a yellow microcrystalline complex **2d** (85%) as the single product after workup. Complexes **3a** and **3b** were prepared from the tetratopic tetrakis(bipyridine) (or octapyridine, octapy) **4b**, **5a** and the copper(I) or silver(I) salt by procedures similar to those used for **2a**–**d** above and were isolated in 61% and 95% yields, respectively. In the case of **3a**, the reaction had to be conducted in pure acetonitrile at 60 °C in order to drive the self-assembly to completion.

Evidence that the products from the above reactions possessed multicellular cage-type structures (Figure 1) in solution came from inspection of their ^1H NMR spectra (Figures 2 and 3; connectivities were determined by ^1H-^1H COSY and NOESY experiments; see Experimental Section



Scheme 1. Self-assembly of the multicompartmental cylindrical inorganic architectures **2** and **3** from linear oligobipyridine **4** and hexaazatriphenylene (hat) **5** ligands through Cu^+ and Ag^+ metal ion coordination.

for signal assignment). In all cases, the spectra were particularly simple and indicative of the presence of a highly symmetrical species in nitromethane. The signals observed agreed with the assigned structures. In **2a, 2b** and **2d** the peaks due to the *ortho-* and *meta*-protons of the phenyl rings of **5a** were divided into two groups in a ratio of 2:1 corresponding to the two outer and single inner ligands **5a** in **2** (Figure 2). In **3a** and **3b**, the above-mentioned protons were divided into two groups in a 1:1 ratio corresponding to the two outer and two inner ligands **5a** (Figure 3). The H6′ and H6″ protons of ligand **4a** in **2a, 2b** and **2d** were found to be shielded relative to the remaining protons (H3′, H4′, H4″, H3″) of the four central pyridine rings of **4a**. This shielding effect is exactly what would be expected for protons pointing towards the interior of the cage cavity. In all complexes studied, the protons on the outer pyridine rings of ligands **4a** and **4b** (H3, H4 and H5) were clearly distinguishable from the remaining protons as a doublet, a triplet and a doublet in a 1:1:1 ratio.

One also observes that the signals of the *ortho*-protons of the phenyl rings on the inner and outer hat ligands are broadened for both **2a** and **3a** (Figures 2 and 3). This indicates that a slow kinetic process is taking place, possibly linked to the presence of anions inside the cavities. More detailed studies are required in order to provide insight into the nature of this phenomenon.

The electrospray (ES) mass spectra of complexes **2a** and **2b** were especially informative. Six bands were clearly observable in each spectrum, corresponding to the species $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_7\}^{2+}$, $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_6\}^{3+}$, $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_5\}^{4+}$, $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_4\}^{5+}$, $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_3\}^{6+}$ and $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](X)_2\}^{7+}$, ($X = PF_6^-$, $CF_3SO_3^-$), formed by successive anion loss. All spectra were recorded at a concentration of 10^{-4} mol dm^{-3} in nitromethane and no other peaks were seen, showing that **2** was the only species present in solution and was stable to dissociation down to at least 10^{-4} mol dm^{-3}.

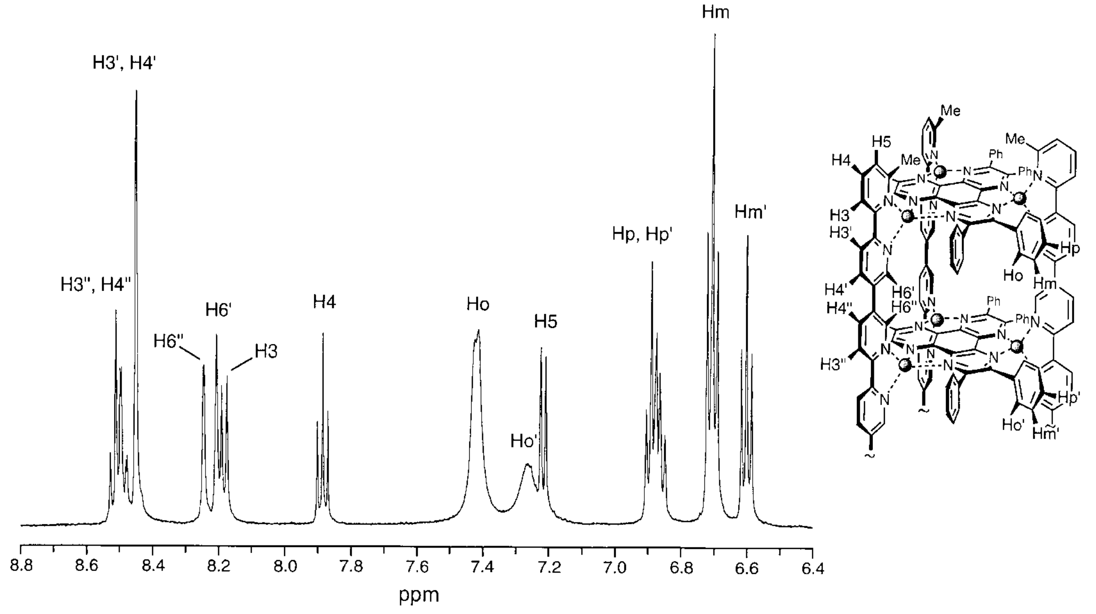


Figure 2. ^1H NMR spectrum of the bicompartmental complex **2a** at 500 MHz in CD_3NO_2 (25 °C).

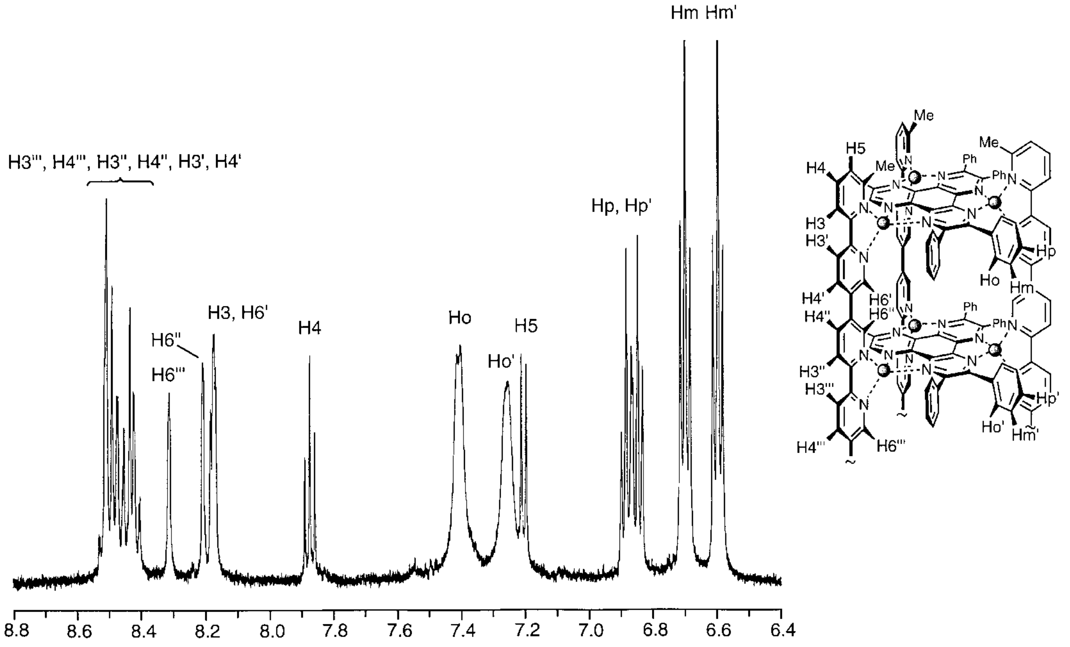


Figure 3. ^{1}H NMR spectrum of the tricompartmental complex **3a** at 500 MHz in CD_3NO_2 (25 °C).

Crystal structures of the multicompartmental architectures 2 and 3: Confirmation that the structures of **2a–d**, **3a** and **3b** were indeed of multicellular type was obtained by determination of the x-ray crystal structures of **2a** and **3a** (see Figures 4 and 5). The cation **2a** is constructed from nine Cu$^+$ ions, three **4a** and three **5a** ligands, and **3a** from twelve Cu$^+$ ions, three **4b** and four **5a** ligands. Both complexes are shaped into beautiful expanded triple helical cylindrical cages. The overall dimensions of **2a** of 26.4(height) × 20.2(diameter) Å, and **3a** of 35.3 (height) × 20.3(diameter) Å places them within the nanostructural domain.

In **2a** three platelike hat **5a** ligands are incorporated in the cation as shown in structure **2**, two forming the top and bottom of the cylindrical cage and the third centrally positioned between the outer pair, dividing the cage into two compartments (Figure 4). The two outer and single inner hat ligands are close to planarity (maximum deviation from mean plane, 0.142(30) Å), and are approximately parallel to one another. However, each outer hat is slightly tilted to different degrees relative to the central hat (angle between normals to their mean planes, 2.39(13)° (outer′-inner) and 11.84(13)°(outer″-inner **5a** ligands). The average distances between the mean planes through the hat ligands are 7.7 Å (outer′/outer″-inner) and 15.3 Å (outer′-outer″) respectively. As a result of the helical twist of the cation, the hat ligands **5a** are not eclipsed as shown in **2** but sequentially rotated with respect to each other by 30.0° (outer′-inner) and 40.5° (inner-outer″), (70.6° outer′-outer″). The helical screw sense of the complex arises mainly from a combination of the distorted tetrahedral coordination polyhedron about the Cu$^+$ ions (N(**4a**)-Cu-N(**5**) 109.45(33) – 141.69(34)°; N(**4a**)-Cu-N(**4a**) and N(**5a**)-Cu-N(**5a**) 81.23(41) – 85.24(33)°) and the dihedral twist angles between the bipyridine chelating subunits in the spy (**4a**) ligands, and to a lesser extent upon the dihedral twisting within the bipyridine units themselves. The overall geometry of each spy ligand is therefore that of a propeller blade in which the bipyridine units are twisted by 19.5 – 32.9° with respect to each other, as well as the pyridine rings within each bipyridine unit where twist angles fall within the range 3.8 – 17.7°. The two halves of each spy ligand are also inclined by 21° and 28° with respect to the axis passing vertically through the centre of the hat units. The hat phenyl rings are tilted by 42.03 – 61.20° relative to the mean plane through the hat ligands, and are mostly within Van der Waals contact (shortest distance = 3.2 Å) with the spy ligands. The Cu–N bond lengths fall within the range 1.97 – 2.15 Å and are unexceptional. The complex **2a** possesses two internal cavities of radius 5.4 Å (based on the N atoms of the three spy ligands), which are each of slightly different size and provide a space of 6.5 × 4.5 Å and 6.5 × 4.0 Å taking Van der Waals radii into account. One PF_6^- ion with full occupancy and one PF_6^- ion and a nitromethane molecule with 50% occupancy are present inside the smaller compartment. The larger compart-

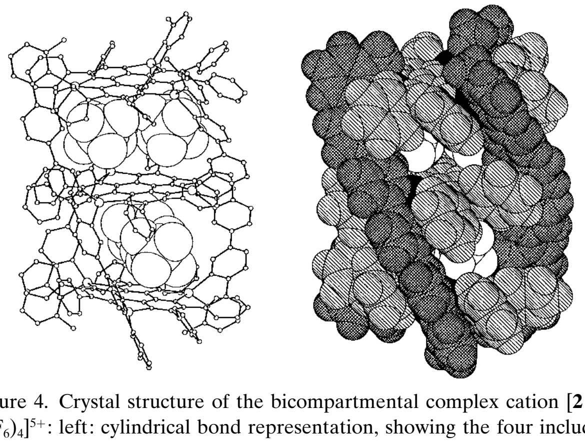


Figure 4. Crystal structure of the bicompartmental complex cation $[\mathbf{2a} \subset (PF_6)_4]^{5+}$: left: cylindrical bond representation, showing the four included PF_6^- ion guests (space-filling representation); right: space-filling representation with the included PF_6^- ions.

ment contains two PF_6^- ions and a water molecule with full occupancy such that almost all available internal space is filled. The remaining five PF_6^- ions and solvent molecules of crystallisation lie within the interstices between the cations, which are themselves arranged in layers with the anions in between. The cations are in Van der Waals contact with each other, (the shortest H–H distance of 2.29 Å occurs within each layer).

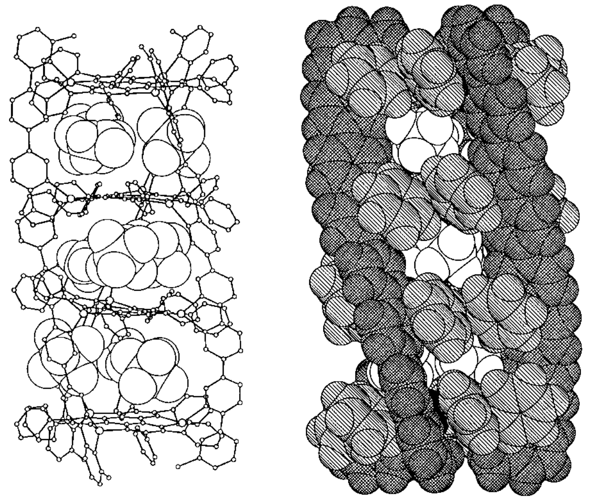


Figure 5. Crystal structure of the tricompartmental complex cation $[\mathbf{3a} \subset (\mathrm{PF}_6)_6]^{6+}$: left: cylindrical bond representation, showing the six included PF_6^- ion guests (space-filling representation); right: space-filling representation with the included PF_6^- ions.

Cation **3a** is also triple-helical and comprises four hat (**5a**) ligands, two outer ones defining the ends of the cylinder, and two inner ones dividing the cylindrical cage into three compartments (Figure 5). The hat ligands **5a** are close to planarity and sequentially rotated with respect to each other by 22° (each outer-inner) and 33° (inner-inner) and 77° (outer-outer). The bipyridine subunits of **4b** are twisted relative to each other by 19.4–31.7° and the N-Cu-N angles and Cu–N lengths fall within the range 106.6–137.5° (N**4b**-Cu-N**5a**), 78.7–89.0° (N**4b**-Cu-N**4b**), 79.1–90.7° (N**5a**-Cu-N**5a**), and Cu–N distances 1.91–2.19 Å. Extensive contacts (within 3.4 Å) exist between the phenyl rings of **5a** and the octapy **4b** ligands which presumably also help to stabilise the resulting superstructure. The average distances between the mean planes through the hat **5a** ligands are 7.97 Å (both outer-inner), 7.87 Å (inner-inner), and 23.81 Å (outer-outer), and define three cavities of dimensions 4.5 × 8.0 Å (outer two cavities), and 5.0 × 7.5 Å (inner cavity). As in **2a**, the cavities are occupied by guests, that is two PF_6^- ions and one $\mathrm{MeNO_2}$ molecule in the outer two, and two PF_6^- ions and a MeOH molecule in the inner compartment. The unprecedented structures of the complexes **2a** and **3a** might be described as molecular skyscrapers with occupants residing on each level!

The slight difference in cavity size apparent in the crystal structure of **2a** and **3a** is not observed in the ^{1}H NMR spectra of the complexes **2a**–**d**, **3a** and **3b** which each show the presence of a single highly symmetric species with both halves of the molecule in a chemically and magnetically equivalent environment. The complexes must therefore be undergoing intramolecular motions in solution which are rapid on the NMR timescale and confer an average cylindrical symmetry to the species.

Anion inclusion and anion exchange: As revealed by the crystal structures, anions are contained in the cavities of the complexes **2a** and **3a**. Their presence is also reflected in the spectral properties of these species. Interestingly, the ^{1}H NMR signals of **2a** and **2b** in $\mathrm{CD_3NO_2}$ have very similar chemical shifts except for those of the protons H6′ and H6″ of ligands **4a** which point into the interior of the cavities. The chemical shifts of the latter differ by 0.90 ($\delta(\mathbf{2b}\mathrm{H6'}) - \delta(\mathbf{2a}\mathrm{H6'})$) and 0.10 ($\delta(\mathbf{2b}\mathrm{H6''}) - \delta(\mathbf{2a}\mathrm{H6''})$) ppm (**2a**: H6′ 8.21, H6″ 8.25 ppm and **2b**: H6′ 8.30, H6″ 8.35 ppm) and provide clear evidence for the presence of anions within the cavities of **2a** and **2b** in solution. When nine equivalents of $n\mathrm{Bu_4NCF_3SO_3}$ were added to **2a** the chemical shifts of H6′ and H6″ became identical to those of **2b** after 24 h. When nine equivalents of $n\mathrm{Bu_4NPF_6}$ were added to **2b**, the chemical shifts of H6′ and H6″ remained unchanged on standing for 24 h in $\mathrm{CD_3NO_2}$. The anions are therefore able to move into and out of the cavities at room temperature but cation **2** appears to have a distinct preference for the inclusion of $\mathrm{CF_3SO_3^-}$ in the presence of PF_6^-. Inspection of the crystal structure of **2a** shows that the six portals in the walls of the cage are slightly smaller than a PF_6^- ion. Intramolecular breathing of the complex by unwinding of the helix may result in opening up the windows thus facilitating anion exchange into and out of the cavities. Further studies on anion inclusion and exchange in and out of the cavities are underway in order to further characterise these interesting processes.

Conclusions

The formation of complexes **2a–d, 3a** and **3b** represents a demonstration of multicomponent self-assembly, which, in the case of **3a** involves seven ligand components of two different types and 12 metal ions, that is 19 particles plus six anions, one methanol and two nitromethane molecules, and generates a closed three-dimensional coordination architecture maintained by 48 Cu, N coordination bonds.

The superstructures of **2** and **3** display a unique combination of unusual properties: i) they possess novel architectures of nanoscopic dimension, laterally expanded to provide an internal cavity; ii) they have the features *of multicompartmental or multicellular* containers; iii) their formation represents a *self compartmentalisation* process presenting biological analogies,[5] and iv) operates by way of *multicomponent mixed-ligand self-assembly*, in which preferential association occurs between different ligands; this represents a step forward in informational complexity compared to that of self-assembling systems consisting of metal ions and a single ligand species; v) they behave as cryptands exhibiting *multiple guest inclusion* with four (**2a**) and six (**3a**) PF_6^- ions and solvent molecules encapsulated within a single receptor entity. Hydrogen-bonding aggregates that formally are of the multicompartmental type have been described but not structurally characterised.[17]

Multiple guest inclusion and compartmentalisation are characteristic features of the organisation of living organisms, ensuring that the correct chemical events take place within spatially confined, well-defined domains that may either be intracellular or belong to different cells in multicellular organisms.

The present results demonstrate that it is possible to access supramolecular architectures of nanometric size presenting a high level of structural complexity by metal ion-mediated self-assembly. The formation of **2a–d**, **3a** and **3b** results from the operation of a programmed, informational process that involves three main stages: a) initiation, b) propagation, and finally c) termination of the assembly leading to a discrete supramolecular entity. Entropic and solvation factors are also expected to play an important role in the generation of such species. Of particular interest is also the simultaneous occurence of two processes: the self-assembly of a multitopic receptor and the selection of substrate entities possessing features compatible with inclusion in the internal cavities.

Extension of the above work is pursued towards the preparation of larger multicompartmental architectures which may present cells of different size, shape and content, as well as towards the exploration of communication between different cellular compartments.

From another point of view, the ability to generate large complex architectures spontaneously through programmed self-organization represents a powerful alternative to nanofabrication and nanomanipulation, that may be expected to have a profound impact in nanoscience and nanotechnology.[1]

In a broader perspective, the present results represent a further step in the progressive design of programmed systems undergoing spontaneous but controlled complexification.

Experimental Section

General techniques: The metal-ion-containing salts $[Cu(CH_3CN)_4]PF_6$ and $AgCF_3SO_3$ were purchased from Aldrich. The former was recrystallised from MeCN and the latter from benzene prior to use. The solvents nitrobenzene and nitromethane (Fluka, puriss) were redistilled under vacuum before use. Adsorption column chromatography was performed by using aluminium oxide (neutral, activity II/III, MERCK) and gel permeation chromatography by using S-X1 Bio-beads (200–400 mesh, BIO-RAD) pre-swelled in nitrobenzene. Ligands **4a** and **4b** were prepared by using standard organometallic coupling protocols.[18] 1,2-Bis(4-*tert*-butylphenyl)ethane-1,2-dione was prepared from 4-*tert*-butylbenzaldehyde (Aldrich) by using the published procedure for benzil.[19] Ultraviolet/visible spectra were recorded on a Varian, CARY 3 spectrophotometer in CH_2Cl_2 redistilled from CaH_2 under argon. 500 MHz ^1H and 125 MHz ^{13}C NMR spectra were recorded on a Bruker ARX 500 spectrometer and 300 MHz ^1H and 75 MHz ^{13}C NMR spectra on a Bruker AM 300 spectrometer, and were referenced to residual CH_3NO_2 in the CD_3NO_2 solvent. ES-MS studies were performed on a VG BioQ triple quadrupole mass spectrometer upgraded in order to obtain the Quattro II performances (Micromass, Altrincham, UK). Samples were dissolved in $MeNO_2$ at 10^{-4}–10^{-5} M and were continuously infused into the ion source at a flow rate of 6 mL min^{-1}, by a Harvard Model 55 1111 syringe pump (Harvard Apparatus, South Natick, MA, USA). The extraction cone voltage (Vc) was at 20 V to avoid fragmentations. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur.

General procedure for 2a–d: Nitromethane (3 mL) was added by syringe to a 1:1 stoichiometric mixture of **4a** (finely powdered) and **5a** or **5b** under an atmosphere of argon. A solution of three equivalents of $[Cu(CH_3CN)_4]X$ in acetonitrile (2 mL) was then added by syringe, the mixture ultrasonicated for 0.25 h then stirred at 20 °C for five days. All solvent was removed under vacuum and the remaining solid purified by either size exclusion chromatography or recrystallisation by liquid-liquid diffusion. In the case of chromatography, the solid was dissolved in nitrobenzene (2 mL) and eluted down a column of SX-1 Biobeads with nitrobenzene as eluant. The product was collected in one fraction, reduced in volume to 3ml then precipitated by the addition of excess toluene. The solid was isolated by filtration under vacuum, washed with excess toluene and pumped dry. Further purification was achieved by adding toluene to a nitromethane solution of the complex over a 2 h period until 90 % of the product had come out of solution. The process was repeated and the solid finally dried under vacuum at 70 °C/2×10^{-6} mmHg. Purification by recrystallisation was achieved by slow diffusion of benzene into a nitromethane solution of the crude reaction product. The crystals which grew over a three week period were isolated by vacuum filtration, washed with benzene and dried under vacuum as described above.

2a: From **4a** (0.030 g, 6.09×10^{-5} mol), **5a** (0.042 g, 6.08×10^{-5} mol) and $[Cu(CH_3CN)_4](PF_6)$ (0.068 g, 1.83×10^{-4} mol) was isolated **2a** (0.097 g, 88 %) as permanganate-coloured microcrystals after purification by size exclusion chromatography. ^1H NMR (CD_3NO_3, 500 MHz, 25 °C): $\delta = 8.52$ (d, $J_{3'',4''}=8.3$ Hz, 6H; **4a**H-3″), 8.49 (dd, $J_{4'',3''}=8.8$ Hz, $J_{4'',6''}=2.0$ Hz, 6H, **4a**H-4″), 8.45 (s, 12H; **4a**H-3′, 4′), 8.25 (s, 6H; **4a**H-6″), 8.21 (s, 6H; **4a**H-6′), 8.18 (d, $J_{3,4}=8.2$ Hz, 6H; **4a**H-3), 7.88 (t, $J_{4,3;4,5}=8.0$ Hz, 6H; **4a**H-4), 7.42 (d, $J_{o,m}=6.7$ Hz, 24H; H-*ortho* (outer **5a**)), 7.27 (s, 12H; H-*ortho* (inner **5a**)), 7.22 (d, $J_{5,4}=7.8$ Hz, 6H; **4a**H-5), 6.89 (t, $J_{p,m}=$ 7.5 Hz, 12H; H-*para* (outer **5a**)), 6.87 (t, $J_{p',m'}=7.5$ Hz, 6H; H-*para* (inner **5a**)), 6.71 (t, $J_{m,o;m,p}=7.9$ Hz, 24H; H-*meta* (outer **5a**)), 6.61 (t, $J_{m',o';m',p'}=8.0$ Hz, 12H; H-*meta* (inner **5a**)), 2.14 (s, 18H; **4a**-CH_3); ^{13}C NMR (CD_3NO_3, 75 MHz, 25 °C): $\delta = 159.11$, 157.82, 157.20, 153.52, 151.87, 151.49, 146.61, 146.47, 140.56, 140.40, 140.28, 138.48, 138.32, 137.71, 137.27, 134.77, 133.78, 131.52, 131.45, 130.56, 130.49, 129.08, 128.96, 127.83, 124.77, 124.46, 121.42, 25.93 (CH_3). ES MS (CH_3NO_2): *m*/*z* (relative intensity; %): 2569.2 (0.5) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_7\}^{2+}$, 1664.4 (11.9) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_6\}^{3+}$, 1211.5 (33.2) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_5\}^{4+}$, 940.0 (47.0) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_4\}^{5+}$, 759.3 (81.2) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_3\}^{6+}$, 630.1 (100.0) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](PF_6)_2\}^{7+}$; UV/Vis ($CH_2Cl_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]); 313 (206377), 361 (413976), 379 (335957)sh, 545 (43759), 676 (20797); elemental analysis calcd. for $C_{240}H_{162}Cu_9F_{54}N_{36}P_9$ (%); C 53.12, H 3.01, N 9.29; found C 52.87, H 3.27, N 9.41.

2b: From **4a** (0.030 g, 6.09×10^{-5} mol, **5a** (0.042 g, 6.08×10^{-5} mol) and $Cu(CF_3SO_3)_2$ (0.066 g, 1.82×10^{-4} mol) and hydrazine hydrate (0.053 mL, 1.09×10^{-3} mol) as reducing agent was isolated **2b** (0.104 g, 93 %) as permanganate-coloured microcrystals. ^1H NMR (CD_3NO_3, 500 MHz, 25 °C): $\delta = 8.53$ (d, $J_{3'',4''}=8.3$ Hz, 6H; **4a**H-3″), 8.49 (dd, $J_{4'',3''}=8.8$ Hz, $J_{4'',6''}=2.1$ Hz, 6H; **4a**H-4″), 8.45 (d, 12H; **4a**H-3′, 4′), 8.35 (d, $J_{6'',4''}=1.5$ Hz, 6H; **4a**H-6″), 8.30 (s, 6H; **4a**H-6′), 8.18 (d, $J_{3,4}=8.1$ Hz, 6H; **4a**H-3), 7.88 (t, $J_{4,3;4,5}=8.0$ Hz, 6H; **4a**H-4), 7.40 (d, $J_{o,m}=$ 6.9 Hz, 24H; H-*ortho* (outer **5a**)), 7.25 (s, 12H; H-*ortho* (inner **5a**)), 7.22 (d, $J_{5,4}=7.8$ Hz, 6H; **4a**H-5), 6.89 (t, $J_{p,m}=7.6$ Hz, 12H; H-*para* (outer **5a**)), 6.88 (t, $J_{p',m'}=8.9$ Hz, 6H; H-*para* (inner **5a**)), 6.71 (t, $J_{m,o;m,p}=7.9$ Hz, 24H; H-*meta* (outer **5a**)), 6.61 (t, $J_{m',o';m',p'}=7.9$ Hz, 12H; H-*meta* (inner **5a**)), 2.15 (s, 18H; **4a**-CH_3); ^{13}C NMR (CD_3NO_3, 75 MHz, 25 °C): $\delta = 162.94$, 161.28, 160.41, 157.29, 155.69, 155.32, 150.62, 150.50, 145.02, 144.81, 144.09, 142.34, 142.15, 141.52, 141.12, 138.66, 137.69, 135.31, 135.24, 134.37, 134.27, 132.93, 132.84, 131.63, 128.59, 128.25, 125.23, 29.83 (CH_3), 123.98 (CF_3SO_3); ES MS (CH_3NO_2): *m*/*z* (relative intensity; %): 1672.2 (1.6) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](CF_3SO_3)_6\}^{3+}$, 1216.9 (35.3) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](CF_3SO_3)_5\}^{4+}$, 943.7 (65) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](CF_3SO_3)_4\}^{5+}$, 761.6 (100.0) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](CF_3SO_3)_3\}^{6+}$, 631.5 (96.5) $\{[Cu_9(\mathbf{4a})_3(\mathbf{5a})_3](CF_3SO_3)_2\}^{7+}$; UV/Vis ($CH_2Cl_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]): 311 (220567), 360 (428454), 376 (378144)sh, 544 (41203), 676 (19296); elemental analysis calcd. for $C_{249}H_{162}Cu_9F_{27}N_{36}O_{27}S_9$ (%): C 54.74, H 2.99, N 9.23; found C 54.76, H 3.22, N 9.37.

2c: From **4a** (0.025 g, 5.08×10^{-5} mol), **5b** (0.052 g, 5.06×10^{-5} mol) and $[Cu(CH_3CN)_4](PF_6)$ (0.057 g, 1.53×10^{-4} mol) was obtained **2c** (0.085 g, 78 %) as dark-brown/black microcrystals after purification by size exclusion chromatography. ^1H NMR (CD_3NO_3, 500 MHz, 25 °C): $\delta = 8.59$ (d, $J_{3'',4''}=8.5$ Hz, 6H; **4a**H-3″), 8.53 (d, $J_{3',4'}=8.8$ Hz, 6H; **4a**H-3′), 8.48 (dd,

$J_{4'',3''}=8.6$ Hz, $J_{4'',6''}=2.2$ Hz, 6H; **4a**H-4''), 8.44 (dd, $J_{4',3'}=4.5$ Hz, $J_{4',6'}=2.0$ Hz, 6H; **4a**H-4'), 8.43 (s, 6H; **4a**H6''), 8.39 (d, $J_{6',4'}=1.9$ Hz, 6H; **4a**H-6'), 8.22 (d, $J_{3,4}=8.2$ Hz, 6H; **4a**H-3), 7.95 (t, $J_{4,3;4,5}=8.0$ Hz, 6H; **4a**H-4), 7.31 (m, 30H; H-*ortho* (outer **5b**) and H-5), 7.18 (d, $J_{o',m'}=8.0$ Hz, 12H; H-*ortho* (inner **5b**)), 6.72 (d, $J_{m,o}=8.8$ Hz, 24H; H-*meta* (outer **5b**)), 6.62 (d, $J_{m',o'}=8.8$ Hz, 12H; H-*meta* (inner **5b**)), 2.16 (s, 18H; **4a**-CH$_3$), 0.98 (s, 54H; H-*t*Bu (inner **5b**)), 0.97 (s, 108H; H-*t*Bu (outer **5b**)); ^{13}C NMR (CD$_3$NO$_3$, 75 MHz, 25 °C): $\delta=159.31$, 157.75, 157.37, 155.13, 153.71, 151.92, 151.11, 146.66, 146.57, 140.63, 140.45, 140.37, 137.96, 137.76, 135.85, 135.68, 134.66, 133.59, 130.45, 127.90, 125.71, 125.45, 124.63, 124.23, 121.24, 35.42 (*C*(CH$_3$)$_3$,**5b**), 31.36 (C(*C*H$_3$)$_3$,**5b**), 25.88 (CH$_3$,**4a**); ES MS (CH$_3$NO$_2$): *m*/*z* (relative intensity; %): 3075.1 (0.2) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_7\}^{2+}$, 2002.0 (8.1) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_6\}^{3+}$, 1464.2 (37.5) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_5\}^{4+}$, 1141.9 (94.1) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_4\}^{5+}$, 927.3 (100.0) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_3\}^{6+}$, 774.2 (71.3) $\{[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5b})_3](\mathrm{PF}_6)_2\}^{7+}$; UV/Vis (CH$_2Cl_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]): 312 (192760), 360 (369432), 532 (38957), 663 (19305); elemental analysis calcd. for $C_{312}H_{306}Cu_9F_{54}N_{36}P_9$ (%): C 58.22, H 4.79, N 7.83; found: C 58.08, H 4.66, N 7.78.

2d: To a mixture of **4a** (0.034 g, 6.90×10^{-5} mol, finely powdered), **5a** (0.048 g, 6.94×10^{-5} mol) and AgCF$_3$SO$_3$ (0.053 g, 2.06×10^{-4} mol) was added nitromethane (7 mL), and the mixture ultrasonicated for 1 h, then left to stir at ambient temperature for three days. During ultrasonication most of the suspended solid reacted and passed into solution, which, finally became clear after 24 h. All solvent was removed under vacuum and the remaining solid twice recrystallised by adding excess benzene over a 2 h period to a solution of the complex in nitromethane. The product was then isolated by vacuum filtration, washed with benzene and air dried. Finally drying under vacuum at 65–70 °C/2×10^{-6} mmHg, yielded **2d** (0.115 g, 85%) as yellow, light insensitive fibrous microcrystals. ^{1}H NMR (CD$_3$NO$_3$, 500 MHz, 25 °C): $\delta=8.58$–8.50 (m, 30H; **4a**H-4', 6', 3'', 4'', 6''), 8.45 (d, $J_{3',4'}=8.7$ Hz, 6H; **4a**H-3'), 8.20 (d, $J_{3,4}=8.1$ Hz, 6H; **4a**H-3), 7.96 (t, $J_{4,3;4,5}=7.9$ Hz, 6H; **4a**H-4), 7.64 (d, $J_{o,m}=7.3$ Hz, 24H; H-*ortho* (outer **5a**)), 7.49 (d, $J_{o',m'}=7.2$ Hz, 12H; H-*ortho* (inner **5a**)), 7.30 (d, $J_{5,4}=7.8$ Hz, 6H; **4a**H-5), 6.88 (t, $J_{p,m}=7.5$ Hz, 12H; H-*para* (outer **5a**)), 6.84 (t, $J_{p',m'}=7.6$ Hz, 6H; H-*para* (inner **5a**)), 6.79 (t, $J_{m,o;m,p}=7.7$ Hz, 24H; H-*meta* (outer **5a**), 6.65 (t, $J_{m',o';m',p'}=7.9$ Hz, 12H; H-*meta* (inner **5a**)), 2.28 (s, 18H; **4a**-CH$_3$); ^{13}C NMR (CD$_3$NO$_3$, 75 MHz, 25 °C): $\delta=159.99$, 158.78, 158.20, 153.11, 151.73, 151.33, 148.68, 148.35, 140.60, 140.01, 139.85, 139.40, 137.84, 137.67, 134.04, 133.27, 131.60, 131.39, 130.35, 130.28, 129.42, 129.20, 126.75, 124.69, 124.60, 121.66, 27.26 (CH$_3$), {128.66, 124.40, 120.13, 115.88 CF$_3$SO$_3$}; UV/Vis (CH$_2$Cl$_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]): 304 (175848), 352 (351372); elemental analysis calcd. for $C_{249}H_{162}Ag_9F_{27}N_{36}O_{27}S_9$ (%): C 51.01, H 2.79, N 8.60; found C 50.80, H 3.02, N 8.72.

3a: To **4b** (0.0168 g, 2.60×10^{-5} mol, finely powdered), **5a** (0.024 g, 3.47×10^{-5} mol) and [Cu(CH$_3$CN)$_4$](PF$_6$) (0.038 g, 1.04×10^{-4} mol) under an atmosphere of argon was added acetonitrile (7 mL) by syringe, the dark-brown mixture ultrasonicated for 0.25 h, then left to stir at ambient temperature for 48 h. During this time the suspended solids slowly dissolved to give a dark-purple solution. The reaction mixture was then heated with continued stirring in a bath at 60 °C for 120 h. All solvent was removed under vacuum, the remaining solid dissolved in nitromethane (4 mL) and gravity filtered, then reduced in volume under vacuum to 2 mL. This solution was then layered with benzene and left to crystallise by liquid–liquid diffusion over a 2–3 week period. The crystallisation mixture was then vigorously shaken and the solvent containing the less-dense contaminants decanted off. Benzene was added and the process repeated five times. The crystals of product were isolated by filtration under vacuum, washed with benzene, air dried and further dried under vacuum at 90 °C/2×10^{-6} mmHg to yield **3a** (0.038 g, 61%) as permanganate-coloured blocks. ^{1}H NMR (CD$_3$NO$_3$, 500 MHz, 25 °C): $\delta=8.51$ (m, 12H; **4b**H-3''', 4'''), 8.50 (d, $J_{3'',4''}=8.4$ Hz, 6H; **4b**H-3''), 8.47 (dd, $J_{4'',3''}=8.9$ Hz, $J_{4'',6''}=2.0$ Hz, 6H; **4b**H-4''), 8.45 (d, $J_{3',4'}=9.6$ Hz, 6H; **4b**H-3'), 8.41 (dd, $J_{4',3'}=8.9$ Hz, $J_{4',6'}=1.9$ Hz, 6H; **4b**H-4'), 8.31 (s, 6H; **4b**H-6'''), 8.21 (d, $J_{6'',4''}=1.3$ Hz, 6H; **4b**H-6''), 8.18 (d, $J_{3,4}=7.7$ Hz, 6H; **4b**H-3), 8.17 (d, $J_{6',4'}=1.6$ Hz, 6H; **4b**H-6'), 7.88 (t, $J_{4,3;4,5}=7.9$ Hz, 6H; **4b**H-4), 7.41 (d, $J_{o,m}=6.4$ Hz, 24H; H-*ortho* (outer **5a**)), 7.26 (s, 24H; H-*ortho* (inner **5a**)), 7.21 (d, $J_{5,4}=7.7$ Hz, 6H; **4b**H-5), 6.88 (t, $J_{p,m}=7.7$ Hz, 12H; H-*para* (outer **5a**)), 6.85 (t, $J_{p',m'}=7.6$ Hz, 12H; H-*para* (inner **5a**)), 6.70 (t, $J_{m,o;m,p}=7.8$ Hz, 24H; H-*meta* (outer **5a**)), 6.60 (t, $J_{m',o';m',p'}=7.8$ Hz, 24H; H-*meta* (inner **5a**)), 2.13 (s, 18H; **4b**-CH$_3$); ^{13}C NMR (CD$_3$NO$_3$, 125.8 MHz, 25 °C): $\delta=159.04$, 157.78, 157.33, 153.48, 152.15, 151.71, 151.47, 146.54, 146.39, 146.33, 140.49, 140.42, 140.26, 138.37, 137.81, 137.41, 137.04, 134.90, 134.01, 133.84, 131.51, 131.40, 130.55, 130.45, 129.05, 128.92, 127.82, 124.81, 124.67, 124.48, 121.42, 25.91 (CH$_3$); ES MS (CH$_3$NO$_2$): *m*/*z* (relative intensity; %): 2254 (6) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_9\}^{3+}$, 1656.5 (30) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_8\}^{4+}$, 1296.8 (53) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_7\}^{5+}$, 1056.4 (83) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_6\}^{6+}$, 884.5 (100) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_5\}^{7+}$, 755.3 (99) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_4\}^{8+}$, 654.6 (47) $\{[\mathrm{Cu}_{12}(\mathbf{4b})_3(\mathbf{5a})_4](\mathrm{PF}_6)_3\}^{9+}$; UV/Vis (CH$_2Cl_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]: 317 (262076), 371 (521269), 387sh (438140), 543 (52429), 670 (25768); elemental analysis calcd. for $C_{318}H_{210}Cu_{12}F_{72}N_{48}P_{12}$ (%): C 53.01, H 2.94, N 9.33; found C 53.22, H 3.15, N 9.54.

3b: To a mixture of **4b** (0.010 g, 1.55×10^{-5} mol, finely powdered), **5a** (0.0142 g, 2.06×10^{-5} mol) and AgCF$_3$SO$_3$ (0.016 g, 6.23×10^{-5} mol) was added nitromethane (4 mL) and the mixture ultrasonicated for 1.5–2 h. The resulting pale yellow solution was then left to stir at ambient temperature for 48 h. All solvent was removed under vacuum and the remaining solid redissolved in warm nitromethane (4 mL) and injected through a microporous filter. The product was then reduced in volume under vacuum to 3 mL and purified by recrystallisation in the same way as that described for **2d** above. After washing with benzene and drying under vacuum, **3b** (0.038 g, 95%) was obtained as a pale yellow microcrystalline powder. ^{1}H NMR (CD$_3$NO$_3$, 500 MHz, 25 °C): $\delta=8.67$ (s, 6H), 8.56–8.42 (m, 48H), **4b**H-3', 4', 6', 3'', 4'', 6'', 3''', 4''', 6''', 8.19 (d, $J_{3,4}=8.0$ Hz, 6H; **4b**H-3), 7.94 (t, $J_{4,3;4,5}=7.9$ Hz, 6H; **4b**H-4), 7.61 (d, $J_{o,m}=7.3$ Hz, 24H; H-*ortho* (outer **5a**)), 7.51 (d, $J_{o',m'}=7.2$ Hz, 24H; H-*ortho* (inner **5a**)), 7.28 (d, $J_{5,4}=7.7$ Hz, 6H; **4b**H-5)), 6.87 (t, $J_{p,m}=7.6$ Hz, 12H; H-*para* (outer **5a**), 6.82 (t, $J_{p',m'}=7.6$ Hz, 12H; H-*para* (inner **5a**)), 6.77 (t, $J_{m,o;m,p}=7.8$ Hz, 24H; H-*meta* (outer **5a**)), 6.64 (t, $J_{m',o';m',p'}=7.9$ Hz, 24H; H-*meta* (inner **5a**)), 2.25 (s, 18H; **4b**-CH$_3$); ^{13}C NMR (CD$_3$NO$_3$, 125.8 MHz, 25 °C): $\delta=159.91$, 158.73, 158.23, 153.02, 153.00, 151.78, 151.62, 151.30, 148.95, 148.67, 148.30, 140.59, 139.91, 139.28, 137.85, 137.70, 137.59, 134.10, 133.68, 133.29, 131.63, 131.33, 130.30, 129.72, 129.39, 129.16, 126.73, 124.67, 124.57, 124.52, 121.66, 27.21 (CH$_3$); UV/Vis (CH$_2$Cl$_2$): λ [nm] (ε [mol^{-1}dm^{3}cm^{-1}]): 313 (239087), 362 (450389), 379sh (351758); elemental analysis calcd. for $C_{330}H_{210}Ag_{12}F_{36}N_{48}O_{36}S_{12}$ (%): C 50.90, H 2.72, N 8.63; found: C 50.63, H 2.84, N 8.64.

5b: A warm solution of hexaaminobenzene[16] (0.102 g, 6.06×10^{-4} mol) in distilled water (3.5 mL) was prepared under argon and added by syringe to a stirred solution of 1,2-bis-(4-*tert*-butylphenyl)ethane-1,2-dione[19] (2.0 g, 6.20×10^{-3} mol) in acetic acid (8 mL), heated in a bath at 50 °C. During addition, a khaki-coloured solid (crude **5b**) rapidly developed. Ethanol (3 mL) was then added, the temperature increased to 80 °C, and the reaction maintained at this temperature with continued stirring for 24 h. The precipitated solid was isolated by filtration uder vacuum, washed with excess MeOH and air dried. The solid was then powdered, briefly boiled in MeOH (30 mL) and re-isolated by vacuum filtration as above. The crude product was finally twice chromatographed on columns of neutral Alumina, eluting with 1:1 hexane/CH$_2$Cl$_2$. Removal of solvent on a water bath and drying under vacuum yielded **5b** (0.451 g, 72%) as a pale yellow powdery solid. Microanalytically pure material was obtained by further recrystallisation from methylcyclohexane and drying under vacuum at 100–120 °C/0.05 mmHg. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): $\delta=7.84$ (d, $J_{o,m}=8.4$ Hz; 12H; H-*ortho*), 7.43 (d, $J_{m,o}=8.5$ Hz, 12H; H-*meta*), 1.36 (s, 54H; *para*-C(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): $\delta=153.70$, 152.58, 139.09, 136.04, 129.98, 125.37, 34.82 *C*(CH$_3$)$_3$, 31.30 C(*C*H$_3$)$_3$; FAB+ MS (CHCl$_3$): *m*/*z* (relative intensity; %): 895.6 (4) $[\mathbf{5b}-\mathrm{C_6H_4(C(CH_3)_3)}+\mathrm{H}]^+$, 996.7 (7) $[\mathbf{5b}-2\,\mathrm{CH_3}-\mathrm{H}]^+$, 1012.7 (24) $[\mathbf{5b}-\mathrm{CH_3}-\mathrm{H}]^+$, 1027.7 (100) $[\mathbf{5b}]^+$, 1043,7 (11) $[\mathbf{5b}+\mathrm{CH_3}+\mathrm{H}]^+$; elemental analysis calcd. for $C_{72}H_{54}N_6$ (%): C 84.17, H 7.65, N 8.18; found C 84.12, H 7.64, N 8.04.

Crystallographic measurements: $[\mathbf{2a}\subset(\mathrm{PF}_6)_4](\mathrm{PF}_6)_5$: Crystals suitable for measurement were grown by slow diffusion of toluene into a nitromethane solution of the complex. X-ray data: $[\mathrm{Cu}_9(\mathbf{4a})_3(\mathbf{5a})_3](\mathrm{PF}_6)_9\cdot0.5\,\mathrm{MeNO_2}\cdot\mathrm{H_2O}$: STOE IPDS (−70 °C), graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å), triclinic, space group $P\bar{1}$ (no. 2), $a=18.588(4)$, $b=18.790(3)$, $c=39.737(7)$ Å, $\alpha=76.34(2)$, $\beta=82.86(2)$, $\gamma=85.88(2)$; $V=13369(4)$ Å^3, $Z=2$, $\mu=0.853$ mm^{-1}, $F(000)=5706$, $\rho_{\mathrm{calcd}}=1.403$ Mg m^{-3}, $2\theta_{\max}=42.00°$. Structure solution and refinement: Primary structure solution by direct methods (SHELXS-92).[20] Anisotropic refinement for all non-hydrogen atoms of the cationic complex molecule (SHELXL-93).[21] A riding model starting from calculated positions was employed for the hydrogen atoms—no hydrogen positions were calculated for solvent molecules. A total of 63054 reflections were measured and of these 27302 were independent [R(int) = 0.0689], 26996 of which were used for the refinement of 3375 parameters. The solvent and the anion structure shows multifold disorder, therefore atoms of the solvent molecules were refined isotropically using splitpositions. The structure was refined against F^2 (full-matrix least-squares). $R_1 = 0.0931$ (for 19569 reflections with $F > 4\sigma F$) [$R_1 = 0.1225$ (all data)] and $wR_2 = 0.3115$ (all data), *GooF* on $F^2 = S = 1.032$, max./ min. residual density: $+1.11/-0.54\,e\,Å^{-3}$, ($R_1 = \Sigma F_o| - |F_c/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $GooF = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n = no. of reflections and p = no. of parameters). **[3a ⊂ (PF$_6$)$_6$](PF$_6$)$_6$:** Crystals suitable for measurement were grown by slow diffusion of toluene into a nitromethane solution of the complex. X-ray data: [Cu$_{12}$(**4b**)$_3$(**5a**)$_3$](PF$_6$)$_{12}$C$_6$H$_6$ · 3MeNO$_2$ · 3MeOH: STOE IPDS (−70 °C), graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), orthorhombic, space group *Pcca* (no. 54), $a = 30.615(6)$, $b = 32.515(7)$, $c = 39.436(8)$ Å; $V = 39256(14)$ Å^3, $Z = 4$, $\mu = 0.775$ mm^{-1}, $F(000) = 15456$, $\rho_{calcd} = 1.293$ Mg m^{-3}, $2\theta_{max} = 47.40°$. Structure solution and refinement: Primary structure solution by direct methods (SHELXS-92).[20] Anisotropic refinement for all non-hydrogen atoms of the cationic complex molecule (SHELXL-93)[21] and benzene and one PF$_6$. A riding model starting from calculated positions was employed for the hydrogen atoms. A total of 75697 reflections were measured and of these 23987 were independent [R(int) = 0.0681], 14978 of which were used for the refinement of 1786 parameters. Parts of the solvent and the anion structure shows multifold disorder, therefore atoms of the solvent molecules were refined isotropically using splitpositions. The structure was refined against F^2 (full-matrix least-squares). $R_1 = 0.1342$ (for 8718 reflections with $F > 4\sigma F$) [$R1 = 0.2343$ (all data)] and $wR_2 = 0.3328$ (all data), GooF on $F^2 = S = 3.407$, max./ min. residual density: $+1.03/-0.63\,e\,Å^{-3}$. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410248 (**2a**) and CSD-410249 (**3a**).

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