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Synthesis and Characterization of Poly-NHC-Derived Silver (I) Assemblies and Their Transformation into Poly-Imidazolium Macrocycles

Ana Gutiérrez-Blanco,[a, b] Christian Dobbe,[a] Alexander Hepp,[a] Constantin G. Daniliuc,[c] Macarena Poyatos,*[b] F. Ekkehardt Hahn,*[a] and Eduardo Peris*[b]

Three metallosupramolecular assemblies composed of two bis-NHCs and two silver atoms, [**4**]$(PF_6)_2$, two tetra-NHCs and four silver atoms, [**7**]$(PF_6)_4$, and two tri-NHCs and three silver atoms [**8**]$(BF_4)_3$, have been prepared. Assemblies [**4**]$(PF_6)_2$ and [**7**]$(PF_6)_4$ feature NHC ligands decorated with terminal olefin groups. Irradiation of [**4**]$(PF_6)_2$ yielded complex [**5**]$(PF_6)_2$ with two terminal cyclobutane rings linking the two bis-NHC ligands. Liberation of the macrocyclic tetrakisimidazolium salt H_4-**6**$(PF_6)_4$ was achieved by reaction of [**5**]$(PF_6)_2$ with NH_4Cl/NH_4PF_6. No [2 + 2] cycloaddition was observed upon irradiation of [**7**]$(PF_6)_4$, apparently due to an unfavorable orientation of the olefin groups. Irradiation of complex [**8**]$(BF_4)_3$ with three internal pairs of olefin groups leads to [**9**]$(BF_4)_3$ as a mixture of two isomers that differ on the relative orientation of the internal cyclobutane rings. Reaction of [**9**]$(BF_4)_3$ with NH_4Cl/NH_4BF_4 yields an isomer mixture of the novel cage-line hexakisimidazolium salt H_6-**10**$(BF_4)_6$.

Introduction

Over the last three decades, research on supramolecular coordination complexes (SCCs)[1] has emerged as an important sub-discipline of coordination chemistry. Particularly, the wide range of applications has stimulated interest in these compounds. Among others, SCCs have found applications in catalysis,[2] molecular recognition,[3] the stabilization of highly reactive species,[4] and as drug delivery/release vectors.[5] Coordination-driven self-assembly[1e,6] arguably constitutes the most widely used method for the construction of discrete SCCs. From the ligand perspective, metallosupramolecular assemblies have been mainly constructed from O-, N-, and P-donor Werner-type polydentate ligands. More recently, poly N-heterocyclic carbene ligands (poly-NHCs)[7] have emerged as an alternative for the generation of organometallic metallosupramolecular assemblies.[8] The rapid development of organometallic supramolecular assemblies is illustrated by the coinage of the term supramolecular organometallic complexes (SOCs),[9] referring to all metal-containing assemblies in which the linker-metal connection is established by M–C bonds.

Over the last 10 years, the number of metallosupramolecular assemblies featuring M–C_{NHC} bonds has grown steadily. Among them, a large number of NHC-derived SOCs is based on group 11 metals. These metals in oxidation state of +1 offer certain advantages for the preparation of metal assemblies such as the trend to form linear C_{NHC}–M–C_{NHC} moieties and therefore facilitate the construction of assemblies in which the metal is sandwiched between two polydentate NHCs.[10] In addition, the Ag–C_{NHC} bond is usually labile allowing rearrangements to the thermodynamically most stable assembly. Known poly-NHC derived assemblies with group 11 metals, include diverse architectures such as rectangles, triangles[11] and cylinders.[12]

Metallosupramolecular assemblies that are amenable of post-assembly modification (PAM) reactions can be modified at their ligands after the assembly has formed.[8a,12h,13] This constitutes a very interesting feature, because PAM reactions facilitate the generation of architectures with tailored functionalities normally not directly accessible from metal ions and ligands. The combination of poly-NHC ligands and group 11 metals has been found to be a promising strategy for the design of PAM-amenable metallosupramolecular assemblies.[8a,14]

Cationic imidazolium salts have been widely used as anion receptors because they combine potential hydrogen bonding with favorable electrostatic interactions in their interactions

[a] *A. Gutiérrez-Blanco, Dr. C. Dobbe, Dr. A. Hepp, Prof. Dr. F. E. Hahn*
Institut für Anorganische und Analytische Chemie,
Westfälische Wilhelms-Universität Münster,
Corrensstrasse 28–30, 48149 Münster, Germany
E-mail: fehahn@uni-muenster.de
https://www.uni-muenster.de/chemie.ac/hahn/index.html
[b] *A. Gutiérrez-Blanco, Dr. M. Poyatos, Prof. Dr. E. Peris*
Institute of Advanced Materials (INAM), Centro de Innovación en Química Avanzada (ORFEO-CINQA)
Universitat Jaume I
Avda Vicente Sos Baynat s/n, 12071 Castellón, Spain
E-mail: poyatosd@uji.es
eperis@uji.es
http://www.inam.uji.es/users/macarena-poyatos
http://www.inam.uji.es/users/eduardo-peris
[c] *Dr. C. G. Daniliuc*
Organisch-Chemisches Institut,
Westfälische Wilhelms-Universität Münster,
Corrensstrasse 40, 48149 Münster, Germany

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with selected substrates.[15] However, finding effective ways for preparing imidazolium-based multivalent anion receptors still constitutes a challenge. The PAM methodology may constitute a valuable approach for the preparation of poly-imidazolium salts as anion receptors with enhanced binding affinities, as suggested by Jin and co-workers.[14d] Our first progress in this area was recently described with the template-controlled preparation of an oktakisimidazolium salt starting from a tetrakisimidazolium salt.[14a] The oktakisimidazolium salt turned out to be an efficient multivalent anion receptor with a binding affinity significantly larger than that shown by the original tetrakisimidazolium salt.

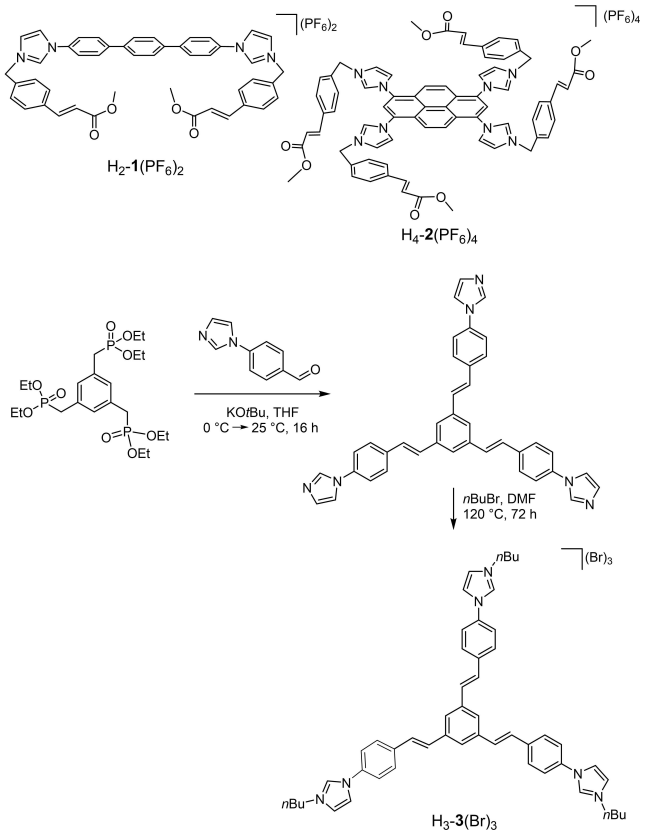
Based on these previous findings, we describe here the preparation and characterization of a series of metallosupramolecular assemblies from poly-imidazolium salts featuring terminal or internal olefins and Ag^{I} ions. The resulting poly-NHC-Ag^{I} assemblies were then subjected to photochemically induced [2 + 2] cycloaddition reactions, by activation of the pendant cinnamic ester groups or the internal olefins. This procedure linked the individual poly-NHC ligands to larger macrocyclic or cage-like poly-NHCs. Demetallation of the poly-NHC complexes yielded novel poly-imidazolium salts not accessible by conventional organic synthesis.

Results and Discussion

The poly-imidazolium salts H_2-**1**$(PF_6)_2$ and H_4-**2**$(PF_6)_4$ (Scheme 1, top) featuring terminal olefins were prepared by standard methods from the bis- or tetrakisimidazolyl compounds by *N*-alkylation with methyl-3-(4-bromomethyl)cinnamate. A different strategy was used for the preparation of H_3-**3**$(Br)_3$ featuring internal olefins (Scheme 1, bottom). First 1,3,5-tris (diethoxyphosphinylmethylene)benzene was reacted with 4-imidazolylbenzaldehyde in the presence of KO*t*Bu.[14a] The trisimidazolyl derivative was then triply *N*-alkylated using *n*BuBr to give H_3-**3**$(Br)_3$ in 83% yield. The poly-imidazolium salts H_2-**1**$(PF_6)_2$-H_3-**3**$(Br)_3$ were characterized by NMR spectroscopy and mass spectrometry.

Reaction of H_2-**1**$(PF_6)_2$ with a slight excess of Ag_2O yielded the metallorectangle [**4**]$(PF_6)_2$ in 83% yield (Scheme 2). The formation of the rectangular assembly was confirmed by NMR spectroscopy and mass spectrometry. The ^{1}H NMR spectrum of [**4**]$(PF_6)_2$ is consistent with the pseudo-D_{2h} symmetry of the molecule. This is exemplified by the appearance of two resonances assigned to the protons of the imidazolylidene rings ($\delta = 7.98$ and 7.78 ppm), the three signals due to the protons of the terphenylene linker ($\delta = 7.88$, 7.80 and 7.64 ppm) and the two doublets assigned to the olefin protons ($\delta = 7.52$ and 6.48 ppm). The metallation of the NHC donors with Ag^{I} has been confirmed by the resonance at $\delta = 179.4$ ppm observed in the $^{13}C\{^1H\}$ NMR spectrum for the C_{NHC} carbon atom. The dimetallic nature of the complex is evident from the electrospray mass spectrum, which shows the base peak at $m/z =$ 818.4, assigned to $[\mathbf{4}]^{2+}$.

The dinuclear NHC complex [**4**]$(PF_6)_2$ was irradiated at ambient temperature with a high pressure mercury lamp for 3 h



Scheme 1. Poly-imidazolium salts H_2-**1**$(PF_6)_2$ and H_4-**2**$(PF_6)_4$ (top), and synthetic procedure for the preparation of H_3-**3**$(Br)_3$ (bottom).

in acetonitrile to initiate a [2 + 2] cycloaddition of two adjacent cinnamic acid groups. Under these reaction conditions, [**4**]$(PF_6)_2$ was quantitatively converted into complex [**5**]$(PF_6)_2$ featuring two cyclobutane units linking the two *p*-terphenylene-bisimidazolylidene ligands (Scheme 2). The ^{1}H NMR spectrum of [**5**]$(PF_6)_2$ lacks the signals due to the olefin protons that were observed for [**4**]$(PF_6)_2$ at $\delta = 7.52$ and 6.48 ppm. Instead, two new resonances at $\delta = 4.25$ and 4.08 ppm for the protons of the cyclobutane rings are observed, confirming that the [2 + 2] cycloaddition did proceed (Figure 1).

Finally, the two Ag^{I} cations in [**5**]$(PF_6)_2$ were removed by reaction with NH_4Cl in methanol to give the soluble macrocyclic tetrakisimidazolium salt H_4-**6**$(Cl)_4$ and solid AgCl. Anion exchange with NH_4PF_6 allowed precipitating H_4-**6**$(PF_6)_4$ in 80% yield (Scheme 2). The ^{1}H NMR spectrum of H_4-**6**$(PF_6)_4$ showed the characteristic signal for the four chemically equivalent NC*H*N protons of the imidazolium groups at $\delta = 10.02$ ppm as a clear indication for the formation of four imidazolium units (Figure 1). The signals for the cyclobutane protons were observed as doublets at $\delta = 4.31$ and 4.06 ppm. The ESI mass spectrum of H_4-**6**$(PF_6)_4$ showed the most intensive peaks at $m/z = 356.0$ and 523.5, assigned to cations $[H_4\text{-}\mathbf{6}]^{4+}$ and $[H_4\text{-}\mathbf{6} + PF_6]^{3+}$, respectively.

Next, the tetranuclear metallocage [**7**]$(PF_6)_4$ was prepared from the pyrene-bridged tetrakisimidazolium salt H_4-**2**$(PF_6)_4$ and Ag_2O (Scheme 3). In previous studies, we observed a series of

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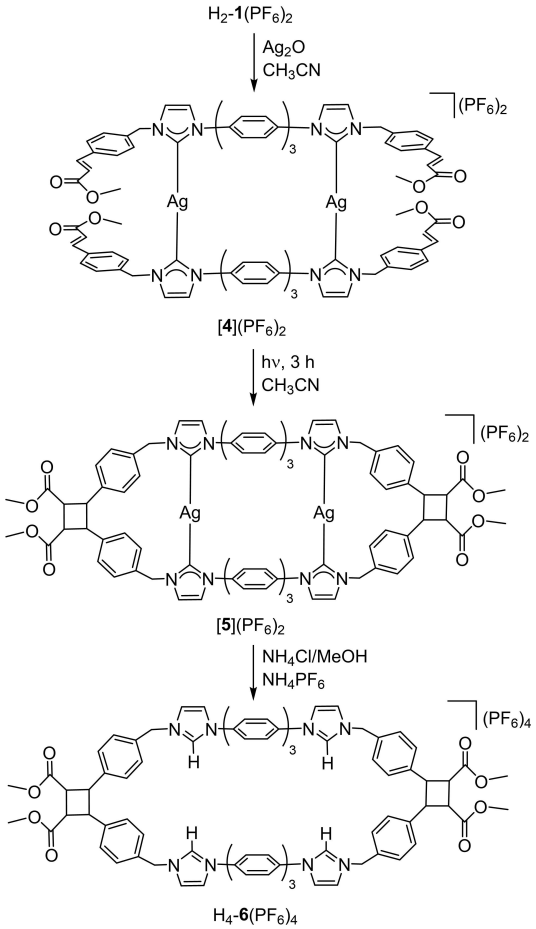
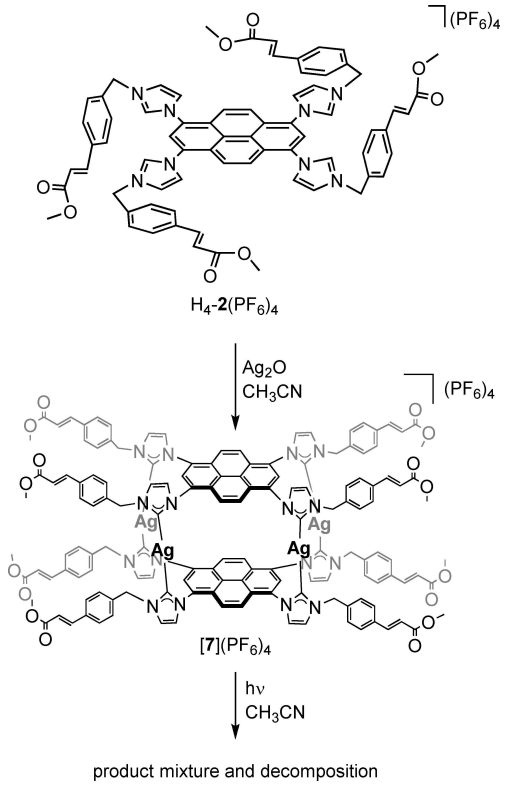


Scheme 2. Preparation of the metallosupramolecular assembly [**4**]$(PF_6)_2$, its PAM to give [**5**]$(PF_6)_2$ and liberation of the macrocyclic tetrakisimidazolium salt H_4-**6**$(PF_6)_4$.



Scheme 3. Synthesis of [**7**]$(PF_6)_4$ and attempted PAM.

tetranuclear Rh^I and Ir^I complexes obtained from a related pyrene-bridged tetrakisimidazolylidene ligand displaying interesting structural and catalytic features.[16] The reaction of H_4-**2**$(PF_6)_4$ with Ag_2O, affords the tetranuclear cylinder-like assembly [**7**]$(PF_6)_4$ in 74% yield. Compound [**7**]$(PF_6)_4$ was characterized by NMR spectroscopy and mass spectrometry. The ^1H NMR spectrum displays a set of signals in accord with a pseudo-D_{2h} symmetric molecule. For example, two resonances due to the protons of the pyrene bridge were observed at $\delta = 8.18$ and 7.96 ppm. In addition, two signals due to the protons of the imidazolylidene rings ($\delta = 7.56$ and 7.45 ppm) and two doublets assigned to the olefin protons ($\delta = 7.52$ and 6.39 ppm) were observed. The $^{13}C\{^1H\}$NMR spectrum shows a signal at $\delta =$ 182.8 ppm assigned to the metallated carbene carbon atom. The tetrametallic nature of the complex was unambiguously confirmed by electrospray mass spectrometry, which reveals peaks at $m/z = 689.6$ and 967.8 assigned to $[\mathbf{7}]^{4+}$ and $[\mathbf{7} + PF_6]^{3+}$, respectively.

Attempts to perform a post synthetic modification on [**7**]$(PF_6)_4$ *via* a photochemically induced [2 + 2] cycloaddition reaction were next investigated. A solution of [**7**]$(PF_6)_4$ in acetonitrile was irradiated with a high pressure mercury lamp at ambient temperature for 3 h. Under these reaction conditions, the expected cycloaddition product was not formed and only a mixture of unidentified reaction products was obtained. For the [2 + 2] cycloaddition to proceed, the olefins must be oriented in a parallel fashion with a distance between the midpoints measuring about 3.6 Å.[17] While these geometric features were observed for a related cylinder-like assembly obtained from two tetra-NHC ligand and four silver atoms,[14a] we believe that the orientation of the olefin groups in [**7**]$(PF_6)_4$ does not meet the geometric requirements. Unfortunately, we were not able to obtain crystals suitable for an X-ray diffraction study with [**7**]$(PF_6)_4$ to confirm this assumption.

In order to shed more light on the geometric requirements for the [2 + 2] cycloaddition and the possible outcome of this reaction, we decided to extend our studies to tri-NHC ligands featuring internal olefin groups. In this regard, the reaction of H_3-**3**$(Br)_3$ with Ag_2O followed by anion exchange with $AgBF_4$ yielded assembly [**8**]$(BF_4)_3$ (Scheme 4). Complex [**8**]$(BF_4)_3$ was characterized by NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum shows the characteristic resonance for the C_{NHC} carbon atom at $\delta = 178.0$ ppm. The ^1H NMR spectrum features the resonances for the olefin protons at $\delta = 7.19$ and 7.14 ppm with the typical *trans*-coupling constant of $^3J_{H\text{-}H} = 16.5$ Hz.

The molecular structure of [**8**]$(BF_4)_3$ was established by an X-ray diffraction analysis with crystals of composition [**8**]$(BPh_4)_3 \cdot 2CH_3CN$ obtained from [**8**]$(BF_4)_3$ by anion exchange with $NaBPh_4$. The molecular structure determination confirms the formation of a cylinder-like, trinuclear assembly (Figure 2).

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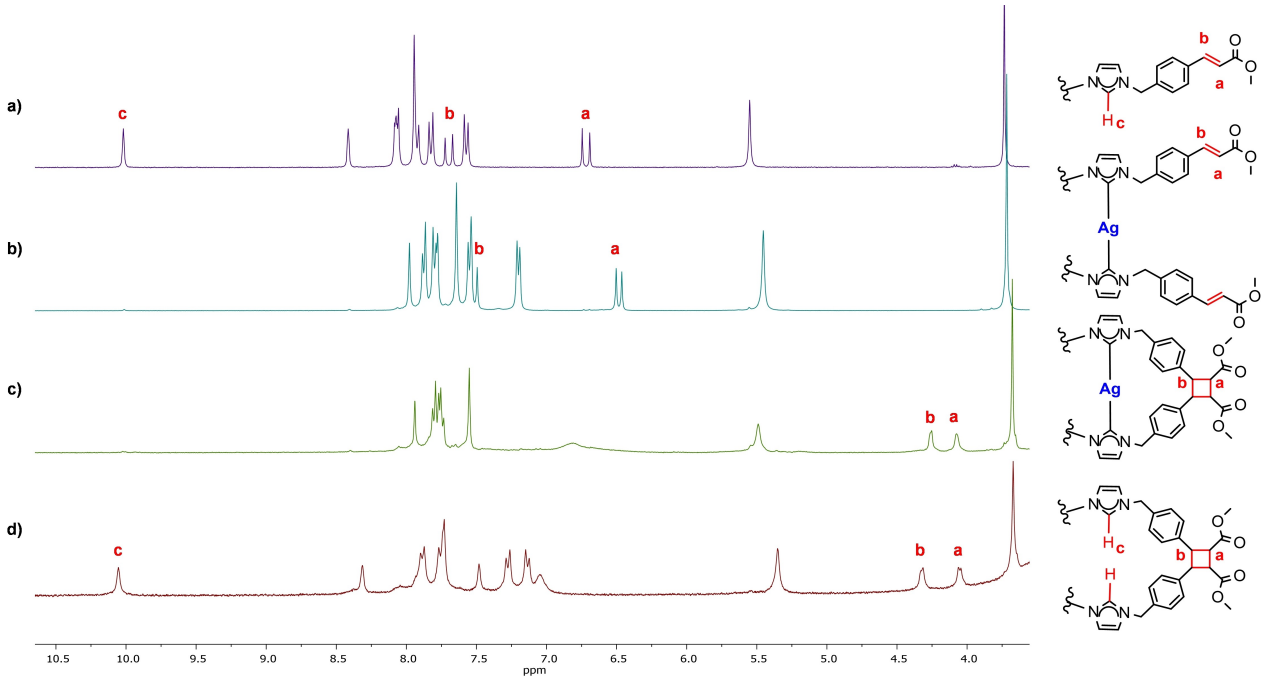

Figure 1. Section of the ^{1}H NMR spectra (DMSO-d_6) of (a) H_2-**1**$(PF_6)_2$, (b) [**4**]$(PF_6)_2$, (c) [**5**]$(PF_6)_2$ and (d) H_4-**6**$(PF_6)_4$. Only characteristic signals mentioned in the text are labelled in the spectra.

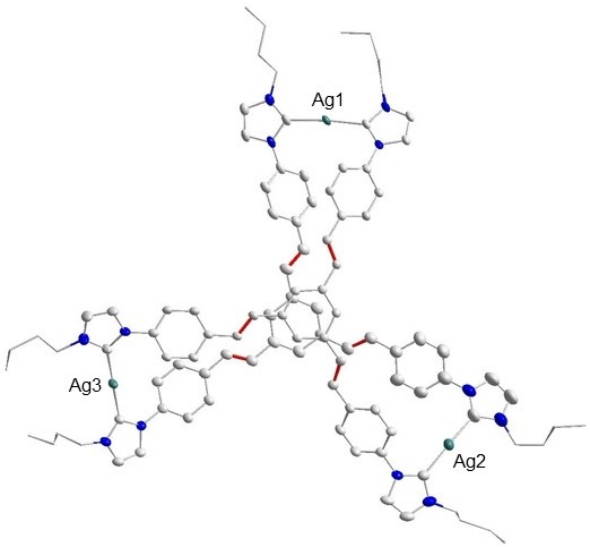

Figure 2. Molecular structure of cation $[\mathbf{8}]^{3+}$ in [**8**]$(BPh_4)_3$·$2CH_3CN$ showing the non-parallel orientation of the olefin groups (in red).

The three silver atoms form a rather symmetrical triangle with an average non-bonding Ag···Ag separation of 17.6 Å. The average Ag–C_{NHC} distance measures 2.08 Å and falls in the typical range for this type of bond.[14] The central benzene rings are arranged parallel but twisted by about 4° relative to each other. Interestingly, the three pairs of olefin groups are not oriented in a parallel fashion.

While the separation between the olefins in the three pair measures between 3.35 to 3.83 Å and thus fall in the range required for a subsequent [2+2] cycloaddition,[17] their non-parallel orientation might prevent this reaction. Such behavior has been previously observed for dinuclear silver-NHC complexes featuring internal olefin bonds.[14f]

Nevertheless, complex [**8**]$(BF_4)_3$ was irradiated with a high-pressure lamp in order to prove our hypothesis. We observed changes in the ^{1}H NMR spectra, thus indicating that the cycloaddition reaction might be taking place. After 16 h of reaction, no more changes were observed in the ^{1}H NMR and it was assumed that the formation of the triple cyclobutane was complete (Scheme 4).

This assumption was corroborated by the ^{1}H NMR spectrum of the reaction product [**9**]$(BF_4)_3$, showing no resonances for the olefin protons. However, the ^{1}H NMR spectrum features a total of 12 new resonances for the cyclobutane protons (Figure 3) instead of the two resonances expected and observed after cyclobutane formation in [**5**]$(PF_6)_2$ and related compounds.[14] This observation is consistent with the formation of two isomeric complexes (Figure 4) in the cycloaddition, featuring either three different (isomer **A**) or three identical cyclobutane rings (isomer **B**).

Assuming the formation of the isomers **A** and **B** of [**9**]$(BF_4)_3$, all resonances in the ^{1}H NMR spectrum (Figure 3, bottom) can be assigned. For the unsymmetric isomer **A**, three resonances are observed for each of the protons H10, H11 and H13. The symmetric isomer **B** gives only one set of resonances for H10, H11 and H13. The resonances for the other protons of the isomers fall together in additional multiplets, which could not be resolved.

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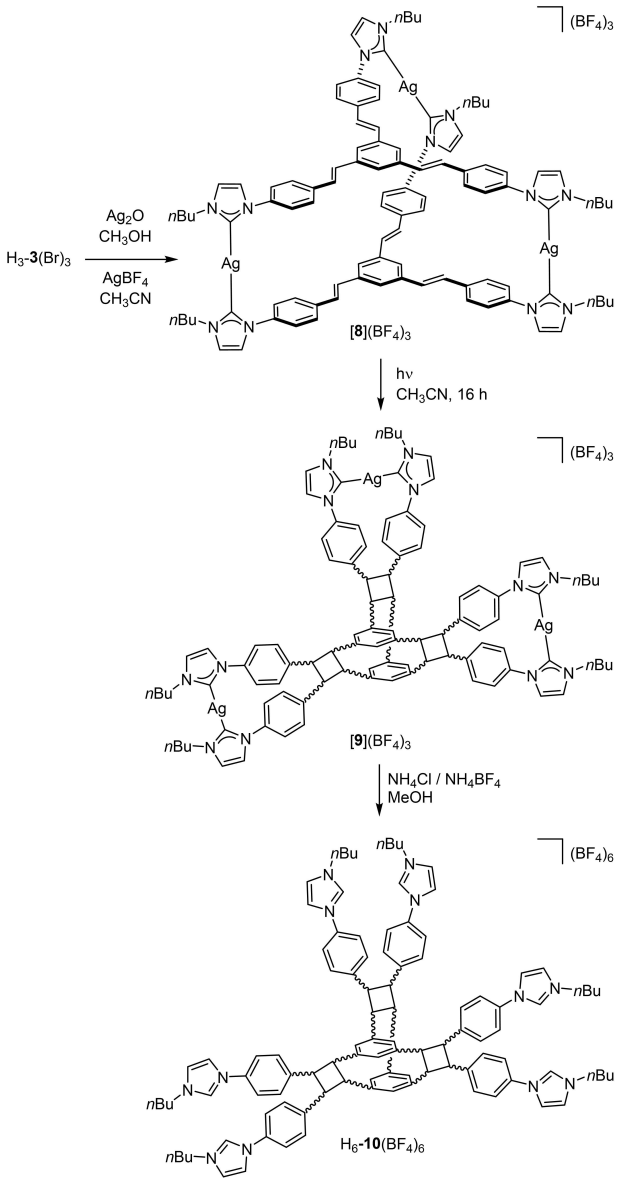

Scheme 4. Synthesis of [**8**](BF$_4$)$_3$, its PAM to [**9**](BF$_4$)$_3$ and liberation of hexakisimidazolium salt H$_6$-**10**(BF$_4$)$_6$.

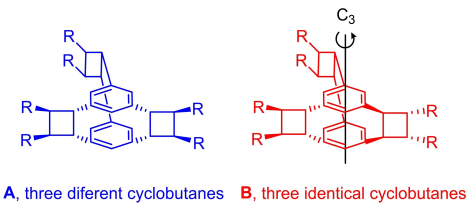

Figure 4. Schematic representation of isomers **A** and **B** of [**9**](BF$_4$)$_3$.

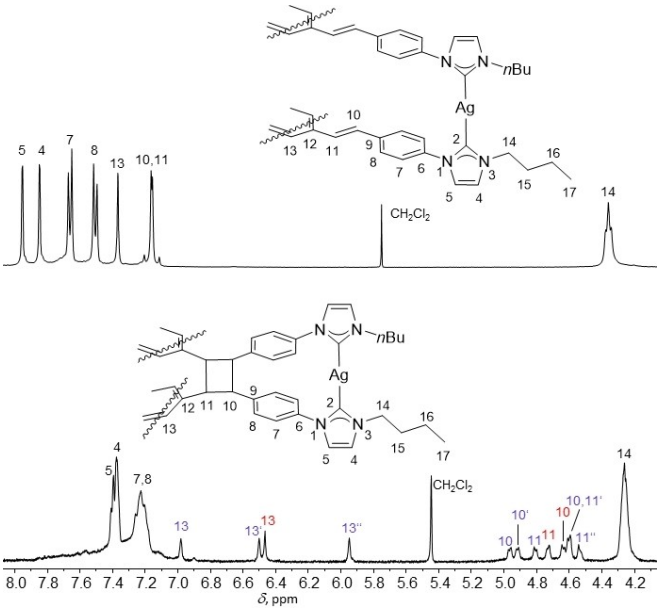

Figure 3. Sections of the ^{1}H NMR spectra of [**8**](BF$_4$)$_3$ (top) and [**9**](BF$_4$)$_3$ (bottom). The resonances for isomers **A** and **B** are labelled in blue and red, respectively. Overlapping resonances for both isomers are depicted in black.

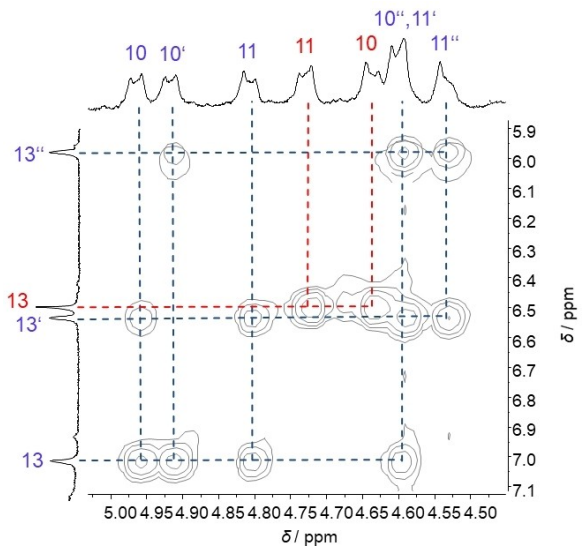

Figure 5. Section of the ^{1}H,^{1}H ROESY NMR spectrum for the isomers of [**9**](BF$_4$)$_3$ showing the two independent spin systems (resonances for the unsymmetrical isomer **A** in blue and for the symmetrical isomer **B** in red).

The formation of the isomer mixture should lead to two separate spin systems. These two spin systems were indeed observed by ^{1}H,^{1}H-ROESY NMR spectroscopy (Figure 5). The ROESY spectrum clearly shows the correlation between protons H13 and H10/H11 for the two isomers. Resonances for the isomer mixture of [**9**](BF$_4$)$_3$ were also observed by ^{13}C{^{1}H} NMR spectroscopy (see the Supporting Information).

Finally, the hexakisimidazolium salt H$_6$-**10**(BF$_4$)$_6$ was liberated from compound [**9**](BF$_4$)$_3$ by reaction with NH$_4$Cl/NH$_4$BF$_4$ in methanol (Scheme 4). The salt was characterized by mass spectrometry showing the strongest peaks at *m/z* (%) = 251.1542 (100, calcd. for [H$_6$-**10**]$^{6+}$ 251.1548) and 318.9866 (40, calcd. for [H$_6$-**10** + BF$_4$]$^{5+}$ 318.9872). Both the ^{1}H and the ^{13}C{^{1}H} NMR spectra of H$_6$-**10**(BF$_4$)$_6$ confirm the presence of two isomers, one featuring three different cyclobutane rings and

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one composed of three identical ones, similar to the situation in [**9**]$(BF_4)_3$ (see the Supporting Information).

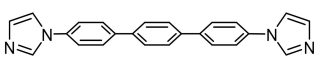
Conclusions

In summary, new bis- and tetrakisimidazolium salts with terminal olefins and a trisimidazolium salt with internal olefins have been prepared and used for the synthesis of di-, tetra- and trinuclear silver-NHC assemblies. The di-silver tetra-NHC metallorectangle [**4**]$(PF_6)_2$ underwent effective photochemically induced [2 + 2] cycloaddition to form a new macrocycle in which the two di-NHC ligands are linked by two terminal cyclobutane units. Removal of the Ag^I ions with NH_4Cl/NH_4PF_6 afforded a novel macrocyclic tetrakisimidazolium salt H_4-**6**$(PF_6)_4$. The pyrene-bridged tetrakismidazolium salt H_4-**2**$(PF_6)_4$ reacted with Ag_2O to give the cylinder-like tetrasilver assembly [**7**]$(PF_6)_4$ featuring four pairs of terminal olefins. Irradiation of this assembly did not yield the derivative with bridging cyclobutanes, most likely due to an unfavorable orientation of the olefin groups. Finally, trisimidazolium salt H_3-**3**$(Br)_3$ reacted with Ag_2O to give the trinuclear assembly [**8**]$(BF_4)_3$ featuring three internal pairs of olefins. Irradiation of this assembly proceeded *via* triple cyclobutane formation leading to a mixture of two isomeric complexes [**9**]$(BF_4)_3$ with either three different or three identical cyclobutane linkers. Liberation of two isomeric hexakisimidazolium cages from [**9**]$(BF_4)_3$ proved possible. We present an efficient method for the synthesis of macrocyclic or cage-like poly-imidazolium salts *via* photochemical [2 + 2] cycloaddition at a silver-carbene template. We are confident that this methodology can be extended to the synthesis of novel cyclic poly-azolium salts not accessible by conventional organic synthesis.

Experimental Section

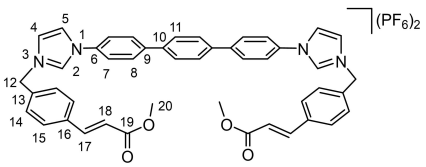
General considerations. 1,3,6,8-Tetraimidazolylpyrene was prepared according to a reported method.[16] All other reagents were used as received from commercial suppliers. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or were distilled by standard procedures prior to use. NMR spectra were recorded on Bruker AVANCE III 400 or 300 MHz spectrometers. NMR spectra were obtained at room temperature in acetonitrile-d_3 or DMSO-d_6. Electrospray mass spectra were recorded on a Micromass Quatro LC instrument, MeOH or CH_3CN were used as mobile phase, and nitrogen was employed as drying and nebulizing gas. Satisfactory microanalytical data for most ligands and metal complexes could not be obtained due to the large fluorine content in the hexafluorophosphate counterions. A complete set of NMR spectra is provided instead.

Synthesis of bisimidazolyl-p-terphenylene



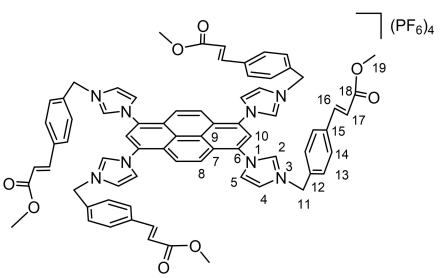
4,4′-Dibromoterphenyl (500 mg, 1.29 mmol), imidazole (173 mg, 2.54 mmol), K_2CO_3 (710 mg, 5.14 mmol) and CuI (49 mg, 0.26 mmol) were placed together in a high pressure Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. The solids were suspended in anhydrous DMF (20 mL) and the resulting mixture was heated under reflux for 72 h. The reaction mixture was then allowed to reach ambient temperature. Distilled water (75 mL) was added, and the resulting suspension was stirred for 2 h. The solid was collected by filtration and washed with water. Compound bisimidazolyl-*p*-terphenylene was isolated as a white solid. Yield: 440 mg (1.21 mmol, 94 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.89–7.83 (m, 8H (2H H4, 4H H7, 2H H2)), 7.80–7.66 (m, 10H (2H H5, 8H H8, H11)). ESI MS *m/z* = 362.7 (calcd. for $[M]^+$ 362.2).

Synthesis of H_2-1$(PF_6)_2$



Bisimidazolyl-*p*-terphenylene (80 mg, 0.22 mmol) and methyl 3-(4-bromomethyl)cinnamate (113 mg, 0.44 mmol) were placed together in a thick-walled Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. The solids were suspended in anhydrous DMF (16 mL) and the resulting mixture was heated to 145 °C for 24 h. Once at ambient temperature, the solvent was distilled under vacuum. The resulting white solid was washed several times with diethyl ether and dried under vacuum. The obtained bromide salt H_2-**1**$(Br)_2$ (101 mg, 0.12 mmol) was suspended in MeOH (20 mL), heated to 40 °C and treated with NH_4PF_6 (56 mg, 0.34 mmol). The resulting suspension was stirred at 40 °C for 16 h. Filtration of the suspension yielded compound H_2-**1**$(PF_6)_2$ as a light brown solid. Yield: 154 mg (0.15 mmol, 68 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.02 (s, 2H, H2), 8.42 (s, 2H, H4), 8.09–8.06 (m, 6H (2H, H5; 4H, H11), 7.93 (m, 8H, H7 and H8), 7.83 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, H14), 7.70 (d, $^3J_{H\text{-}H}$ = 16.1 Hz, 2H, H17), 7.58 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, H15), 6.72 (d, $^3J_{H\text{-}H}$ = 16.1 Hz, 2H, H18), 5.55 (s, 4H, H12), 3.73 (s, 6H, H20). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6): δ = 166.6 (C19), 143.7 (C17), 140.6, 138.1, 136.5 (C6, C9, C10), 135.7 (C2), 134.6, 134.1, 129.0, 128.9 (C13, C14, C15, C16), 128.1, 127.6 (C7, C8), 122.5 (C11, C5), 121.7 (C4), 118.7 (C18), 52.14 (C12), 51.54 (C20). ^{19}F {^{1}H NMR (282 MHz, DMSO-d_6): δ = −70.2 (d). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6): δ = −144.2 (m). ESI MS *m/z* = 355.9 (calcd. for $[H_2\text{-}\mathbf{1}]^{2+}$ 356. 2), 857.3 (calcd. for $[H_2\text{-}\mathbf{1} + PF_6]^+$ 857.3).

Synthesis of H_4-2$(PF_6)_4$



The neutral precursor 1,3,6,8-tetraimidazolylpyrene (100 mg, 0.21 mmol) and methyl 3-(4-bromomethyl)cinnamate (230 mg, 0.90 mmol) were placed together in a thick-walled Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. The solids were suspended in anhydrous DMF (20 mL) and the resulting mixture was heated to 145 °C for 24 h. Once at ambient temperature, the solvent was distilled. The resulting brown solid was washed several times with diethyl ether

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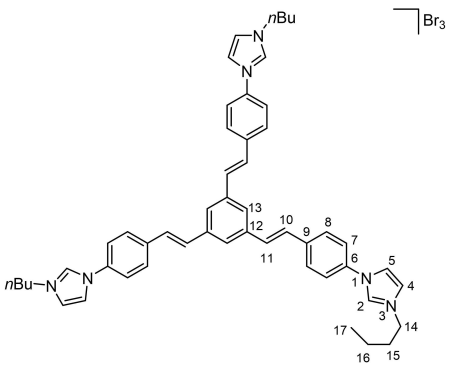
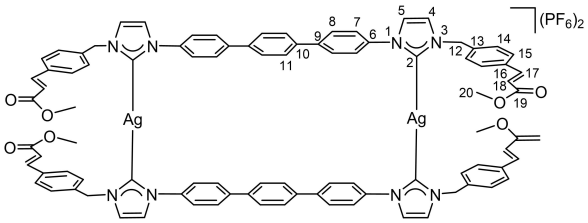
and dried under vacuum. The obtained bromide salt H_4-**2**$(Br)_4$ (267 mg, 0.18 mmol) was suspended in MeOH (30 mL), heated at 40 °C and treated with NH_4PF_6 (176 mg, 1.1 mmol). The suspension was stirred at 40 °C for 16 h. Compound H_4-**2**$(PF_6)_4$ was collected by filtration as a brown solid. Yield: 225 mg (0.13 mmol, 61 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 9.14 (s, 4H, H2), 8.59 (s, 2H, H10), 8.27 (s, 4H, H8), 7.92 (s, 4H, H5), 7.83 (s, 4H, H4), 7.75 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 8H, H14), 7.73 (d, $^3J_{H\text{-}H}$ = 16 Hz, 4H, H16), 7.61 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 8H, H13), 6.60 (d, $^3J_{H\text{-}H}$ = 16 Hz, 4H, H17), 5.61 (s, 8H, H11), 3.77 (s, 12H, H19). ^{13}C {^{1}H} NMR (101 MHz, CD_3CN): δ = 167.9 (C18), 144.3 (C16), 138.8 (C2), 136.6 (C15), 135.9 (C12), 131.0 (C6), 130.8 (C13), 130.7 (C9), 130.02 (C14), 128.9 (C7), 126.8 (C10), 126.7 (C5), 125.9 (C8), 124.8 (C4), 120.4 (C17), 54.4 (C11), 52.4 (C19). ^{19}F{^{1}H} NMR (376 MHz, CD_3CN): δ = −72.6 (d). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ = −144.6 (m). ESI MS *m/z* = 437.1 (calcd. for [H_4-**2** + PF_6]$^{3+}$ 437.1), 728.2 (calcd. for [H_4-**2** + 2PF_6]$^{2+}$ 728.2).

Synthesis of H_3-3$(Br)_3$



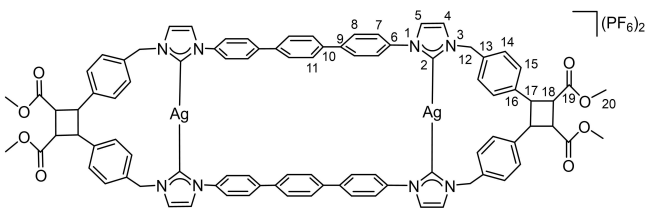
A solution of potassium *tert*-butoxide (2.76 g, 24.6 mmol) in THF (50 mL) was added slowly to a solution of 4-imidazolbenzaldehyde (2.12 g, 12.3 mmol) and 1,3,5-tris (diethoxyphosphosphinylmethylen)benzene (1.30 g, 2.46 mmol) in THF (50 mL) at 0 °C. The solution was stirred for 1 h at 0 °C and was then slowly warmed to 25 °C for 12 h while stirring. Methanol (25 mL) and water (25 mL) were added to the reaction mixture, leading to the precipitation of a light brown solid. The solid was isolated by filtration and washed with diethyl ether (3 × 15 mL). The solid was dried under vacuum to give the trisimidazole. Yield 1.0 g (1.72 mmol, 70 %). The so-isolated trisimidazole (500 mg, 0.86 mmol) was reacted with 1-bromobutane (3.59 g, 2.8 mL, 26.2 mmol) in DMF (40 mL). The suspension was stirred at 120° C for 72 h, then allowed to reach ambient temperature and filtered. The obtained solid was washed with DMF (2 × 10 mL), acetone (3 × 15 mL) and diethyl ether (3 × 15 mL). The solid was dried under vacuum to give compound H_3-**3**$(Br)_3$ as a light brown solid. Yield: 0.71 g (0.71 mmol, 83 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.02 (s, 3H, H2), 8.40 (s, 3H, H5), 8.10 (s, 3H, H4), 7.95 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 6H, H8), 7.89 (s, 3H, H13), 7.87 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 6H, H7), 7.58 (d, $^3J_{H\text{-}H}$ = 16.5 Hz, 3H, H11), 7.51 (d, $^3J_{H\text{-}H}$ = 16.5 Hz, 3H, H10), 4.27 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 6H, H14), 1.91 (m, 6H, H15), 1.37 (m, 6H, H16), 0.96 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 9H, H17). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 138.3 (C9), 137.5 (C12), 135.1 (C2), 133.6 (C6), 130.0 (C11), 127.8 (C8), 127.6 (C10), 124.7 (C13), 123.3 (C4), 122.0 (C7), 120.8 (C5), 49.0 (C14), 31.0 (C15), 18.8 (C16), 13.2 (C17). HRMS (ESI, positive ions): *m/z* (%) = 251.1543 (100, calcd. for [H_3-**3**]$^{3+}$ 251.1548).

Synthesis of [4]$(PF_6)_2$



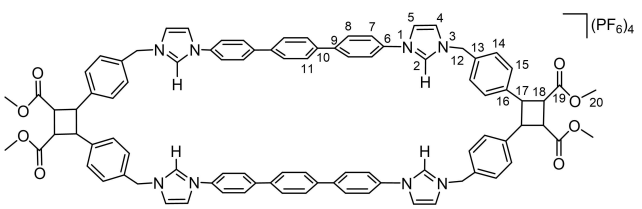
Ag_2O (70 mg, 0.3 mmol) was added to a solution of H_2-**1**$(PF_6)_2$ (100 mg, 0.1 mmol) in acetonitrile (30 mL). The mixture was stirred under exclusion of light for 48 h at 70 °C. After reaching ambient temperature, the obtained suspension was filtered through Celite. The filtrate was concentrated. Addition of diethyl ether yielded [**4**]$(PF_6)_2$ as a grey solid which was collected by filtration, washed with diethyl ether and dried under vacuum. Yield: 80 mg (0.042 mmol, 83 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.98 (s, 4H, H5), 7.88 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 8H, H11), 7.80 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 8H, H7), 7.78 (s, 4H, H4), 7.64 (s, 8H, H8), 7.55 (d, $^3J_{H\text{-}H}$ = 8 Hz, 8H, H14), 7.52 (d, $^3J_{H\text{-}H}$ = 16 Hz, 4H, H17), 7.20 (d, $^3J_{H\text{-}H}$ = 8 Hz, 8H, H15), 6.48 (d, $^3J_{H\text{-}H}$ = 16 Hz, 4H, H18), 5.45 (s, 8H, H12), 3.72 (s, 12H, H20). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ = 179.4 (C2), 166.4 (C19), 143.6 (C17), 139.0, 138.8, 138.7, 137,5, 133,7 (C6, C9, C10, C13, C16), 128.6 (C14), 127.41 (C7), 127.38 (C15), 126.9 (C11), 124.1 (C8), 123.6 123.1 (C4, C5), 117.9 (C18), 54.4 (C12), 51.4 (C20). ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6): δ = −70.2 (d). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ = −144.2 (m). ESI MS *m/z* = 818.4 (calcd. for [**4**]$^{2+}$ 818.2).

Synthesis of [5]$(PF_6)_2$



A quartz tube was charged with a sample of [**4**]$(PF_6)_2$ (18 mg, 0.009 mmol) and CH_3CN (10 mL). Under air and at ambient temperature, the solution was irradiated with a Philips high-pressure mercury lamp for 3 h. The solution was then filtered through Celite and the filtrate was concentrated under vacuum. Conversion was quantitative as judged from the ^{1}H NMR data. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.94 (s, 4H, H5), 7.80 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 8H, H8), 7.77 (s, 4H, H4), 7.74 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 8H, H7), 7.55 (s, 8H, H11), 6.81 (br s, 16H, H14, H15), 5.49 (s, 8H, H12), 4.25 (s, 4H, H17), 4.08 (s, 4H, H18), 3.68 (s, 12H, H20).

Synthesis of H_4-6$(PF_6)_4$



NH_4Cl (2 mg, 0.038 mmol) was added to a solution of [**5**]$(PF_6)_2$ (18 mg, 0.009 mmol) in MeOH (10 mL), and the mixture was stirred for 1 h. The suspension was then filtered and NH_4PF_6 (6 mg, 0.037 mmol) was added to the filtrate. After stirring the mixture for

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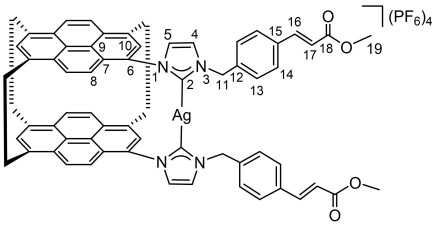
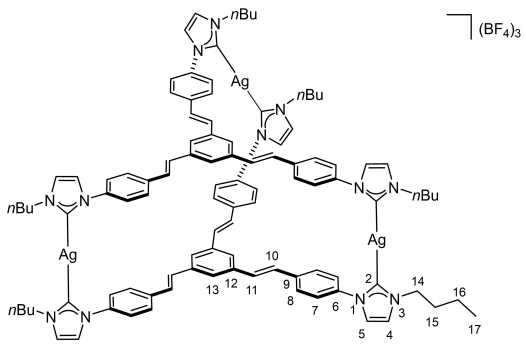
another 2 h, the desired tetrakisimidazolium salt precipitated. The salt was isolated by filtration, washed with diethyl ether and dried under vacuum to give H_4-**6**$(PF_6)_4$ as a white solid. Yield: 13.7 mg (0.0072 mmol, 80 %). ^{1}H NMR (300 MHz, CD_3CN): $\delta = 8.80$ (s, 4H, H2), 7.74 (d, $^3J_{H\text{-}H} = 8.6$ Hz, 8H, H8), 7.59 (m, 12H (8H, H11; 4H, H5)), 7.49 (d, $^3J_{H\text{-}H} = 8.6$ Hz, 8H, H7), 7.21 (d, $^3J_{H\text{-}H} = 8.1$ Hz, 8H, H14), 7.10 (d, $^3J_{H\text{-}H} = 8.1$ Hz, 12H (8H, H15; 4H H4), 5.13 (s, 8H, H12), 4.42 (d, $^3J_{H\text{-}H} = 6.1$ Hz, 4H, H17), 3.97 (d, $^3J_{H\text{-}H} = 6.1$ Hz, 4H, H18) 3.71 (s, 12H, H20). ^{13}C {^{1}H} NMR (101 MHz, CD_3CN): $\delta = 173.7$ (C19), 142.3, 141.3, 139.0, 135.1 (C6, C9, C10, C13), 134.7 (C2), 131.6 (C16), 129.9 (C14), 129.9 (C15), 129.3 (C7), 128.4 (C11), 123.5 (C5), 123.3 (C8), 122.5 (C4), 53.8 (C12), 52.7 (C20), 45.7 (C18), 43.2 (C17). ^{19}F {^{1}H} NMR (282 MHz, CD_3CN): $\delta = -72.8$ (d). ^{31}P {^{1}H} NMR (121 MHz, CD_3CN): $\delta = -144.6$ (m). ESI MS $m/z = 356.0$ (calcd. for $[H_4\text{-}\mathbf{6}]^{4+}$ 356.2), 523.5 (calcd. for $[H_4\text{-}\mathbf{6} + PF_6]^{3+}$ 523.2).

Synthesis of [7]$(PF_6)_4$



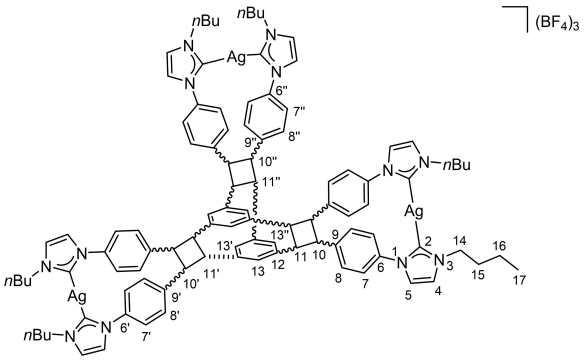
Under aerobic conditions, Ag_2O (39.6 mg, 0.171 mmol) was added to a solution of H_4-**2**$(PF_6)_4$ (100 mg, 0.057 mmol) in acetonitrile (20 mL). The mixture was stirred under exclusion of light for 72 h at 70 °C. After reaching ambient temperature, the resulting suspension was filtered through Celite. The filtrate was concentrated, and addition of diethyl ether (15 mL) produced a grey solid, which was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield 70 mg (0.021 mmol, 74 %). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 8.18$ (s, 4H, H10), 7.96 (s, 8H, H8), 7.56 (s, 8H, H5), 7.52 (d, $^3J_{H\text{-}H} = 16$ Hz, 8H, H16), 7.45 (m, 24H (16H, H13; 8H, H4)), 7.22 (d, $^3J_{H\text{-}H} = 7.8$ Hz, 16H, H14), 6.39 (d, $^3J_{H\text{-}H} = 16$ Hz, 8H, H17), 5.43 (d, $^2J_{H\text{-}H} = 6$ Hz, 16H, H11), 3.78 (s, 24H, H19). ^{13}C {^{1}H} NMR (101 MHz, CD_3CN): $\delta = 182.8$ (C2), 167.9 (C18), 144.3 (C16), 139.4 (C6), 135.5 (C12), 135.3 (C15), 129.9 (C9), 129.7 (C13), 129.6 (C7), 128.5 (C14), 127.4 (C10), 127.0 (C8), 124.2 (C4), 124.2 (C5), 119.5 (C17), 55.7 (C11), 52.4 (C19). ^{19}F {^{1}H} NMR (376 MHz, CD_3CN): $\delta = -72.5$ (d). ^{31}P {^{1}H} NMR (162 MHz, CD_3CN): $\delta = -144.6$ (m). ESI MS $m/z = 689.6$ (calcd. for $[\mathbf{7}]^{4+}$ 689.4), 967.8 (calcd. for $[\mathbf{7} + PF_6]^{3+}$ 967.5).

Synthesis of [8]$(BF_4)_3$



A mixture of H_3-**3**$(Br)_3$ (99 mg, 0.10 mmol) and Ag_2O (37 mg, 0.16 mmol) in methanol (10 mL) was stirred at 55 °C under exclusion of light for 16 h. The solvent was then removed under reduced pressure and $AgBF_4$ (29 mg, 0.15 mmol) and acetonitrile (10 mL) were added. The solution was then stirred for 12 h at 55 °C. Subsequently, the suspension was filtered twice trough Celite. The solvent was removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 (5 mL). This solution was again filtered through Celite. The filtrate was brought to dryness to give compound [**8**]$(BF_4)_3$ as a light brown solid. Yield: 98 mg (0.047 mmol, 94 %). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.95$ (d, $^3J_{H\text{-}H} = 1.6$ Hz, 6H, H5), 7.85 (d, $^3J_{H\text{-}H} = 1.6$ Hz, 6H, H4), 7.66 (d, $^3J_{H\text{-}H} = 8.5$ Hz, 12H, H7), 7.51 (d, $^3J_{H\text{-}H} = 8.5$ Hz, 12H, H8), 7.37 (s, 6H, H13), 7.19 (d, $^3J_{H\text{-}H} = 16.5$ Hz, 6H, H10), 7.14 (d, $^3J_{H\text{-}H} = 16.5$ Hz, 6H, H11), 4.36 (t, $^3J_{H\text{-}H} = 6.9$ Hz, 12H, H14), 2.02–1.88 (m, 12H, H15), 1.48–1.36 (m, 12H, H16), 1.00 (t, $^3J_{H\text{-}H} = 7.3$ Hz, 18H, H17). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): $\delta = 178.0$ (br, C2), 138.1 (C6), 137.1 (C9), 136.8 (C12), 129.4 (C11), 127.2 (C8), 126.8 (C10), 124.1 (C13), 123.1 (C4, C7), 122.1 (C5), 51.6 (C14), 33.2 (C15), 19.4 (C16), 13.5 (C17). HRMS (ESI, positive ions): m/z (%) = 608.5316 (100, calcd. for $[\mathbf{8}]^{3+}$ 608.5332). Anal. Calcd. for [**8**]$(BF_4)_3 \cdot H_2O$ ($C_{102}H_{108}Ag_3N_{12}B_3F_{12} \cdot H_2O$): C, 58.22; H, 5.27; N, 7.99. Found: C, 57.92; H, 4.79; N, 8.11 %.

Synthesis of [9]$(BF_4)_3$



A solution of [**8**]$(BF_4)_3$ (98 mg, 0.047 mmol) in CH_3CN (50 mL) was placed in a quartz Schlenk tube. The solution was irradiated with a Philips high-pressure mercury lamp for 16 h at 25 °C. The suspension was subsequently filtered through Celite and the filtrate was brought to dryness to give compound [**9**]$(BF_4)_3$ as an brownish solid. The conversion from [**8**]$(BF_4)_3$ to [**9**]$(BF_4)_3$ was quantitative as judged by ^{1}H NMR spectroscopy. The NMR spectra indicated the formation of 2 isomers depending on the conformation of the cyclobutane rings. The two isomers could not be separated, but their resonances in the NMR spectra were resolved based on 2D NMR data. Due to signal overlap, the relative amounts of the isomers could not be determined exactly. ^{1}H NMR (400 MHz, CD_3CN, isomer **A** with three different cyclobutanes): $\delta = 7.48$–7.33 (m, 12H, H4, H5), 7.32–7.16 (m, 24H, H7, H8), 6.98 (s, 2H, H13), 6.50 (s, 2H, H13′), 5.95 (s, 2H, H13″), 4.96 (d, $^3J_{H\text{-}H} = 6.2$ Hz, 2H H10), 4.92 (d, $^3J_{H\text{-}H} = 6.2$ Hz, 2H, H10′), 4.81 (d, $^3J_{H\text{-}H} = 6.5$ Hz, 2H, H11), 4.60 (d, $^3J_{H\text{-}H} = 6.7$ Hz, 4H, H10″, H11′), 4.53 (d, $^3J_{H\text{-}H} = 6.5$ Hz, H11″), 4.32–4.22 (m, 12H, H14), 1.96–1.93 (m, 12H, H15), 1.51–1.37 (m, 12H, H16), 1.04–0.96 (m, 18H, H17). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, isomer **A** with three different cyclobutanes): $\delta = 181.5$ (br, C2, only detectable by 2D NMR spectroscopy), 143.6, 143.2, 143.1 (C9, C9′, C9″), 143.1, 142.9, 142.6, (C12, C12′, C12″), 139.3, 139,2 (C6, C6′, C6″), 132.7 (br, C7, only detectable by 2D NMR spectroscopy), 130.5, 130.4, 128.5 (C13, C13′, C13″ only detectable by 2D NMR spectroscopy), 126.0, 125.9 (C8, C8′, C8″), 123.6, (C5), 123.1 (C4), 54.1 (C11), 53.8 (C11′), 53.7 (C11″), 52.8 (C14), 43.9 (C10), 43.8 (C10′), 43.8 (C10″), 34.5 (C15), 20.7 (C16), 14.1 (C17). ^{1}H NMR (400.1 MHz, CD_3CN, isomer **B** with three identical cyclobutanes): $\delta = 7.48$–7.33 (m, 12H, H4, H5), 7.32–7.16 (m, 24H, H7, H8), 6.47 (s, 6H, H13), 4.73 (d, $^3J_{H\text{-}H} = 6.5$ Hz, 6H, H11), 4.64 (d, $^3J_{H\text{-}H} = 6.5$ Hz, 6H, H10), 4.32–4.22 (m, 12H, H14), 1.96–1.93 (m, 12H, H15), 1.51–1.37 (m, 12H, H16), 1.04–0.96 (m, 18H,

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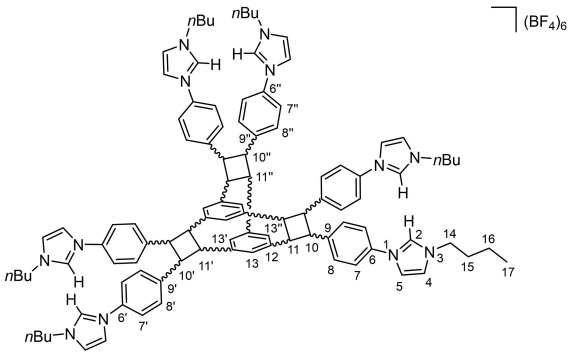
H17). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, isomer **B** with three identical cyclobutanes): $\delta = 181.5$ (br, C2, only detectable by 2D NMR spectroscopy), 143.5 (C9), 142.1 (C12), 139.3 (C6), 132.7 (br, C7, only detectable by 2D NMR spectroscopy), 130.5 (C13), 126.0 (C8), 123.6 (C5), 123.1 (C4), 54.0 (C11), 52.8 (C14), 43.9 (C10), 34.5 (C15), 20.7 (C16), 14.1 (C17). HRMS (ESI, positive ions): $m/z = 608.5326$ (100, calcd. for $[\mathbf{9}]^{3+}$ 608.5332).

Synthesis of H_6-10$(BF_4)_6$



A solution of $[\mathbf{9}](BF_4)_3$ (120 mg, 0.058 mol) and NH_4Cl (19 mg, 0.36 mmol) in MeOH (20 mL) was stirred for 2 h at 25 °C. A white solid (AgCl) immediately precipitated. The suspension was filtered through Celite and NH_4BF_4 (38 mg, 0.36 mmol) was added. The resulting solution was stirred at 25 °C for 2 h. After this time, a white solid precipitated, which was isolated by filtration. The solid was brought to dryness under vacuum to give compound H_6-$\mathbf{10}(BF_4)_6$ as a white powder. Yield: 70 mg (35 mmol, 60 %). Due the low solubility of H_6-$\mathbf{10}(BF_4)_6$, not all the carbon atom resonances were detected in the $^{13}C\{^1H\}$ NMR spectra. NMR spectra showed resonances for two isomeric reaction products, one with three identical and one with three different cyclobutane-units. The two isomers could not be separated, but the two different spin systems were resolved by 2D ^1H NMR spectroscopy. Due of the overlap between the resonances of the two isomers, the relative amounts of the isomers could not be determined exactly. ^1H NMR (400 MHz, DMSO-d_6, isomer **A** with three different cyclobutanes): $\delta = 9.72$ (s, 6H, H2), 8.25 (s, 6H, H4), 8.02 (s, 6H, H5), 7.83–7.46 (m, 24H, H7, H8), 6.80 (s, 2H, H13), 6.41 (s, 2H, H13′), 5.86 (s, 2H, H13″), 4.90 (s, 2H, H10), 4.87 (s, 2H, H10′), 4.69 (s, 2H, H11), 4.60 (s, 2H, H10″), 4.48 (s, 2H, H11′), 4.45 (s, 2H, H11″), 4.22 (m, 12H, H14), 1.84 (m, 12H, H15), 1.32 (m, 12 H, H16), 0.93 (t, $^3J_{H\text{-}H} = 7.5$ Hz, 18H, H17). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, isomer **A** with three different cyclobutanes): $\delta = 143.4$, 143.3, 142.9 (C9, C9′, C9″, by 2D NMR), 136.8, (C12, C12′, C12″, by 2D NMR), 134.8 (C2), 132.5 (C6), 131.1 (C13, by 2D NMR), 129.8 (C8), 128.9 (C13′), 128.8 (C13″), 123.3 (C4), 120.9 (C7), 120.7 (C5), 54.5, 54.0 (C11, C11′, C11″), 49.0 (C14) 44.3 (C10, by 2D NMR), 44.2 (C10′, by 2D NMR), 44.1 (C10″, by 2D NMR), 31.0 (C15), 18.7 (C16), 13.2 (C17). ^1H NMR (400 MHz, DMSO-d_6, isomer **B** with three identical cyclobutanes): $\delta = 9.72$ (s, 6H, H2), 8.25 (s, 6H, H4), 8.02 (s, 6H, H5), 7.83–7.46 (m, 24H, H7, H8), 6.37 (s, 6H, H13), 4.63 (s, 12H, H10, H11), 4.22 (m, 12H, H14), 1.84 (m, 12H, H15), 1.32 (m, 12H, H16), 0.93 (t, $^3J_{H\text{-}H} = 7.5$ Hz, 18H, H17). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, isomer **B** with three identical clobutanes): $\delta = 142.8$ (C9, by 2D NMR) 136.8 (C12, by 2D NMR), 134.8 (C2), 132.5 (C6), 129.8 (C8), 128.9 (C13), 123.3 (C4), 120.9 (C7), 120.7 (C5), 54.5 (C11), 49.0 (C14) 44.2 (C10, by 2D NMR), 31.0 (C15), 18.7 (C16), 13.2 (C17). HRMS (ESI, positive ions): $m/z = 251.1542$ (100, calcd. for $[H_6\text{-}\mathbf{10}]^{6+}$ 251.1548), 318.9866 (40, calcd. for $[H_6\text{-}\mathbf{10} + BF_4]^{5+}$ 318.9872), 420.4844 (10, calcd. for $[H_6\text{-}\mathbf{10} + 2BF_4]^{4+}$ 420.4849), 589.31363 (8, calcd. for $[H_6\text{-}\mathbf{10} + 3BF_4]^{3+}$ 589.3139), 927.4733 (8, calcd. for $[H_6\text{-}\mathbf{10} + 4BF_4]^{2+}$ 927.4727).

X-ray diffraction studies

Compound $[\mathbf{8}](BPh_4)_3 \cdot 2CH_3CN$ was obtained by stirring samples of $[\mathbf{8}](BF_4)_3$ (50 mg, 0.024 mmol) and $NaBPh_4$ (25 mg, 0.073 mmol) in acetonitrile. Crystals suitable for X-ray diffraction studies of $[\mathbf{8}](BPh_4)_3 \cdot 2MeCN$ were obtained by slow diffusion of diethyl ether into a concentrated solution of $[\mathbf{8}](BPh_4)_3$ in acetonitrile. X-ray diffraction data were collected with an Agilent SuperNova diffractometer equipped with an Atlas CCD detector at 100(2) K using Mo Kα ($\lambda = 0.71073$ Å) radiation. Semiempirical multi-scan absorption corrections were applied to the set. The structure solution was found with SHELXT[18] and were refined with SHELXL[19] against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms have been added to the structure models on calculated positions. Crystal data for $[\mathbf{8}](BPh_4)_3 \cdot 2MeCN$: Formula $C_{178}H_{174}N_{14}Ag_3B_3N_{14}$, $M = 2865.36$ g mol^{-1}, colorless prism, $0.02 \times 0.02 \times 0.08$ mm^3, triclinic, space group P-1, $Z = 6$, $a = 21.0858(6)$, $b = 28.4587(8)$, $c = 39.5416(12)$ Å, $\alpha = 75.042(2)$, $\beta = 82.599(2)°$, $\gamma = 76.552(2)$, $V = 22235.5(12)$ Å^3, $\rho_{calcd} = 1.284$ g cm^{-1}, $\mu = 0.451$ mm^{-1}, 223317 measured intensities ($1.5° \leq 2\Theta \leq 50.1°$), semiempirical absorption correction ($0.991 \leq T \leq 0.965$), 78402 independent intensities ($R_{int} = 0.0832$) and 52901 observed intensities ($I \geq 2\sigma(I)$), refinement of 5761 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. $R = 0.0820$, $R_w = 0.2038$, $R_{all} = 0.1226$, $R_{w,all} = 0.2245$. The asymmetric unit contains three formula unit of $[\mathbf{8}](BPh_4)_3$ and six molecules of CH_3CN. In addition, three badly disordered acetonitrile molecules were found in the asymmetric unit. The program PLATON-SQEEZE[20] was therefore used to remove mathematically the effect of these solvent molecules. The quoted formula and derived parameters[21] do not include the squeezed solvent molecules.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbene ligands · Macrocycles · Post-assembly modification · Silver · Supramolecular assemblies

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