PAPER

Synthesis and crystal structures of twisted three-dimensional assemblies of adamantane-bridged tris-NHC ligands and Ag[I]†

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Two adamantane-bridged tripodal trisimidazolium or trisbenzimidazolium salts were designed as C_{3v}-symmetrical tricarbene ligands and synthesized in good yields. The reaction of the tripodal trisazolium salt precursors with silver oxide provided trisilver hexacarbene complexes bearing a three-dimensional framework. Multinuclear NMR spectroscopy and mass spectrometry data showed that the complexes were symmetric structures of two tricarbene ligands, three metal ions, and three counter anions. X-ray crystallographic analyses revealed that both complex cations adopted a highly twisted conformation. The complex cations built from the trisimidazolium salts were arranged into columnar structures through CH/π interactions, which were assembled into a three-dimensional network structure by intermolecular CH/F interactions *via* hexafluorophosphate anions. The complex cations generated from the trisbenzimidazolium salts were aligned into columnar structures, which were arranged into a network structure through CH/π interactions. Solvents and counter anions were accommodated in the spaces of the crystalline lattices.

Introduction

Metal-mediated three-dimensional (3D) structures have gained attention because of their potential applications in molecular encapsulation, cavity-directed catalytic transformations, and stabilization of reactive intermediates.[1–4] Various types of 3D structures including cages, capsules, cylinders, boxes, and tubes have been made from appropriate combinations of multidentate organic ligands and metal ions. These metal–organic frameworks based on Werner-type metal complexes have been of particular interest for the last two decades. Recently, many different N-heterocyclic carbenes (NHCs) and their metal complexes have received interest owing to a wide variety of applications in homogeneous and asymmetric catalysis and luminescence.[5–7] The production of discrete 3D metallosupramolecular complexes in cylinder-like

and tubular structures from organometallic frameworks has been successfully realized through the formation of stable M–C_{NHC} bonds between poly-NHC ligands and metal atoms.[8] For instance, Meyer and co-workers have constructed a silver NHC complex from a neopentane-based tripodal carbene ligand.[9] Hahn and co-workers showed that a series of disk-shaped poly-NHC ligands could self-assemble into multinuclear cylinder-like structures of various sizes and shapes.[10] The preparation of box- and cylinder-like structures from macrocyclic poly-NHC ligands has been reported by several groups.[11] The design of these poly-NHC ligands is crucial in determining the size, shape, and conformation of the resulting organometallic assembly. C_3-symmetric, relatively flexible C_{3v}-symmetrical and macrocyclic NHC ligands have been used; however, the use of rigid C_{3v}-symmetrical tricarbene ligands for the creation of well-defined complexes remains less explored. Herein, we report the efficient preparation of two adamantane-derived tris-NHC ligands bearing imidazolium or benzimidazolium salts and their trisilver hexacarbene complexes. X-ray crystallographic analysis revealed that both complexes possess a 3D organometallic framework that has an exceedingly twisted conformation in the solid state. The helical trisilver complex cations were arranged into columnar structures, which further assembled into network structures by multiple intermolecular interactions.

We have previously shown that adamantane derivatives can be useful building blocks for the design and synthesis

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† Electronic supplementary information (ESI) available: Characterization data of ^{1}H and ^{13}C NMR spectra for all precursors and complexes, mass spectra for complexes 3 and 6, and crystallographic information files (CIFs) of complexes 3 and 6. The crystal structure depository numbers for 3 and 6 are CCDC 1420798 and 1420799. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce01860a
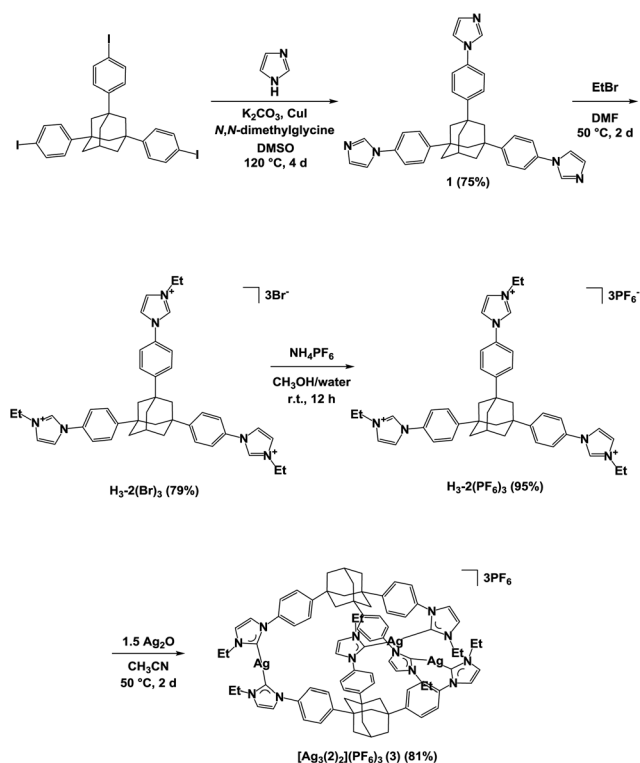
of macrocycles and cages, and allow unique guest-inclusion abilities and self-assembly behaviors over the past few years.[12] We selected trisubstituted adamantane derivatives for further investigation, as they have been versatile candidates for C_{3v}-symmetric tricarbene ligands. They are rigid and well-defined, and have highly symmetric skeletons. Thus, we have designed novel molecular-based organometallic assemblies, which were constructed from two tripodal 1,3,5-triphenyladamantane-derived trisimidazolium or trisbenzimidazolium salts and three metal ions.

Results and discussion

The synthesis of the trisimidazolium salt H_3-2(PF_6)$_3$ is depicted in Scheme 1. The copper(I)-catalyzed reaction of imidazole with 1,3,5-tris(4-iodophenyl)adamantane gave the corresponding tripodal adamantane derivative (1). Alkylation of the three imidazoles in 1 with ethyl bromide gave the product after anion exchange with ammonium hexafluorophosphate, H_3-2(PF_6)$_3$. The reaction of silver oxide (0.15 mmol) with the trisimidazolium salt H_3-2(PF_6)$_3$ (0.10 mmol) in a 3:2 stoichiometry in acetonitrile (10 mL) at 50 °C for 2 days resulted in the formation of the trisilver hexacarbene complex [Ag_3(2)$_2$](PF_6)$_3$ (3) in 81% yield. The ^{1}H NMR spectrum of the product showed that the peak corresponding to the imidazolium proton in H_3-2(PF_6)$_3$ at 8.91 ppm had disappeared, inferring the production of a carbene complex. In the ^{13}C NMR spectrum of 3, the resonance from the

carbene carbon atoms in the complex was observed at 180.0 ppm, which is consistent with values previously reported for other silver carbene complexes.[10] Furthermore, only four signals are observed in the aromatic region of the ^{1}H NMR spectrum of 3, indicating that the ligands are equivalent and symmetric in the product. In addition to the NMR analysis, cold-spray ionization MS (CSI-MS) confirmed the desired composition of 3, having three silver atoms, three hexafluorophosphate anions, and two adamantane-bridged imidazolin-2-ylidene ligands. Two peaks were found in the mass spectrum: at m/z 1907.4020, corresponding to [$M - PF_6$]$^+$, and m/z 881.2183, corresponding to [$M - 2PF_6$]$^{2+}$ (Fig. S1 in the ESI†). The isotopic distributions in the peaks were consistent with their calculated theoretical pattern. Complex 3 can be dissolved in many organic solvents including dimethyl sulfoxide, methanol, acetonitrile, and acetone, but is only sparingly soluble in chloroform, diethyl ether, hexane, and toluene.

The molecular structure of complex 3 was determined by single-crystal X-ray analysis (Fig. 1). Single crystals were obtained from vapor diffusion of 1,4-dioxane into an acetonitrile solution of 3. The compound crystallized in the space group $P2_1/c$, which contains one molecule of 3 and six molecules of 1,4-dioxane in the asymmetric unit. The molecular structure of the complex cation [Ag_3(2)$_2$]$^{3+}$ showed a 3D structure with a twisted conformation. The complex had small internal spaces within the framework, which were too small
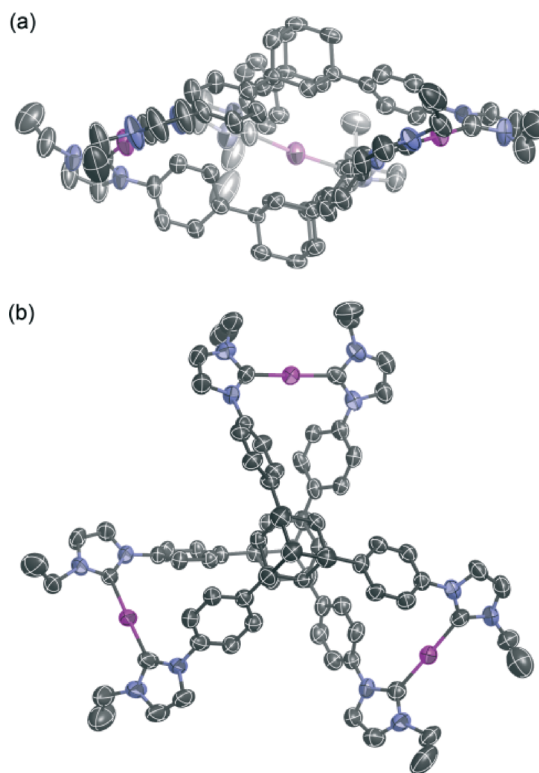

Fig. 1 The molecular structure of the complex cation in 3. (a) Side view and (b) top view. Ellipsoids are drawn at the 50% probability level. Solvent molecules, counter anions, and hydrogen atoms have been omitted for clarity.

Scheme 1 Preparation of the trisimidazolium salt H_3-2(PF_6)$_3$ and the complex [Ag_3(2)$_2$](PF_6)$_3$ (3).

to allow for the encapsulation of small organic molecules. The centroid–centroid distance between the two adamantane moieties is 6.66 Å, and the three distances between the silver atoms are 12.53, 12.92, and 13.36 Å. The complex cation has chirality, arising from the direction of the twist in the triphenyladamantane moieties, where the torsion angle between the two triphenyladamantane parts of **3** is 43.0°. There exist two pairs of enantiomeric conformers of the complex cation with (*M*)- and (*P*)-helicity in the unit cell, meaning that the crystals have no overall chirality. The three pairs of phenyl rings are nearly vertical to each other, where the angles between the planes of the benzene moieties are 65.3, 76.2, and 87.3°. The centers of the three pairs of phenyl rings are separated by 4.99–5.01 Å. The torsion angles between the planes of the phenyl and imidazolin-2-ylidene rings range from 35.6 to 50.5°. The distances of Ag–$C_{carbene}$ and the $C_{carbene}$–Ag–$C_{carbene}$ angles in **3** are 2.06–2.09 Å and 174.8–178.8°, respectively. It is noteworthy that the angles between the plane of the three metal centers and the plane of the metal-mediated imidazolin-2-ylidene rings are 12.0, 14.5, and 20.6°. Each complex cation has a columnar structure formed through CH/π interactions between the adamantane parts and imidazolin-2-ylidene rings and phenyl groups along the *c* axis (Fig. 2a), containing alternating enantiomers of the complex cation. These columns interacted with the hexafluorophosphate anions *via* multiple CH/F interactions[13] between the hydrogen atoms of the imidazolin-2-ylidene, ethyl, and phenyl groups and the fluorine atoms of the hexafluorophosphate anions (Fig. 2b). This gives an overall 3D network. The solvent molecules were accommodated within the spaces of the network structures.

Similarly, we constructed a trisilver hexacarbene complex $[Ag_3(5)_2](PF_6)_3$ (**6**), where an adamantane-derived trisbenzimidazolium salt was used as the tris-NHC ligand. The trisbenzimidazolium salt H_3-$5(PF_6)_3$ was synthesized in good yield according to Scheme 2. Mixing silver oxide (0.15 mmol) and H_3-$5(PF_6)_3$ (0.10 mmol) in a 3 : 2 stoichiometry gave the trisilver hexacarbene complex $[Ag_3(5)_2](PF_6)_3$ (**6**) in 85% yield. ^{1}H and ^{13}C NMR data for the product indicated similar results to the complex $[Ag_3(2)_2](PF_6)_3$ (**3**). The mass spectrum had two peaks: at *m/z* 1031.2670, corresponding to $[M - 2PF_6]^{2+}$, and *m/z* 639.1885, corresponding to $[M - 3PF_6]^{3+}$, indicating that it was the desired complex (Fig. S2 in the ESI†). Complex **6** dissolves in many organic solvents including dimethyl sulfoxide, acetonitrile, and acetone, but is only sparingly soluble in methanol, hexane, chloroform, diethyl ether, and toluene.

Single crystals were obtained from the vapor diffusion of 1,4-dioxane into an acetonitrile solution of **6**. The complex crystallized in the space group $P2_1/c$, and has one molecule of **6**, two molecules of 1,4-dioxane and one molecule of acetonitrile in the asymmetric unit. In the crystal structure of **6**, the complex cation $[Ag_3(5)_2]^{3+}$ adopted a similar conformation to $[Ag_3(2)_2]^{3+}$ despite the introduction of the bulky benzimidazolin-2-ylidene ring (Fig. 3). The centroid–centroid distance between the two adamantane moieties is 6.69 Å, and
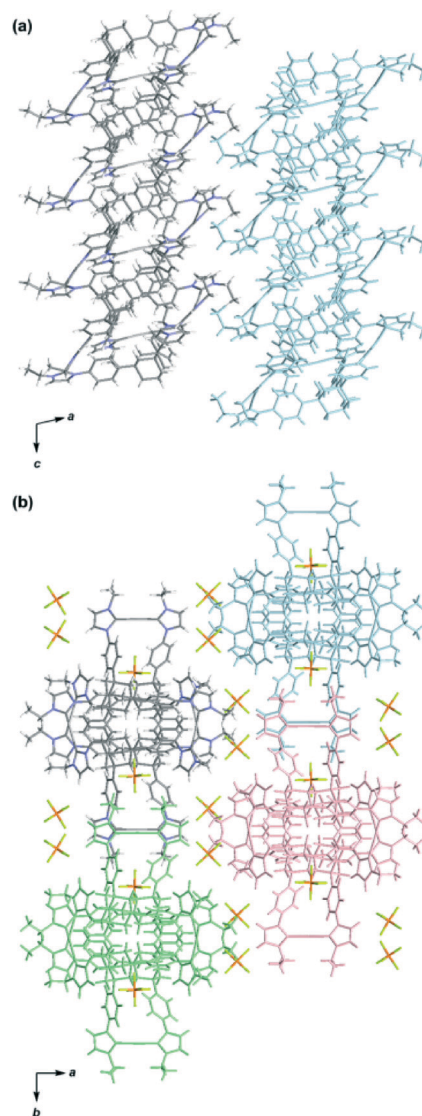

Fig. 2 Packing diagram of the complex $[Ag_3(2)_2](PF_6)_3$ (**3**). (a) Side view of the columns parallel to the *c* axis; included solvent molecules and counter anions were omitted for clarity. (b) Top view of the network structure; solvent molecules were omitted for clarity. The molecules of neighbouring columns are colored light blue, pink, and light green.

the three distances between the silver atoms are 12.46, 12.87, and 12.89 Å. The torsion angle between the two triphenyladamantane parts of **6** is 43.3°. Again, the complex cation contains two helical enantiomers per unit cell. In the three pairs of phenyl rings, the two pairs are nearly vertical, and the other is almost parallel to each other. The angles between the ring planes of the benzene moieties are 7.5, 63.5, and 78.2°. The distances between the centers of the three pairs of phenyl rings are 4.83, 5.13, and 5.25 Å. The torsion angles between the planes of the phenyl and benzimidazolin-2-ylidene rings range from 48.4 to 55.7°. The distances of Ag–$C_{carbene}$ and the angles of $C_{carbene}$–Ag–$C_{carbene}$ in **6** are 2.07–2.10 Å and 175.2–177.9°. The angles between the plane of the three metal centers and the plane of the metal-mediated benzimidazolin-2-ylidene rings are 8.7, 19.4,
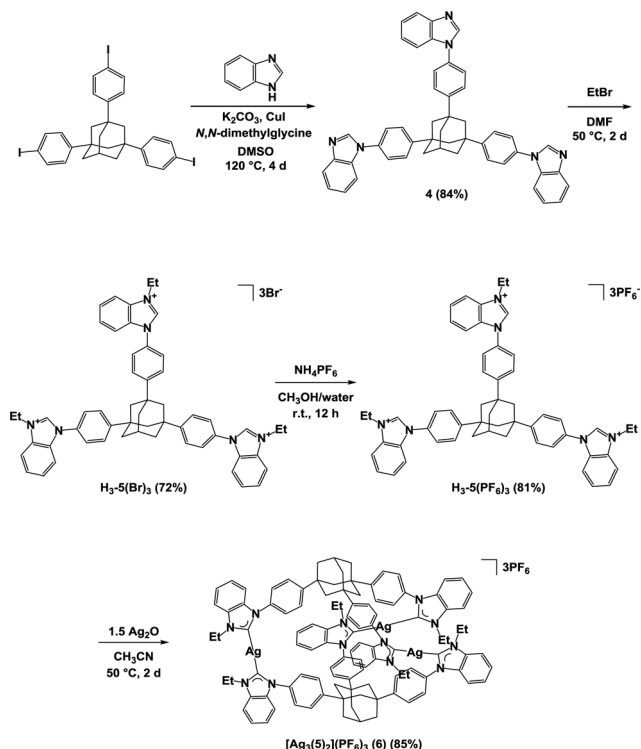
Scheme 2 Preparation of the trisbenzimidazolium salt H_3-5(PF_6)$_3$ and the complex [Ag$_3$(5)$_2$](PF$_6$)$_3$ (6).

and 22.5°. Individual complex cations were arranged into a columnar structure *via* CH/π interactions between benzimidazolin-2-ylidene, phenyl, and adamantyl groups along the *b* axis (Fig. 4a), containing alternating enantiomers of the complex cation. The columns were assembled into a network structure through CH/π interactions between benzimidazolin-2-ylidene, phenyl, and ethyl groups (Fig. 4b). Hexafluorophosphate anions interacted with benzimidazolin-2-ylidene, phenyl, ethyl, and adamantyl groups *via* CH/F interactions. Solvent molecules were included in the spaces of the network structures.

Hahn and Peris *et al.* demonstrated that C_3-symmetrical tricarbene ligands can form trinuclear silver(ɪ), gold(ɪ), and copper(ɪ) carbene complexes, which adopt a twisted conformation in the solid state.[10] In comparison with these complex cations, the distortions between the rigid tripodal parts in 3 and 6 are similar. The angles between the plane of the three metal centers and the plane of the metal-mediated imidazolin-2-ylidene or benzimidazolin-2-ylidene rings were nearly parallel, showing the helical structures having enormously twisted conformations. Recently, a double-stranded NHC-helicate from a pentadentate diNHC ligand was studied by Huynh and co-workers.[14a] The research on extended organometallic frameworks containing this twisted complex cation is quite restricted,[14] whereas there are several examples of twisted structures made up of Werner-type metal–organic frameworks.[15] Accordingly, tripodal adamantane-
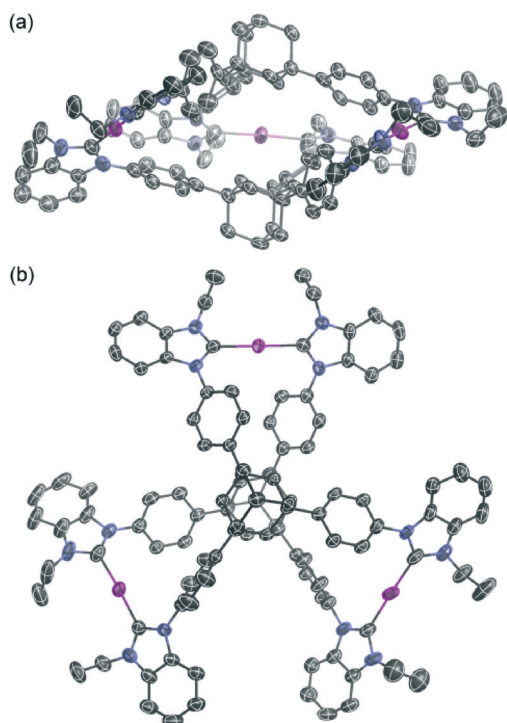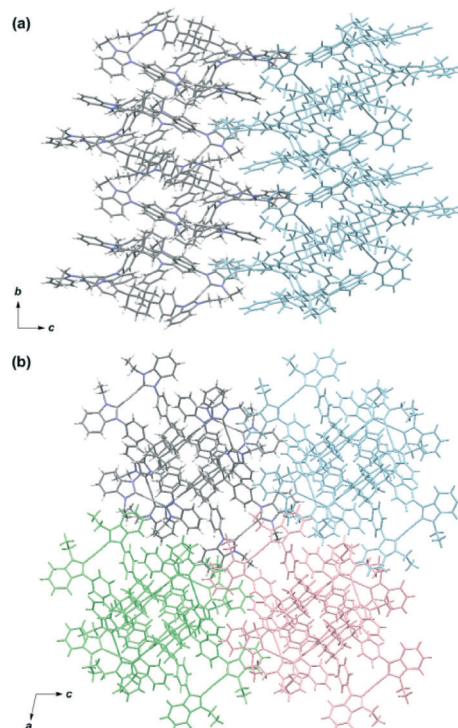

Fig. 3 The molecular structure of the complex cation in 6. (a) Side view and (b) top view. Ellipsoids are drawn at the 50% probability level. Solvent molecules, counter anions, disordered atoms, and hydrogen atoms have been omitted for clarity.

Fig. 4 Packing diagram of the silver complex [Ag$_3$(5)$_2$](PF$_6$)$_3$ (6). (a) Side view of the columnar structure along the *b* axis. (b) Top view of the network structure. Solvent molecules and counter anions were omitted for clarity. The molecules of neighbouring columns are colored light blue, pink, and light green.

based tricarbene ligands of non-disk-shaped C_{3v}-symmetrical molecules to bend disk-shaped C_3-symmetrical compounds are applicable building blocks for the creation of helical organometallic assemblies.

Conclusions

In summary, we have demonstrated that tripodal adamantane-derived tris-NHC ligands can be used for the construction of well-defined 3D trisilver hexacarbene complexes with a twisted conformation. This was achieved through metal-directed self-assembly, where two tricarbene ligands were bridged with three metal atoms. Two metallosupramolecular structures were obtained in high yields without the generation of other oligomeric and polymeric by-products, and this shows that the use of non-disk-shaped C_{3v}-symmetrical ligands does not inhibit the self-assembly process. These results provide a strategy for the design of twisted 3D organometallic assemblies and the exploitation of helical structures. Studies on the preparation and applications of 3D NHC complexes bearing other metal centers and chiral counter anions are ongoing in our laboratory.

Experimental

General procedure

All reagents and solvents were obtained from commercial suppliers and used without further purification. The synthesis of 1,3,5-tris(4-iodophenyl)adamantane was performed according to the literature.[16] Melting points were determined using an ATM-01. IR spectra were recorded on a Jasco FT/IR-6300. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer at 298 K in CDCl₃ or DMSO-d_6 with trimethylsilane as the reference, and CD₃OD or CD₃CN. X-ray crystal structure data were collected using a Bruker SMART APEX II diffractometer with Mo Kα radiation and a Bruker D8 VENTURE diffractometer with Cu Kα radiation. Column chromatography was performed on a Wakogel C200, and thin-layer chromatography was carried out on 2.0 mm Merck precoated silica gel glass plates. Gel permeation chromatography was performed using a recycling preparative HPLC (LC-9204, Japan Analytical Industry Co., Ltd.) and a JAIGEL H series column (Japan Analytical Industry Co., Ltd.). HRMS and CSI-MS measurements were performed using a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS; Apex-Qe 9.4 T, Bruker Daltonics, Inc. Billerica, MA). We could not perform satisfactory elemental analyses of the precursors and the complexes in several attempts, presumably due to their hydroscopic nature and the large amount of fluorine present, and to the capability of their molecules to keep the solvents.

Synthesis of 1,3,5-tris(4-(imidazol-1-yl)phenyl)adamantane (1)

A mixture of 1,3,5-tris(4-iodophenyl)adamantane (7.42 g, 10.0 mmol), potassium carbonate (8.29 g, 60.0 mmol), N,N-dimethylglycine (0.62 g, 6.0 mmol), imidazole (4.08 g, 60.0

mmol), and CuI (0.57 g, 3.0 mmol) in dry dimethyl sulfoxide (100 mL) was stirred at 120 °C for 4 days under an argon atmosphere. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in chloroform and water, and the solution was washed with water and brine and dried over sodium sulfate. After removal of the solvent, silica gel column chromatography (eluent: CHCl₃ : MeOH = 20 : 1) and gel permeation chromatography (eluent: CHCl₃) of the residue afforded the title compound as a white solid (4.20 g, 7.46 mmol) in 75% yield. M.p. 162–163 °C. FT-IR (ATR, cm⁻¹): 2916, 2851, 1521, 1507, 1490, 1304, 1219, 1054, 964, 772, 728. ^{1}H NMR (400 MHz, CDCl₃) δ 7.85 (s, 3H), 7.56 (d, J = 8.8 Hz, 6H), 7.39 (d, J = 8.4 Hz, 6H), 7.28 (s, 3H), 7.21 (s, 3H), 2.65 (br s, 1H), 2.20–2.13 (m, 6H), 2.08 (br d, J = 2.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl₃) δ 148.9, 135.6, 135.5, 130.4, 126.4, 121.5, 118.3, 48.0, 41.2, 38.3, 29.9. HRMS (ESI, m/z) calcd for $C_{37}H_{35}N_6$ [M + H]⁺ 563.2918, found 563.2912.

Synthesis of 1,3,5-tris(4-(3-ethylimidazol-1-yl)phenyl)adamantane tribromide, H₃-2(Br)₃

1,3,5-Tris(4-(imidazol-1-yl)phenyl)adamantane (1) (0.42 g, 0.75 mmol) was dissolved in dry N,N-dimethylformamide (20 mL), and ethyl bromide (0.98 g, 9.0 mmol) was added. The reaction mixture was stirred at 50 °C for 2 days under an argon atmosphere. The reaction mixture was evaporated under reduced pressure. The white solids were dissolved in methanol, and diethyl ether was added. The resulting precipitate was isolated by filtration and, after washing with diethyl ether, the title compound was dried *in vacuo* to give a white solid (0.53 g, 0.60 mmol) in 79% yield. M.p. 244–246 °C. FT-IR (ATR, cm⁻¹): 2922, 2850, 1653, 1550, 1516, 1457, 1260, 1210, 1140, 1071, 1018, 828, 771, 746. ^{1}H NMR (400 MHz, CD₃OD) δ 9.67 (s, 3H), 8.11 (s, 3H), 7.92 (s, 3H), 7.84–7.78 (m, 12H), 4.44 (q, J = 7.2 Hz, 6H), 2.62 (br s, 1H), 2.29–2.11 (m, 12H), 1.65 (t, J = 7.2 Hz, 9H). ^{13}C NMR (100 MHz, CD₃-OD) δ 153.4, 136.0, 134.3, 128.4, 124.2, 123.1, 122.8, 48.6, 46.6, 41.9, 39.8, 31.4, 15.6. HRMS (ESI, m/z) calcd for $C_{43}H_{47}N_6$ [M − 2H − 3Br]⁺ 647.3857, found 647.3855.

Synthesis of 1,3,5-tris(4-(3-ethylimidazol-1-yl)phenyl)adamantane tris(hexafluorophosphate), H₃-2(PF₆)₃

A solution of ammonium hexafluorophosphate (0.38 g, 2.3 mmol) in methanol (3.0 mL) was added to a methanol solution (7.0 mL) of compound H₃-2(Br)₃ (0.53 g, 0.60 mmol). The white hexafluorophosphate salt precipitated instantly. Water was added into the reaction mixture and stirred for 12 h at room temperature. The precipitates were isolated by filtration and, after washing with methanol and diethyl ether, the title compound was dried *in vacuo* to give a white solid (0.62 g, 0.57 mmol) in 95% yield. M.p. 266–267 °C. FT-IR (ATR, cm⁻¹): 2929, 2858, 1653, 1559, 1516, 1507, 1457, 1213, 1078, 1021, 838, 772, 739. ^{1}H NMR (400 MHz, CD₃CN) δ 8.91 (s, 3H), 7.80 (d, J = 8.8 Hz, 6H), 7.78 (t, J = 2.0 Hz, 3H), 7.63–7.60 (d, J = 8.8 Hz and s, 9H), 4.29 (q, J = 7.2 Hz, 6H), 2.60 (br t, J = 2.8 Hz, 1H), 2.25–2.17 (m, 6H), 2.09 (br d, J = 2.4 Hz, 6H),

1.56 (t, J = 7.2 Hz, 9H). ^{13}C NMR (100 MHz, CD$_3$CN) δ 153.3, 135.2, 133.9, 128.3, 123.9, 123.2, 122.7, 47.8, 46.4, 41.5, 39.6, 31.1, 15.3. HRMS (ESI, m/z) calcd for C$_{43}$H$_{49}$F$_{12}$N$_6$P$_2$ [M − PF$_6$]$^+$ 939.3297, found 939.3252.

Synthesis of [Ag$_3$(2)$_2$](PF$_6$)$_3$ (3)

Compound H$_3$-2(PF$_6$)$_3$ (0.11 g, 0.10 mmol) was dissolved in dry acetonitrile (10 mL), and silver oxide (35 mg, 0.15 mmol) was added. The suspension was stirred at 50 °C for 2 days under exclusion of light and an argon atmosphere. After cooling to room temperature, the resulting mixture was filtered over celite to give a solution. The filtrate was concentrated to 2 mL, and the addition of diethyl ether into this solution resulted in the precipitation of a white solid. The precipitate was isolated by filtration upon washing with diethyl ether, and the title compound was dried *in vacuo* to give a white solid (0.08 g, 0.04 mmol) in 81% yield. M.p. > 300 °C (decomposed). FT-IR (ATR, cm^{-1}): 2921, 2852, 1559, 1516, 1471, 1424, 1267, 1223, 1017, 951, 837, 736. ^{1}H NMR (400 MHz, CD$_3$CN) δ 7.55 (d, J = 8.4 Hz, 12H), 7.52 (d, J = 2.0 Hz, 6H), 7.43 (d, J = 1.6 Hz, 6H), 7.27 (d, J = 8.4 Hz, 12H), 4.30 (q, J = 6.4 Hz, 12H), 2.47 (br s, 2H), 2.06 (br d, J = 12.0 Hz, 6H), 1.99 (br s, 12H), 1.89 (br d, J = 12.0 Hz, 6H), 1.53 (t, J = 7.2 Hz, 18H). ^{13}C NMR (100 MHz, CD$_3$CN) δ 180.0, 150.9, 139.2, 127.2, 124.6, 123.1, 122.8, 49.0, 48.2, 41.3, 39.2, 30.7, 17.4. HRMS (CSI, m/z) calcd for C$_{86}$H$_{92}$Ag$_3$F$_6$N$_{12}$P [M − 2PF$_6$]$^{2+}$ 881.2175, found 881.2183.

Synthesis of 1,3,5-tris(4-(benzimidazol-1-yl)phenyl)adamantane (4)

The title compound was synthesized in 84% yield as a white solid in a similar manner to the preparation of 1,3,5-tris(4-(imidazol-1-yl)phenyl)adamantane (1). M.p. 168–169 °C. FT-IR (ATR, cm^{-1}): 2922, 2854, 1516, 1489, 1455, 1340, 1284, 1229, 1048, 976, 839, 738. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (s, 3H), 7.90 (d, J = 5.2 Hz, 3H), 7.70 (d, J = 8.8 Hz, 6H), 7.57–7.52 (m, 9H), 7.37–7.32 (m, 6H), 2.73 (br s, 1H), 2.32–2.24 (m, 6H), 2.17 (br d, J = 2.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.5, 144.1, 142.3, 134.5, 134.0, 126.7, 124.0, 123.7, 122.8, 120.7, 110.5, 48.1, 41.2, 38.5, 30.0. HRMS (ESI, m/z) calcd for C$_{49}$H$_{41}$N$_6$ [M + H]$^+$ 713.3387, found 713.3381.

Synthesis of 1,3,5-tris(4-(3-ethylbenzimidazol-1-yl)phenyl)adamantane tribromide, H$_3$-5(Br)$_3$

The title compound was synthesized in 72% yield as a white solid in a similar manner to the preparation of H$_3$-2(Br)$_3$. M. p. 243–245 °C. FT-IR (ATR, cm^{-1}): 2920, 2854, 1559, 1540, 1507, 1472, 1340, 1233, 1191, 1041, 1013, 986, 839, 779. ^{1}H NMR (400 MHz, CD$_3$OD) δ 9.93 (s, 3H), 8.12 (d, J = 7.6 Hz, 3H), 7.99 (d, J = 8.8 Hz, 6H), 7.87–7.74 (m, 15H), 4.71 (q, J = 7.2, Hz, 6H), 2.73 (br s, 1H), 2.46–2.24 (m, 12H), 1.76 (t, J = 7.2 Hz, 9H). ^{13}C NMR (100 MHz, CD$_3$OD) δ 154.2, 142.6, 133.3, 132.9, 132.7, 128.9, 128.7, 128.6, 126.2, 114.8, 114.7, 44.18, 44.16, 42.0, 40.1, 31.6, 14.6. HRMS (ESI, m/z) calcd for C$_{55}$H$_{54}$BrN$_6$ [M − H − 2Br]$^+$ 877.3588, found 877.3585.

Synthesis of 1,3,5-tris(4-(3-ethylbenzimidazol-1-yl)phenyl)adamantane tris(hexafluorophosphate), H$_3$-5(PF$_6$)$_3$

The title compound was synthesized in 81% yield as a white solid in a similar manner to the preparation of H$_3$-2(PF$_6$)$_3$. M. p. > 300 °C (decomposed). FT-IR (ATR, cm^{-1}): 2922, 2855, 1653, 1559, 1540, 1507, 1472, 1340, 1272, 1231, 1190, 1041, 986, 840, 746. ^{1}H NMR (400 MHz, CD$_3$CN) δ 9.23 (s, 3H), 8.01 (d, J = 8.4 Hz, 3H), 7.94 (d, J = 8.4 Hz, 6H), 7.80–7.72 (m, 15H), 4.60 (q, J = 7.2 Hz, 6H), 2.70 (br s, 1H), 2.39–2.29 (m, 6H), 2.20 (br s, 6H), 1.69 (t, J = 7.6 Hz, 9H). ^{13}C NMR (100 MHz, CD$_3$CN) δ 153.9, 141.5, 133.0, 132.5, 132.2, 128.8, 128.5, 128.4, 126.0, 114.70, 114.68, 48.0, 44.1, 41.5, 39.8, 31.1, 14.5. HRMS (ESI, m/z) calcd for C$_{55}$H$_{55}$F$_{12}$N$_6$P$_2$ [M − PF$_6$]$^+$ 1089.3766, found 1089.3756.

Synthesis of [Ag$_3$(5)$_2$](PF$_6$)$_3$ (6)

The title compound was synthesized in 85% yield as a white solid in a similar manner to the preparation of [Ag$_3$(2)$_2$](PF$_6$)$_3$ (3). M.p. > 300 °C (decomposed). FT-IR (ATR, cm^{-1}): 2922, 2855, 1654, 1559, 1516, 1507, 1472, 1342, 1271, 1229, 1190, 1013, 839, 746. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, J = 8.4 Hz, 6H), 7.74 (d, J = 8.4 Hz, 12H), 7.65–7.61 (m, 6H), 7.54–7.48 (m, 12H), 7.44 (d, J = 8.0 Hz, 12H), 4.75 (br d, J = 6.0 Hz, 12H), 2.15 (br d, J = 11.2 Hz, 6H), 2.03–2.00 (m, 18H), 1.63 (t, J = 7.2 Hz, 18H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.2, 150.0, 135.7, 133.2, 133.0, 126.3, 125.2, 124.8, 112.5, 112.0, 47.9, 44.2, 38.0, 29.2, 16.0. HRMS (CSI, m/z) calcd for C$_{110}$H$_{104}$Ag$_3$N$_{12}$ [M − 3PF$_6$]$^{3+}$ 639.1881, found 639.1885.

X-ray crystallography

X-ray data for crystal 3 were collected on a CCD diffractometer with monochromated Mo Kα (λ = 0.71073 Å) radiation. Data collection was carried out at 150 K using a Japan Thermal Eng. Col., Ltd. Cryostat system equipped with a liquid nitrogen generator. X-ray data for crystal 6 were collected on a CMOS diffractometer (PHOTON 100) with monochromated Cu Kα (λ = 1.54178 Å) radiation. Data collection was carried out at 100 K using a Japan Thermal Eng. Col., Ltd. Cryostat system equipped with a liquid nitrogen generator. The crystal structures of 3 and 6 were solved by direct methods using SHELXS 97 and SHELXTL-2013, respectively.[17] Refinements were carried out by full-matrix least squares (on F^2) with anisotropic temperature factors for non-H atoms. In all of the structures, H atoms were included in their calculated positions. For refinement of the structure and structure analysis, the program package SHELXTL was used. Treatments of included disordered solvent molecules were executed using the program PLATON.[18]

[Ag$_3$(2)$_2$](PF$_6$)$_3$ (3)

C$_{86}$H$_{92}$Ag$_3$N$_{12}$·3(PF$_6$)·6(C$_4$H$_8$O$_2$), M_r = 2580.85, 0.4 × 0.4 × 0.2 mm^3, monoclinic, $P2_1/c$, a = 34.813(3), b = 20.6402(19), c = 16.3040(15) Å, β = 102.6780(10)°, V = 11429.6(18) Å^3, Z = 4, D_c = 1.500 Mg m^{-3}, $2\theta_{max}$ = 52.93°, T = 150 K, 55 296 reflections

measured, 22 635 unique (R_{int} = 0.0442), μ = 0.644 mm^{-1}, T_{max} = 0.88, T_{min} = 0.78. The final R_1 and w$R_2(F^2)$ were 0.0707 and 0.1916 ($I > 2\sigma(I)$), 0.1336 and 0.2158 (all data) for 1340 parameters and 96 restraints. CCDC-1420798.

[Ag$_3$(5)$_2$](PF$_6$)$_3$ (6)

C$_{110}$H$_{104}$Ag$_3$N$_{12}$·3(PF$_6$)·2(C$_4$H$_8$O$_2$)·C$_2$N, M_r = 2566.82, 0.27 × 0.18 × 0.08 mm^3, monoclinic, $P2_1/c$, a = 19.0224(7), b = 15.7764(7), c = 38.4287(15) Å, β = 102.187(2)°, V = 11272.7(8) Å^3, Z = 4, D_c = 1.512 Mg m^{-3}, $2\theta_{max}$ = 130.53°, T = 100 K, 101 361 reflections measured, 19 114 unique (R_{int} = 0.0593), μ = 5.306 mm^{-1}, T_{max} = 0.68, T_{min} = 0.52. The final R_1 and w$R_2(F^2)$ were 0.0532 and 0.1322 ($I > 2\sigma(I)$), 0.0719 and 0.1438 (all data) for 1469 parameters and 40 restraints. CCDC-1420799.

Acknowledgements

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