Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Triarylborane-Centered N-Heterocyclic Carbene Cages with Tunable Photophysical Properties

Yi-Fan Zhang, Ya-Wen Zhang, Xin Li, Li-Ying Sun* and Ying-Feng Han*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Xi'an Key Laboratory of Functional Supramolecular Structure and Materials, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, P. R. China

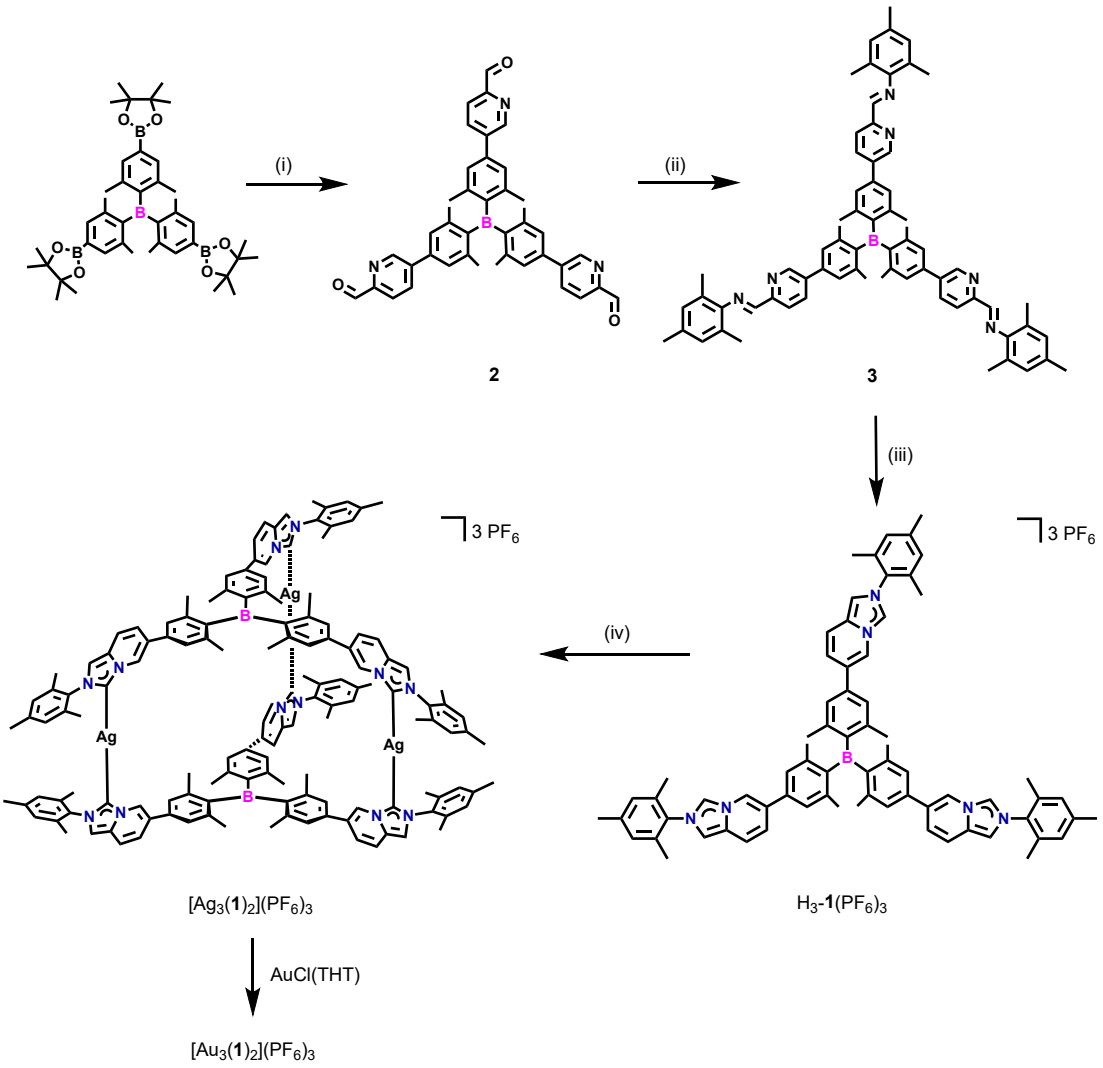
Supporting Information

Table of Contents:

1. Materials and methods

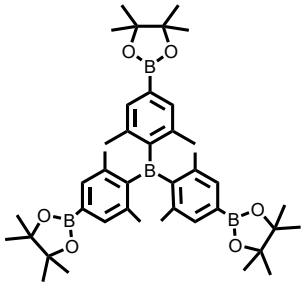
All starting materials were used as received from commercial sources unless otherwise stated, while solvents were freshly distilled by standard procedures before use. All the reagents were of analytical grade. Bis(pinacolato)diboron, $Pd(dppf)Cl_2$, 5-bromo-2-pyridinecarboxaldehyde, and 2,4,6-trimethylaniline were obtained from Bide Pharmatech Co., Ltd. $Pd(PPh_3)_4$ and paraformaldehyde were obtained from Energy Chemical. Ag_2O was purchased from Shanghai Aladdin biochemical Technology Co., Ltd. All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. However, once the reactions were completed, subsequent workups were done without precaution, as the compounds are airstable. The ^1H, $^{13}C\{^1H\}$ and 2D NMR spectra were recorded on Bruker AVANCE III 400 or AVANCE III 600 spectrometers. Chemical shifts for ^1H, $^{13}C\{^1H\}$ and 2D NMR were reported in ppm on the δ scale; ^1H and $^{13}C\{^1H\}$ were referenced to the solvent residual peak. Coupling constants (J) are reported in hertz (Hz). Mass spectra were obtained with a Bruker microTOF-Q II mass spectrometer (Bruker Daltonics Corp., USA) or a Synapt G2 ESI-Q-TOF mass spectrometer in the electrospray ionization (ESI) mode.

2. Synthesis of the triarylborane-bridged NHC precursor and trinuclear hexacarbene complexes



Scheme S1 Synthesis of the triarylborane-bridged NHC precursor H_3-**1**$(PF_6)_3$ and trinuclear hexacarbene complexes $[M_3(\mathbf{1})_2](PF_6)_3$ (M = Ag, Au). (i) 5-bromo-2-pyridinecarboxaldehyde, K_2CO_3, $Pd(PPh_3)_4$, DMF, 110 °C; (ii) 2,4,6-trimethylaniline, $CHCl_3$/EtOH, CH_3COOH, reflux; (iii) (a) paraformaldehyde, HCl, 25 °C; (b) NH_4PF_6, MeOH, 25 °C; (iv) Ag_2O, CH_3CN, 55 °C.

2.1 Synthesis of the boronate ester compound



Tris(4-bromo-2,6-dimethylphenyl)borane (3.30 g, 5.86 mmol), bis(pinacolato)diboron (5.36 g, 21.11 mmol), CH_3COOK (6.91 g, 70.37 mmol) and $Pd(dppf)Cl_2$ (0.43 g, 0.59 mmol) were dissolved in anhydrous 1,4-dioxane (120 mL) and stirred under N_2 atmosphere at 110 °C for 4 d. The resulting mixture was diluted with dichloromethane (200 mL) and washed with water (100 mL × 2) and brine (50 mL). The combined organic layers were dried by $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) to give the boronate ester compound as a white solid. Yield: 57% (2.34 g, 3.32 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 6H), 2.00 (s, 18H), 1.35 (s, 36H) ppm. The ^{1}H NMR spectrum of the boronate ester compound showed clear agreement with the one in the literature.[S1]

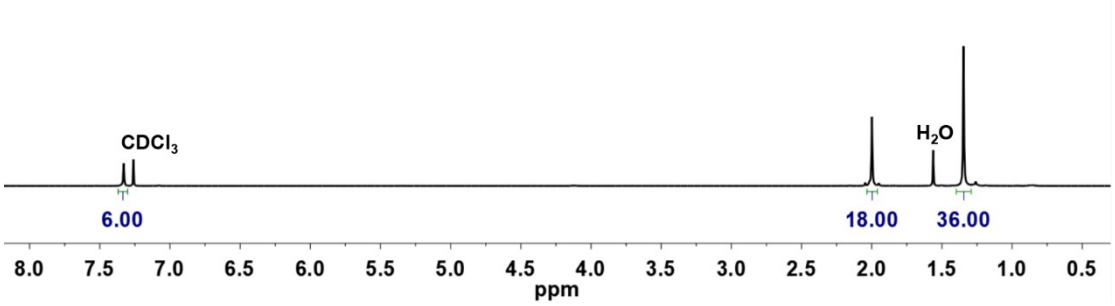
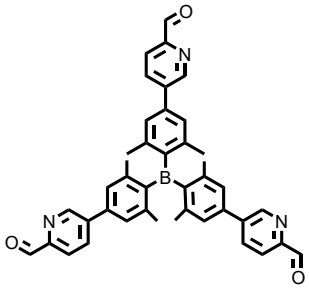


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the boronate ester compound.

2.2 Synthesis of compound 2



A mixture of the boronate ester compound (1.34 g, 1.90 mmol), 5-bromo-2-pyridinecarboxaldehyde (1.59 g, 8.56 mmol), K_2CO_3 (4.20 g, 30.40 mmol), $Pd(PPh_3)_4$ (0.66 g, 0.57 mmol) in anhydrous DMF (80 mL) was degassed and stirred under N_2 atmosphere at 110 ºC for 24 h. The solvent was removed under reduced pressure and the solid residue was triturated with water, collected by filtration, and washed with water (3 × 30 mL), diethyl ether (2 × 10 mL), and *n*-hexane (2 × 10 mL). The crude product was purified by column chromatography

on silica gel (dichloromethane/ethyl acetate = 10:1 to 6:1) to give compound **2** as a pale yellow solid. Yield: 33% (0.40 g, 0.62 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 3H), 9.06 (d, J = 1.7 Hz, 3H), 8.11 (m, 3H), 8.04 (m, 3H), 7.29 (s, 6H), 2.20 (s, 18H) ppm. The ^{1}H NMR spectrum of the compound **2** showed clear agreement with the one in the literature.[S2]

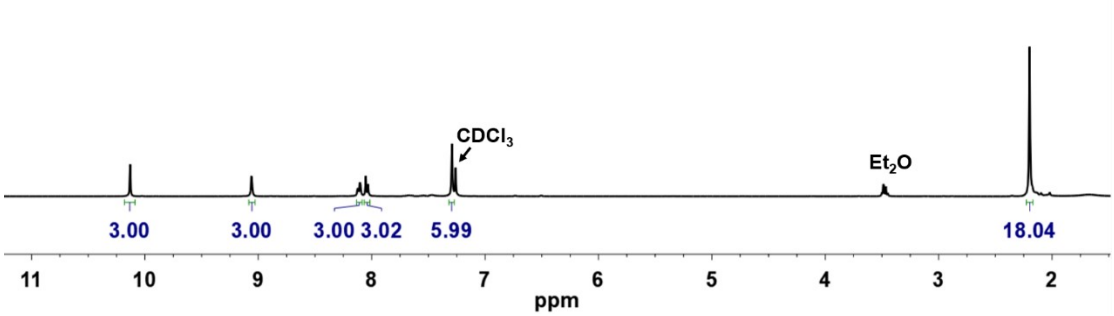
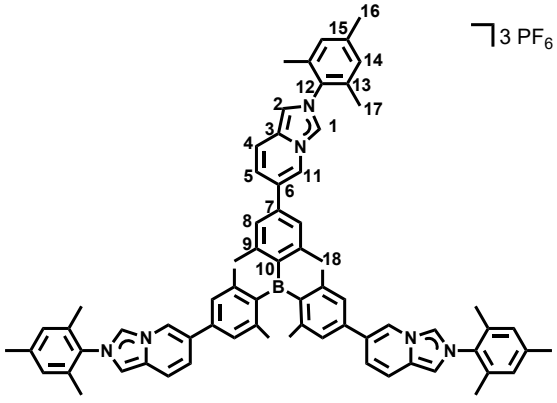


Fig. S2 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2**.

2.3 Synthesis of compound 3

A mixture of compound **2** (0.10 g, 0.16 mmol) was dissolved in chloroform (30 mL) and ethanol (10 mL) and then 2,4,6-trimethylaniline (0.20 mL, 1.41 mmol) and glacial acetic acid (3 μL, 0.053 mmol) were added. The mixture was refluxed for 30 h. The solvent was removed in vacuo and the residue was washed with methanol yielding **3**, as a yellow micro-crystalline powder. The sample was not stable, so the next step was directly carried out without further purification.

2.4 Synthesis of compound H_3-1$(PF_6)_3$



Paraformaldehyde (0.053 g, 0.59 mmol) was dissolved in hot toluene (30 mL) and compound **3** (0.10 g, 0.16 mmol) was added. A solution of 4 M HCl in 1,4-dioxane was added dropwise, whereupon a light-yellow precipitate formed immediately. After stirring for 18 h at ambient temperature, the precipitate was filtered and washed twice with diethyl ether

(2 × 2 mL). To remove unreacted paraformaldehyde, the residue was dissolved in methanol and filtered. Then, a solution of NH_4PF_6 was added and the mixture was stirred for 15 h at ambient temperature to precipitate compound H_3-**1**$(PF_6)_3$ as an off-white solid. Yield: 51% (0.12 g, 0.082 mmol). ^{1}H NMR (600 MHz, CD_3CN): δ = 9.15 (s, 3H, H1), 8.67 (s, 3H, H11), 7.93 (d, J = 9.7 Hz, 3H, H4), 7.90 (s, 3H, H2), 7.71 (d, J = 9.7 Hz, 3H, H5), 7.43 (s, 6H, H8), 7.17 (s, 6H, H14), 2.39 (s, 9H, H16), 2.22 (s, 18H, H18), 2.05 (s, 18H, H17) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ = 148.1 (C10), 142.9 (C9), 142.5 (C15), 137.4 (C7), 135.6 (C13), 132.4 (C12), 132.0 (C6),130.8 (C3), 130.4 (C14), 127.3 (C1), 127.2 (C8),127.0 (C5), 121.9 (C11), 119.5 (C4), 115.8 (C2), 23.3 (C18), 21.1 (C16), 17.3 (C17) ppm. HRMS (ESI, positive ions): m/z = 588.2543 (calcd for [H_3-**1**(PF_6)]$^{2+}$ 588.2777).

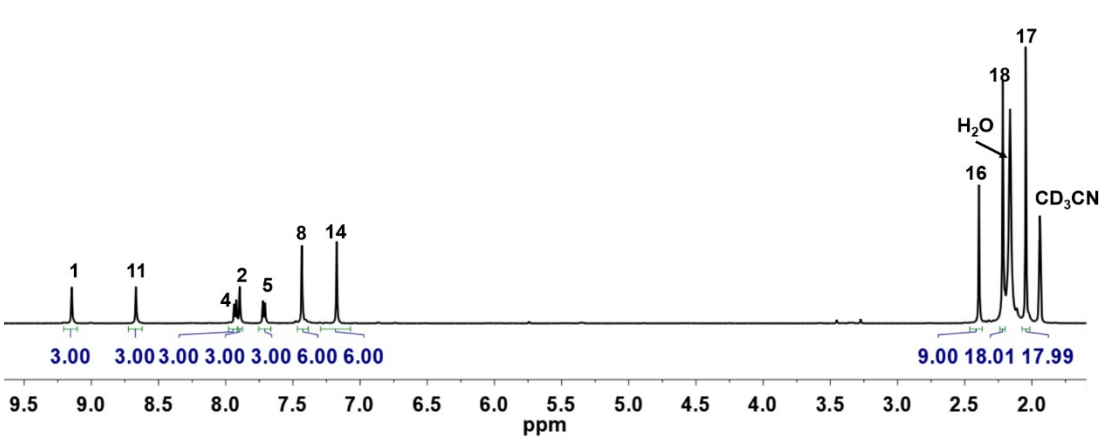


Fig. S3 ^{1}H NMR spectrum (600 MHz, CD_3CN) of H_3-**1**$(PF_6)_3$.

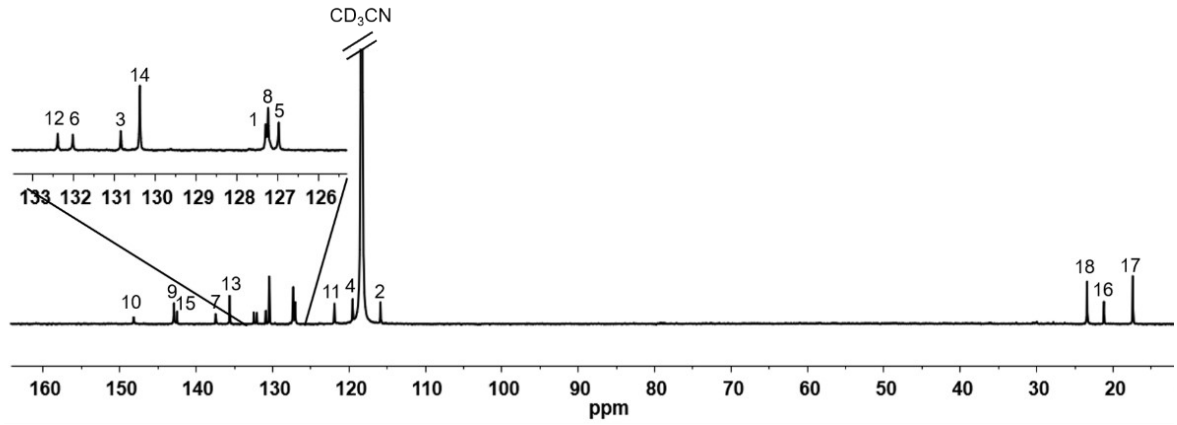


Fig. S4 ^{13}C{^{1}H} NMR spectrum (150 MHz, CD_3CN) of H_3-**1**$(PF_6)_3$.

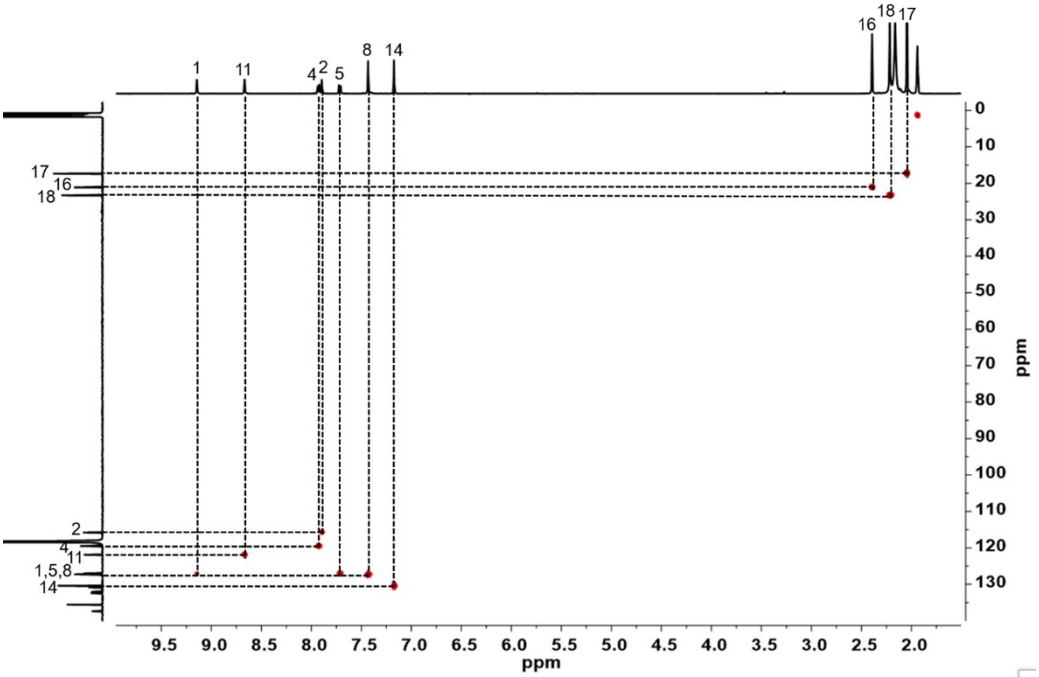


Fig. S5 ^{1}H-^{13}C HSQC spectrum (600 MHz, CD_3CN) of H_3-**1**$(PF_6)_3$.

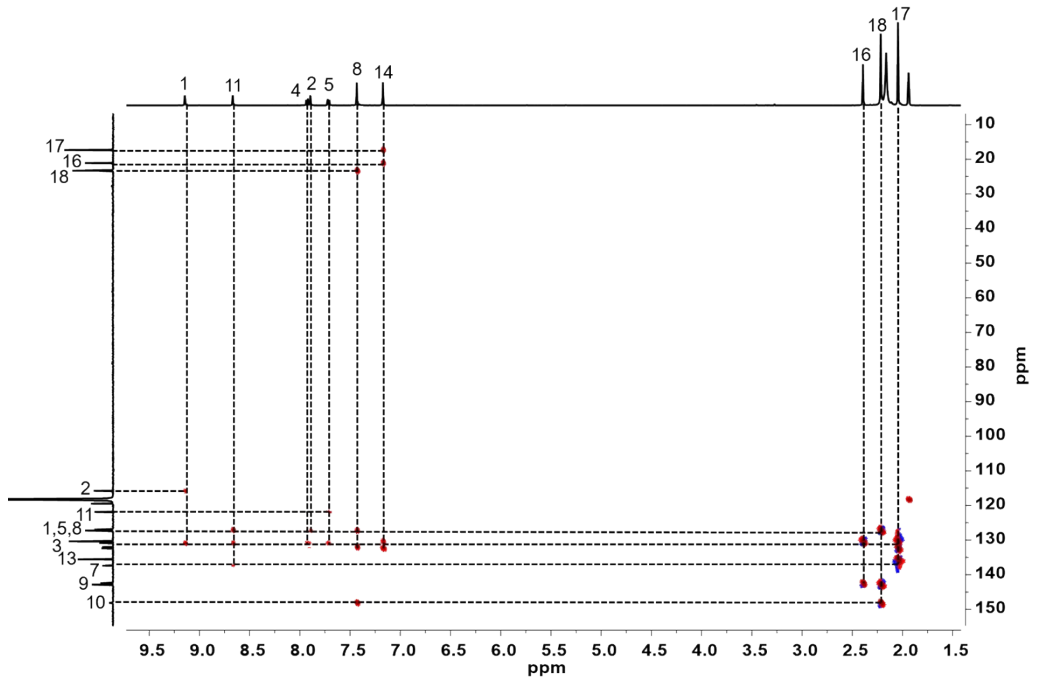


Fig. S6 ^{1}H-^{13}C HMBC spectrum (600 MHz, CD_3CN) of H_3-**1**$(PF_6)_3$.

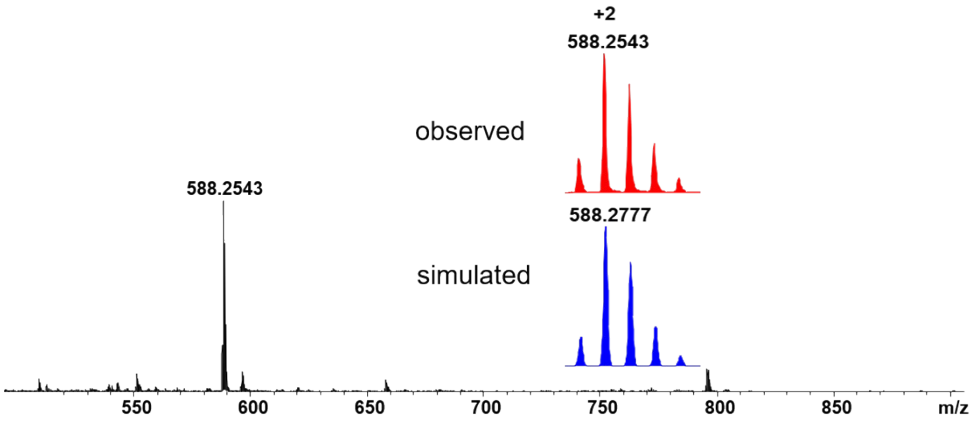
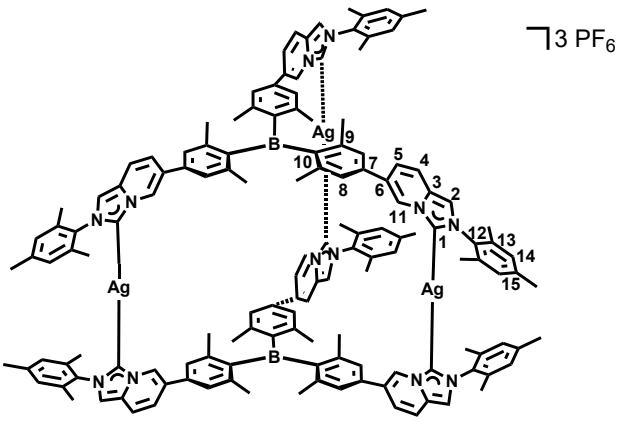


Fig. S7 HR-ESI mass spectrum (positive ions) of H_3-**1**$(PF_6)_3$ (Insert: experimentally observed distribution on top and simulated distribution at the bottom).

2.5 Synthesis of complex $[Ag_3(1)_2](PF_6)_3$



Under a nitrogen atmosphere, a sample of H_3-**1**$(PF_6)_3$ (0.030 g, 0.020 mmol) was dissolved in dry acetonitrile (20 mL) and Ag_2O (0.022 g, 0.092 mmol) was added to this solution. The resulting suspension was heated at 55 ºC for 14 h under the exclusion of light. After cooling the mixture to ambient temperature, the obtained suspension was filtered through a pad of Celite to give a clear solution. The filtrate was concentrated to 3 mL and then adding diethyl ether (30 mL) resulted in the precipitation of a pale yellow solid. The precipitate was filtered, washed with diethyl ether, and dried in vacuo. Yield: 96% (0.027 g, 0.0096 mmol). ^{1}H NMR (600 MHz, CD_3CN): δ = 9.18 (s, 6H, H11), 7.65 (m, 12H, H4, H5), 7.46 (s, 6H, H2), 7.03 (s, 12H, H8), 6.92 (s, 12H, H14), 2.49 (s, 18H, CH_3), 2.15 (s, 36H, CH_3), 1.87 (s, 18H, CH_3), 1.60 (s, 18H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ = 175.8 (C1), 147.7 (C10), 140.2 (C15), 136.8 (C13), 136.5 (C9), 135.3 (C12), 135.0 (C7), 131.3 (C3), 130.4 (C14), 129.7 (C8), 126.2 (C11), 125.8 (C6), 123.1 (C5), 119.0 (C4), 114.7 (C2), 23.8 (CH_3), 21.3 (CH_3), 17.5 (CH_3), 17.1 (CH_3) ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = −73.76 ppm. ^{31}P NMR (162 MHz,

CD_3CN): δ = −144.58 ppm. HRMS (ESI, positive ions): *m/z* = 793.9169 (calcd for $[Ag_3(\mathbf{1})_2]^{3+}$ 793.9517).

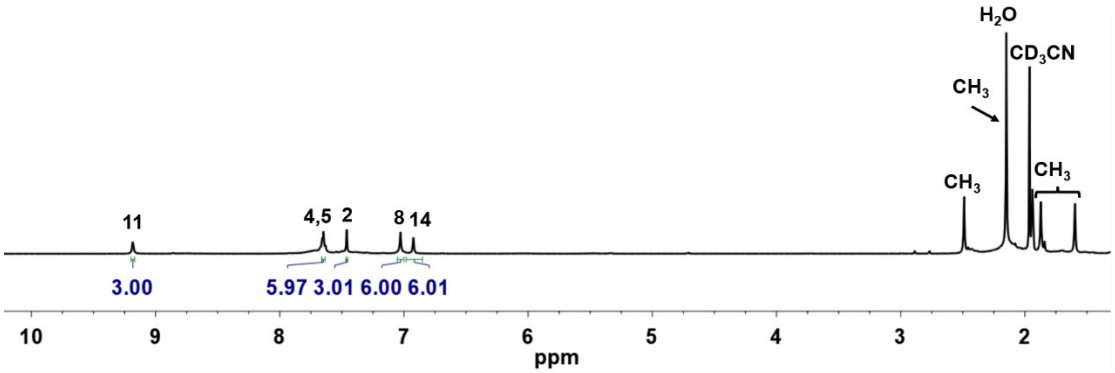


Fig. S8 ^{1}H NMR spectrum (600 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

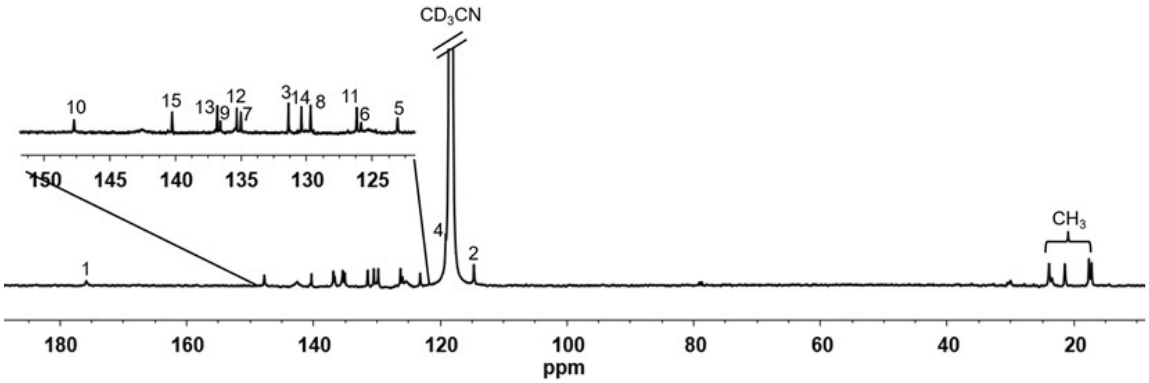


Fig. S9 $^{13}C\{^1H\}$ NMR spectrum (150 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

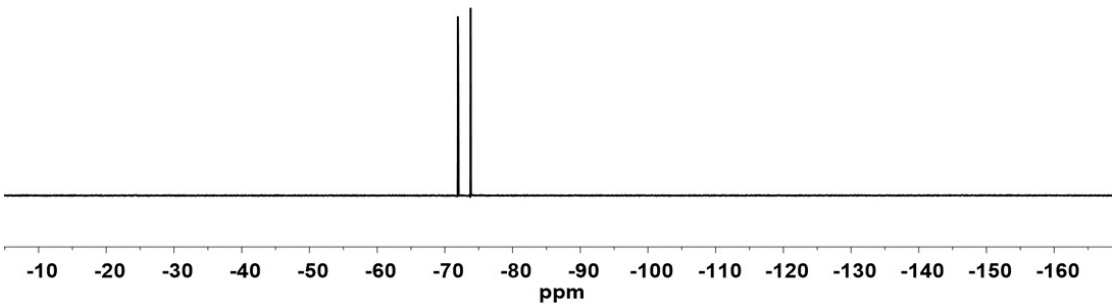


Fig. S10 ^{19}F NMR spectrum (376 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

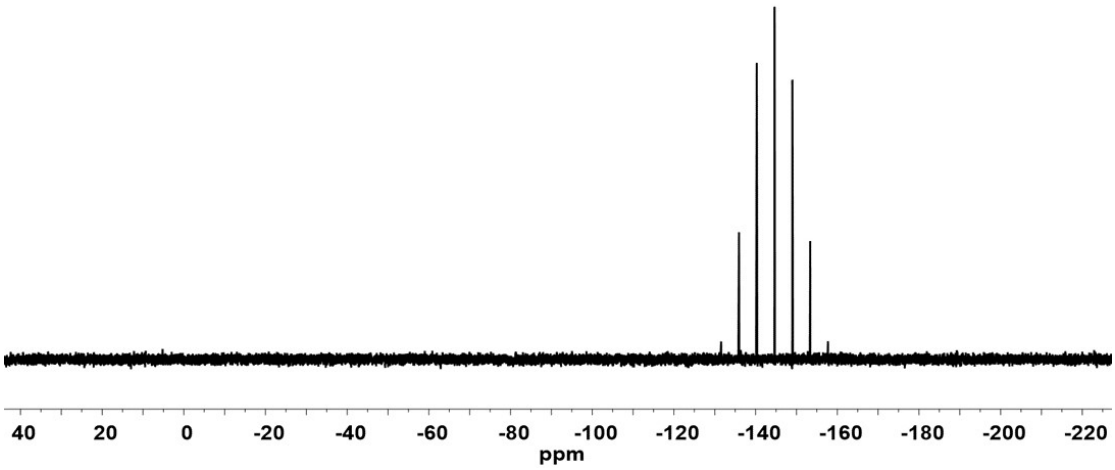


Fig. S11 ^{31}P NMR spectrum (162 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

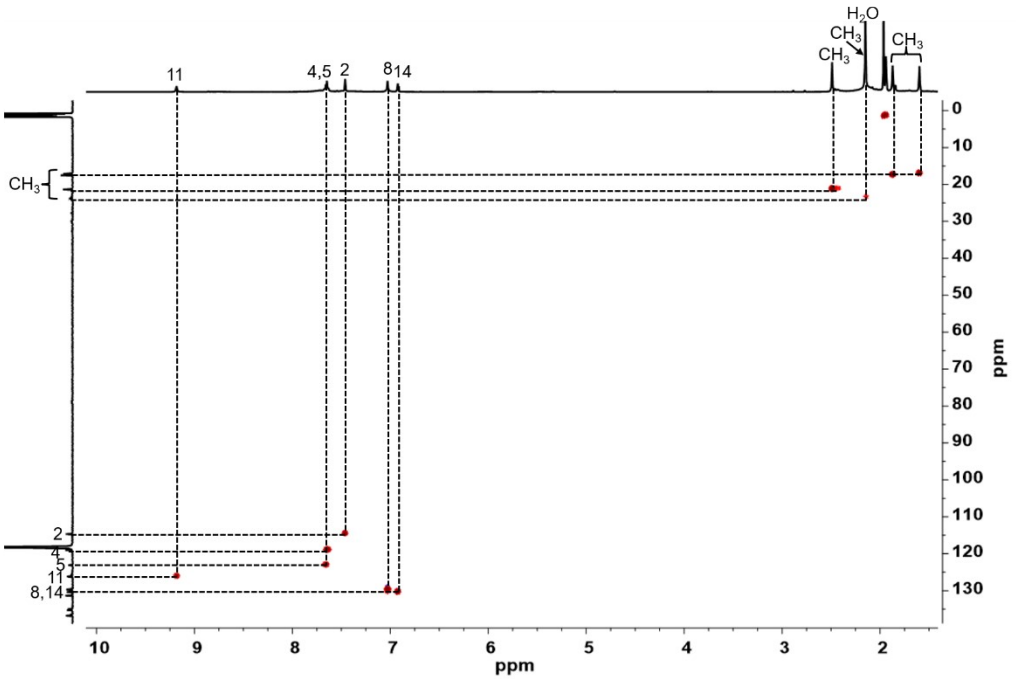


Fig. S12 ^{1}H-^{13}C HSQC spectrum (600 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

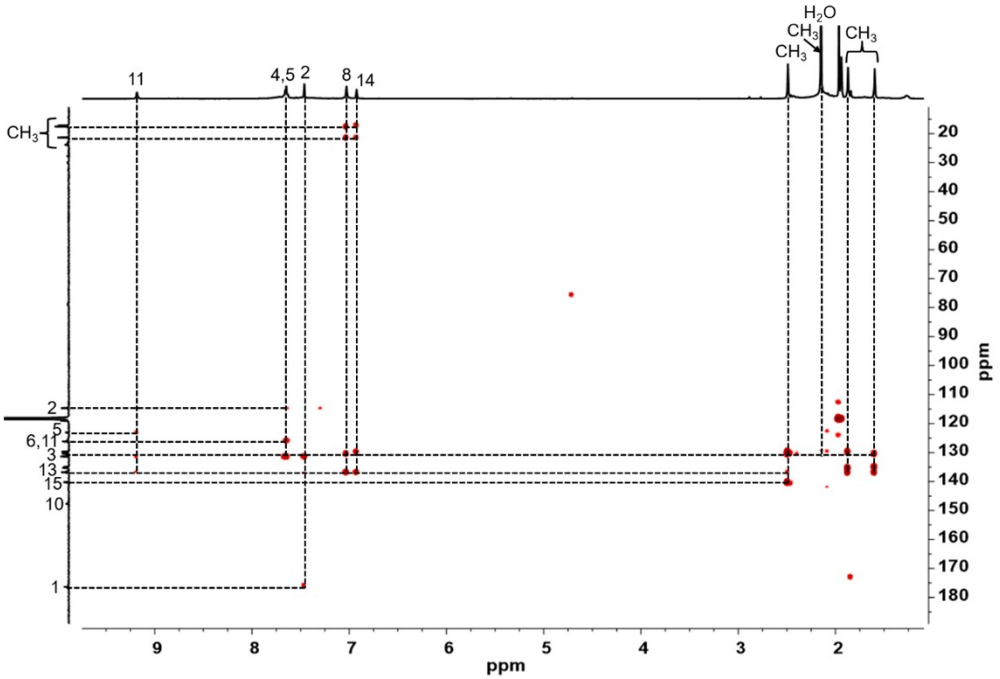


Fig. S13 ^{1}H-^{13}C HMBC spectrum (600 MHz, CD_3CN) of $[Ag_3(\mathbf{1})_2](PF_6)_3$.

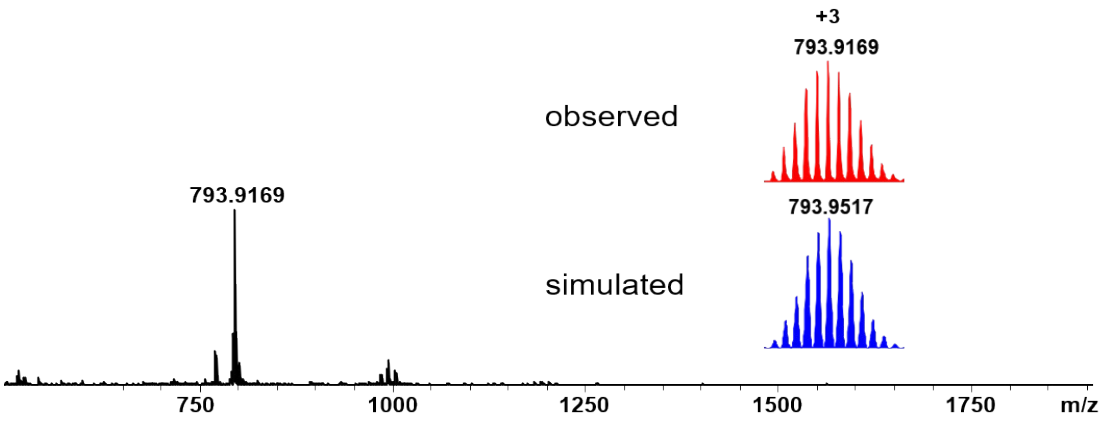
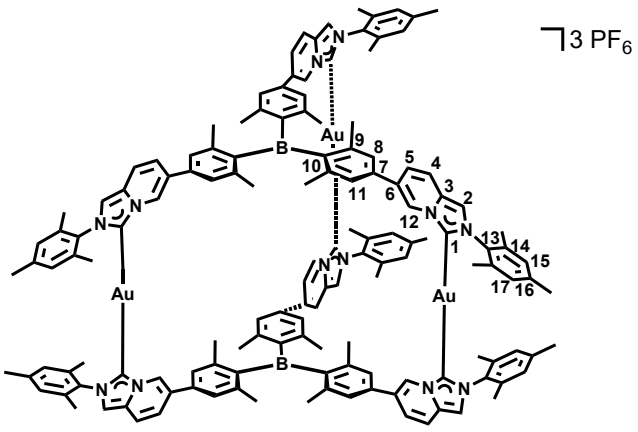


Fig. S14 HR-ESI mass spectrum (positive ions) of $[Ag_3(\mathbf{1})_2](PF_6)_3$ (Insert: experimentally observed distribution on top and simulated distribution at the bottom).

2.6 Synthesis of complex $[Au_3(\mathbf{1})_2](PF_6)_3$



Under a nitrogen atmosphere, a sample of $[Ag_3(\mathbf{1})_2](PF_6)_3$ (0.030 g, 0.011 mmol) was dissolved in dry acetonitrile (20 mL) and to this solution was added [AuCl(THT)] (0.020 g, 0.036 mmol). The reaction mixture was stirred at ambient temperature for 24 h and then slowly filtered through a pad of celite until a clear filtrate was obtained. The filtrate was concentrated to 2 mL, and diethyl ether (20 mL) was added. A purple precipitate formed, which was isolated by filtration, and washed with diethyl ether and dried in vacuo to afford the complex of $[Au_3(\mathbf{1})_2](PF_6)_3$. Yield: 83% (0.028 g, 0.0091 mmol). ^{1}H NMR (400 MHz, CD_3CN): δ = 9.28 (s, 6H), 7.84 (s, 6H), 7.68 (m, 12H), 7.60 (s, 6H), 7.46 (s, 6H), 7.03 (s, 6H), 6.93 (s, 6H), 2.49 (s, 18H, CH_3), 2.34 (s, 18H, CH_3), 1.89 (s, 36H, CH_3), 1.55 (s, 18H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ = 178.2 (C1), 147.5 (C7), 143.3 (C13), 141.3 (C16), 140.2 (C17), 135.9 (C14), 135.7 (C9), 134.5 (C10), 130.7 (C3), 130.2 (C6), 129.3 (C15), 125.9 (C11), 125.5 (C8), 124.4 (C12), 123.1 (C5), 118.8 (C4), 114.5 (C2), 23.4 (CH_3), 21.0 (CH_3), 17.3 (CH_3), 16.8 (CH_3) ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = −73.75 ppm. ^{31}P NMR (162 MHz, CD_3CN): δ = −144.69 ppm. HRMS (ESI, positive ions): *m/z* = 883.0296 (calcd for $[Au_3(\mathbf{1})_2]^{3+}$ 883.0129).

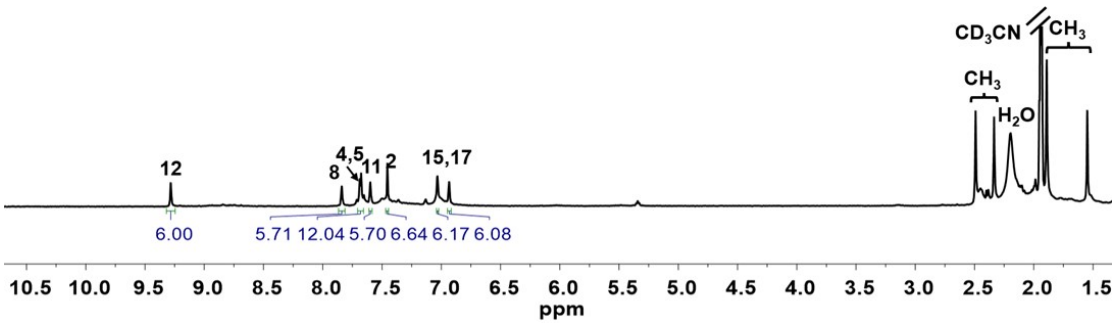


Fig. S15 ^{1}H NMR spectrum (400 MHz, CD_3CN) of $[Au_3(\mathbf{1})_2](PF_6)_3$.

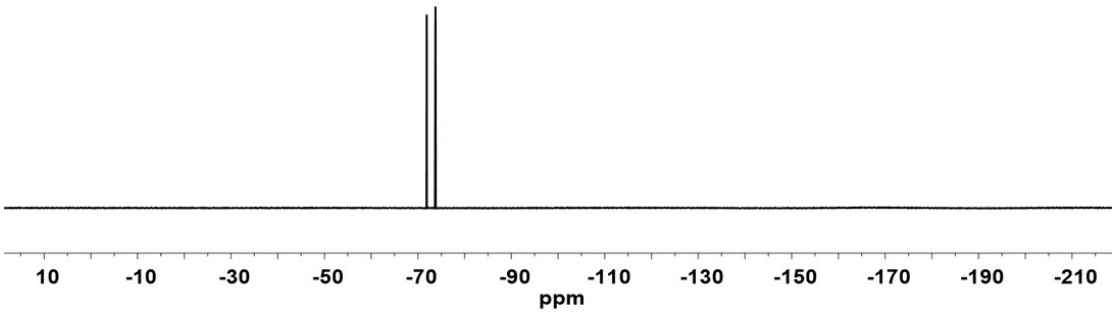


Fig. S16 ^{19}F NMR spectrum (376 MHz, CD_3CN) of $[Au_3(\mathbf{1})_2](PF_6)_3$.

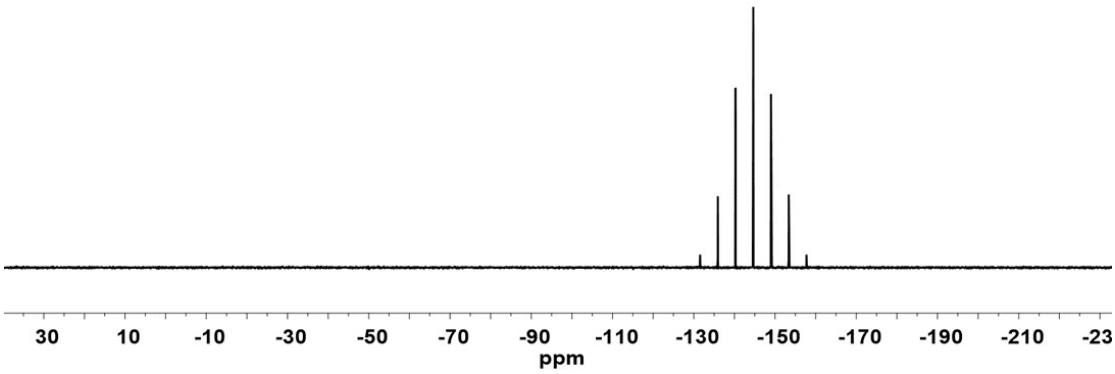


Fig. S17 ^{31}P NMR spectrum (162 MHz, CD_3CN) of $[Au_3(\mathbf{1})_2](PF_6)_3$.

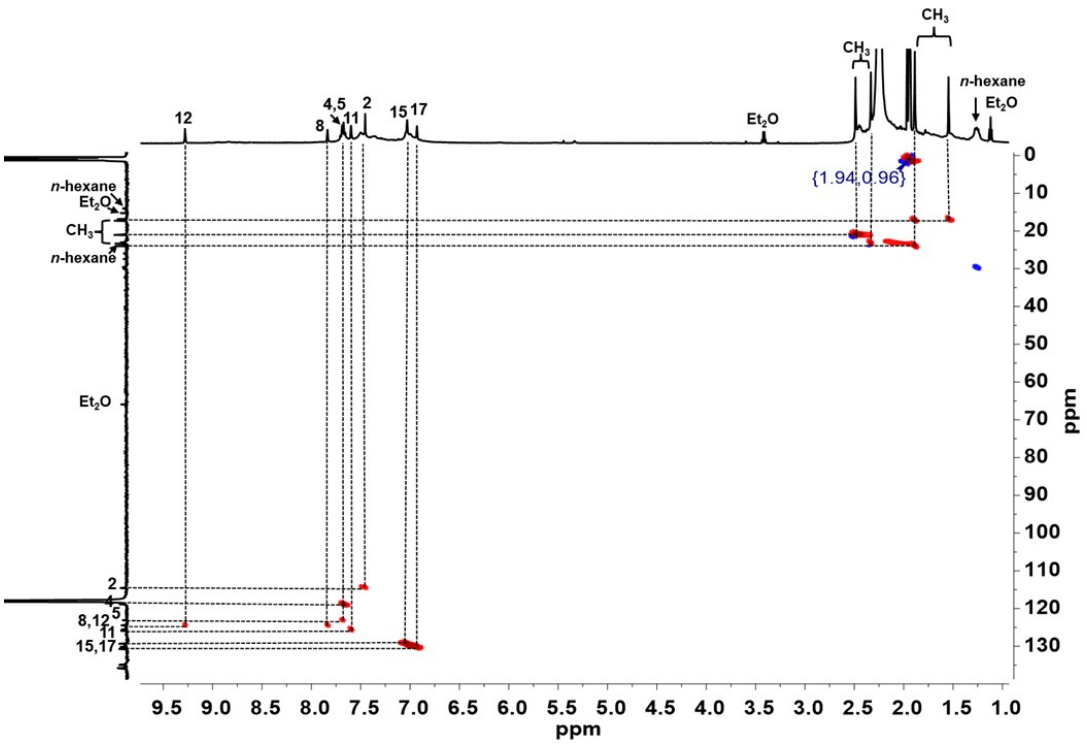


Fig. S18 ^{1}H-^{13}C HSQC spectrum (600 MHz, CD_3CN) of $[Au_3(\mathbf{1})_2](PF_6)_3$.

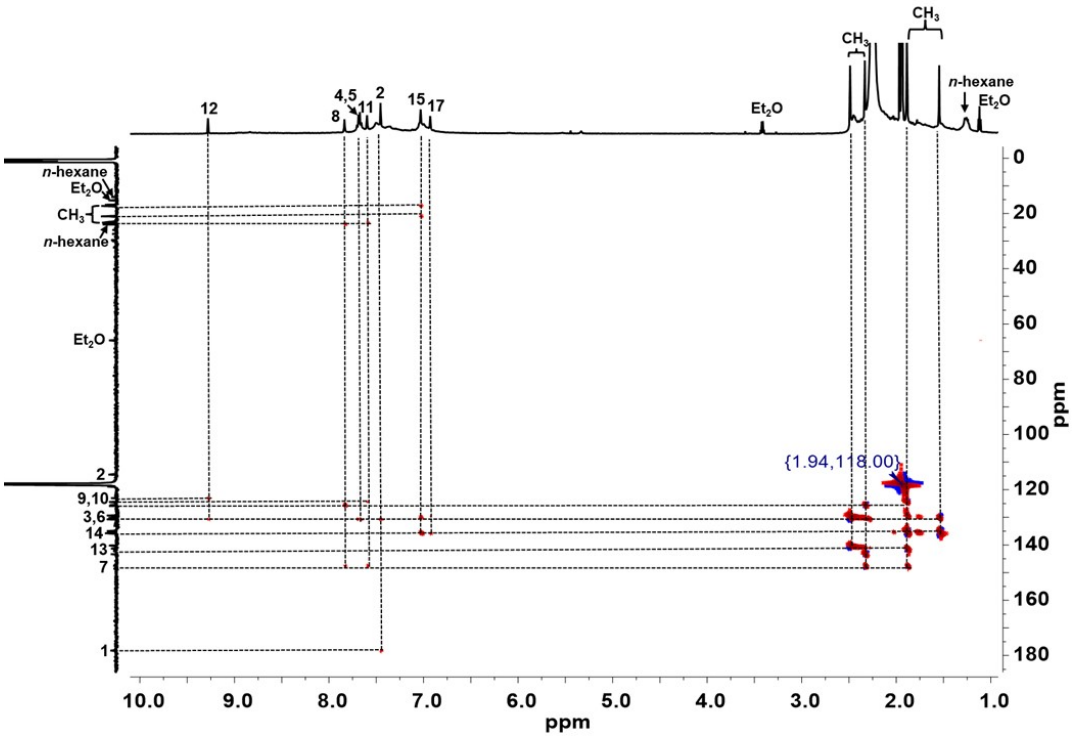


Fig. S19 ^{1}H-^{13}C HMBC spectrum (600 MHz, CD_3CN) of $[Au_3(\mathbf{1})_2](PF_6)_3$.

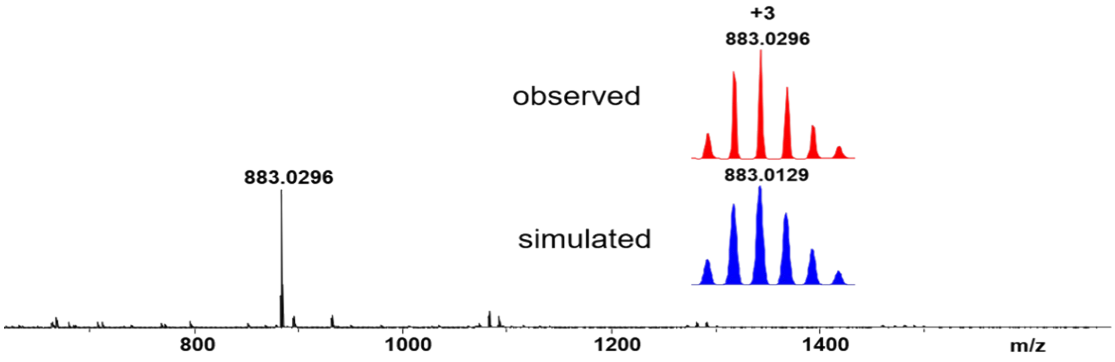


Fig. S20 HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{1})_2](PF_6)_3$ (Insert: experimentally observed distribution on top and simulated distribution at the bottom).

3. X-ray diffraction analysis of $[Ag_3(\mathbf{1})_2](PF_6)_3$

Crystallographic details

Diffraction data of $[Ag_3(\mathbf{1})_2](PF_6)_3$ was collected with a Bruker D8 VENTURE system X-ray diffractometer. Raw data collection and processing were performed with the APEX III software package. The data were corrected for absorption using the SADABS program.[S3] The structure was solved with the olex2 program package. Solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization.[S4,S5] A number of disordered solvent molecules could not be restrained properly and were therefore removed using the SQUEEZE routine. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. The crystal data of $[Ag_3(\mathbf{1})_2](PF_6)_3$ and selected structural parameters are summarized in Table S1.

Table S1 Crystal data of $[Ag_3(\mathbf{1})_2](PF_6)_3$

Empirical formula	$C_{144}H_{138}Ag_3B_2F_{18}N_{12}P_3$
Formula weight	2816.80
Temperature/K	200.0
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	27.755(2)
b/Å	19.4743(14)
c/Å	29.186(2)
α/°	90
β/°	90.276(2)
γ/°	90
Volume/Å^3	15776(2)
Z	4
ρ_{calc} (g·cm^{-3})	1.186
μ (mm^{-1})	0.467
F (000)	5776.0
Crystal size/mm^3	0.23 × 0.22 × 0.20
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.79 to 50.17
Index ranges	-33 ≤ h ≤ 33, -23 ≤ k ≤ 23, -32 ≤ l ≤ 34
Reflections collected	136729
Independent reflections	13938 [R_{int} = 0.1545, R_{sigma} = 0.1018]
Data/restraints/parameters	13938/563/893
Goodness-of-fit on F^2	1.018
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0955, wR_2 = 0.2307
Final *R* indexes [all data]	R_1 = 0.2049, wR_2 = 0.2923
Largest diff. peak/hole / e Å^{-3}	0.59/-0.49
CCDC number	2167062

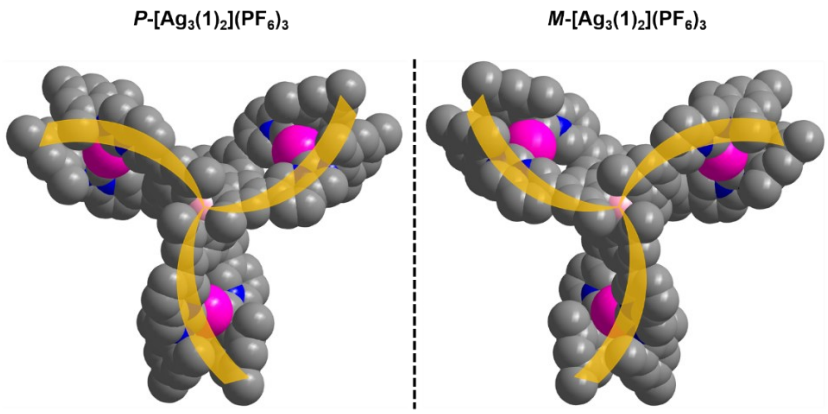


Fig. S21 Space-filling depictions of the two isomers of $[Ag_3(\mathbf{1})_2](PF_6)_3$. Hydrogen atoms and anions are omitted for clarity.

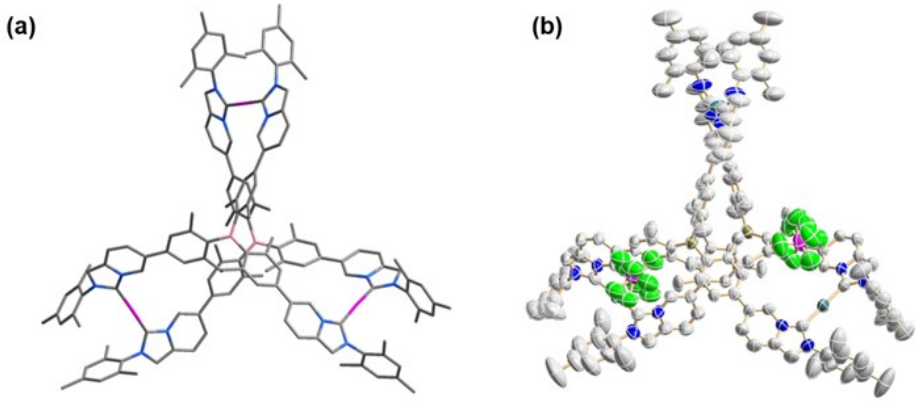


Fig. S22 (a) Sticks and (b) thermal ellipsoid depictions of $[Ag_3(\mathbf{1})_2](PF_6)_3$ at the 50% probability level. Hydrogen atoms are omitted for clarity.

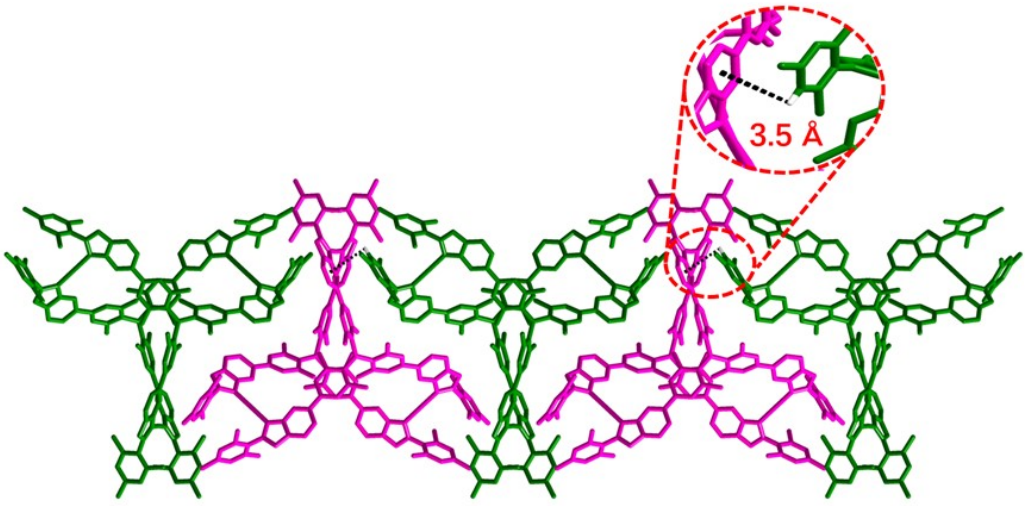


Fig. S23 Five stacks of the trication $[Ag_3(\mathbf{1})_2]^{3+}$ in $[Ag_3(\mathbf{1})_2](PF_6)_3$. Hydrogen atoms and anions are omitted for clarity.

4. Table of photophysical data

The UV-vis experiments were conducted on an Agilent Cary-100 spectrophotometer. The fluorescence experiments were performed on a Horiba QM8000 spectrometer. The experimental quantum yields were determined by recording the emission signals within a K SPHERE-Petite on a Horiba QM 8000 spectrometer equipped with a UXL 75W Xe Lamp, photomultiplier 914D, and double grating emission and excitation monochromators. Fluorescence decay profiles were recorded on an FLS920 instrument. Note: considering the integrity of the spectrum, the excitation wavelength is set at 330 nm.

Table S2 Photophysical data of H_3-**1**$(PF_6)_3$, $[Ag_3(\mathbf{1})_2](PF_6)_3$, and $[Au_3(\mathbf{1})_2](PF_6)_3$ in solution

Sample[a]	λ_{abs}/(nm)	λ_{em}/(nm)	τ^b solution /(ns)	Φ^b solution /(%)
H_3-**1**$(PF_6)_3$	269, 348	418	2.6146	21.76
$[Ag_3(\mathbf{1})_2](PF_6)_3$	269, 361	487	4.2663	19.19
$[Au_3(\mathbf{1})_2](PF_6)_3$	266, 349	478	1.4378	1.46

[a]Solution measurements were carried out with 10^{-5} M acetonitrile solutions. [b]Average lifetimes (τ), and quantum yields (Φ) (T = 298 K).

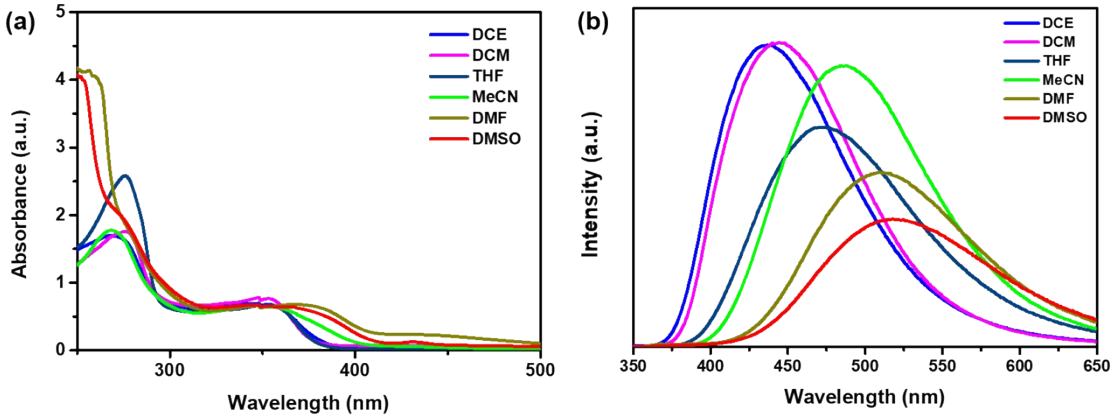


Fig. S24 (a) UV-vis absorption and (b) fluorescence emission spectra of $[Ag_3(\mathbf{1})_2](PF_6)_3$ in various solvents (λ_{ex} = 330 nm, $c = 10^{-5}$ M, T = 298 K).

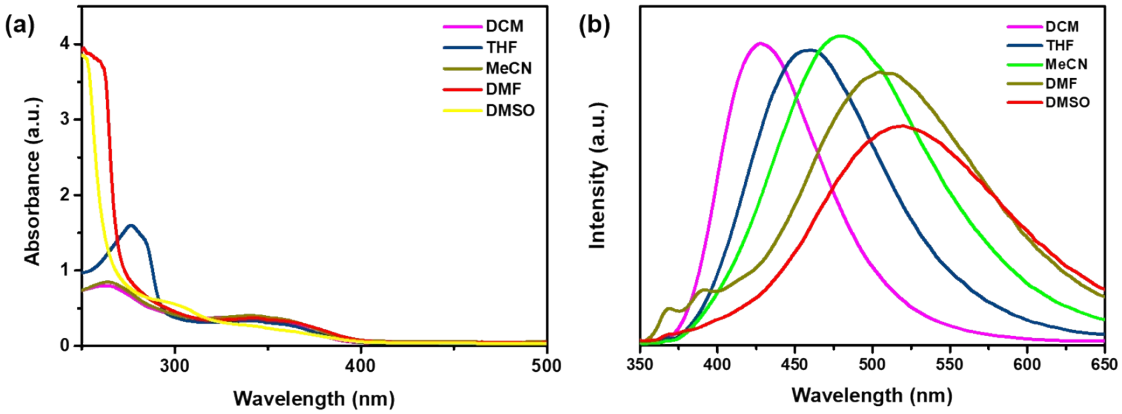


Fig. S25 (a) UV-vis absorption and (b) fluorescence emission spectra of $[Au_3(\mathbf{1})_2](PF_6)_3$ in various solvents (λ_{ex} = 330 nm, $c = 10^{-5}$ M, T = 298 K).

5. DFT calculation

All calculations were performed with the Gaussian(R) 09 program optimizer[S6]. The theoretical approach is based on the framework of density functional theory (DFT)[S7,S8]. Calculations were performed using M06, UM06, and UB3LYP functional[S9] with the LANL2DZ basis set (Au, Ag) and the 6-31G* basis set (H, C, N, B). Cartesian coordinates of all the optimized geometries are listed in the supporting information. Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds.

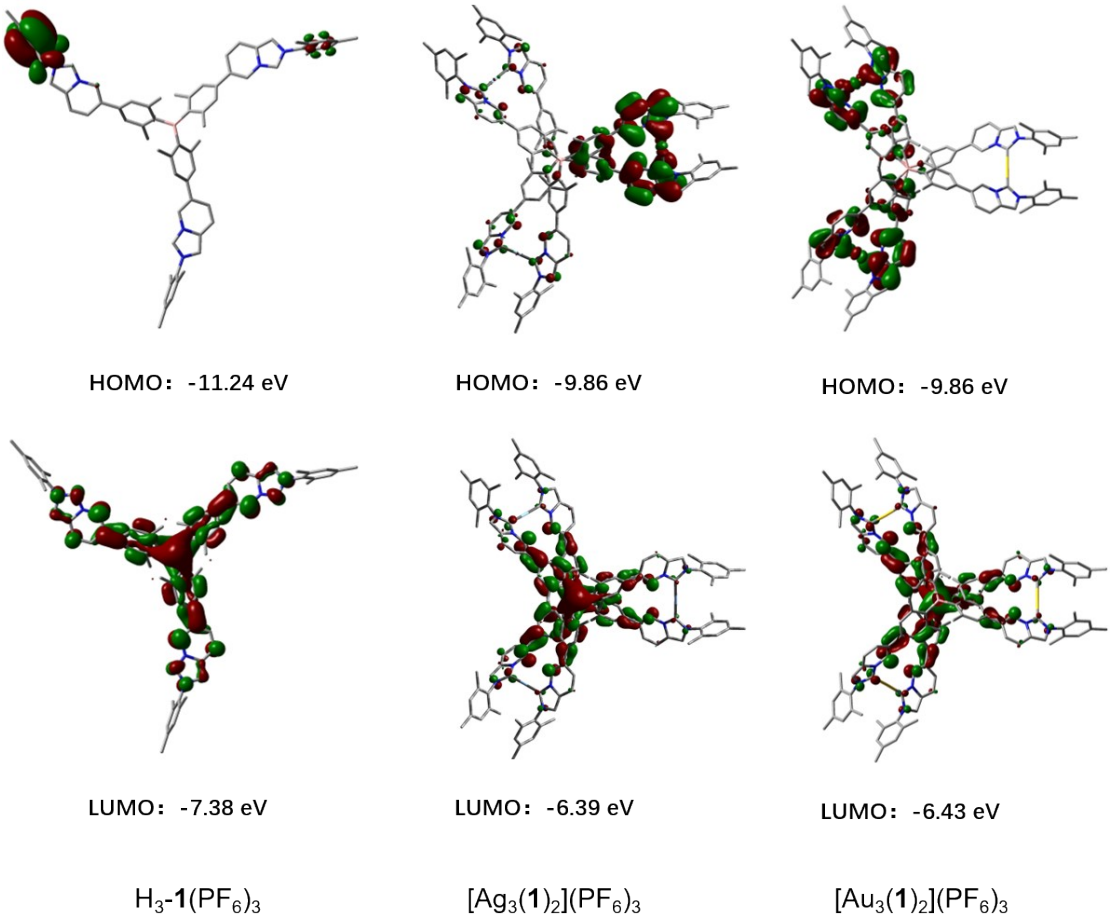


Fig. S26 HOMO (top) and LUMO (bottom) diagrams of H_3-**1**$(PF_6)_3$, $[Ag_3(\mathbf{1})_2](PF_6)_3$, and $[Au_3(\mathbf{1})_2](PF_6)_3$.

Table S3. Cartesians coordinates of calculated (H_3-**1**$(PF_6)_3$) at the UB3LYP/LANL2DZ, 6-31G*.

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.583003	2.624862	-0.283326	C	-0.363497	2.305315	1.710416
N	-7.254254	7.274095	0.081775	H	-0.052974	1.410676	2.259689
N	-5.831209	5.6214	-0.028555	H	-0.7493	3.017596	2.445801
C	-1.410538	2.007694	0.653891	H	0.540307	2.739102	1.26988
C	0.5195	-2.39202	-1.221556	C	-1.146408	-3.61571	0.659134
N	7.793348	2.233678	-0.017997	H	-1.756506	-4.086116	1.426008
C	-1.020099	-2.222803	0.662928	C	-6.087327	2.93581	-0.588765
C	-1.276334	0.945497	-0.284025	H	-6.163199	1.871798	-0.781489
C	-2.555986	2.810525	0.649652	C	-5.957292	6.946638	0.205655
H	-2.65883	3.576436	1.414153	C	-0.478294	-4.414308	-0.276962
C	2.447163	0.230037	0.662545	C	-4.787623	3.491566	-0.292155
C	-0.170465	-1.577974	-0.279728	C	-7.212252	3.707054	-0.601387
C	1.463881	0.642501	-0.280648	H	-8.189941	3.28858	-0.813051

C	3.716216	0.818198	0.659549	N	-2.688802	-9.909939	0.085534
H	4.428565	0.525532	1.426691	C	-3.444803	1.58939	-1.215842
C	1.823415	1.648195	-1.221762	H	-4.210654	1.443008	-1.972789
C	2.176269	-0.820516	1.722878	C	-2.327274	0.74881	-1.223573
H	1.244754	-0.637458	2.268145	C	-4.68908	4.829951	-0.023868
H	2.983127	-0.840634	2.461514	H	-3.758272	5.344024	0.177987
H	2.099522	-1.822026	1.286972	C	-7.10702	5.094758	-0.316934
N	-1.962054	-7.853935	-0.025225	C	5.601373	3.804813	-0.582856
C	3.11066	2.194207	-1.211371	H	4.719974	4.404764	-0.77853
H	3.369645	2.928643	-1.969313	C	-0.631259	-5.890141	-0.284471
C	0.347816	-3.779842	-1.212171	C	-3.050718	-8.621703	0.203279
H	0.853843	-4.371529	-1.970371	B	0.006024	0.003571	-0.280517
C	6.534991	1.64447	-0.013715	C	9.002201	1.675987	0.215733
H	6.51086	0.58169	0.189629	C	-1.843274	-6.469416	-0.022662
C	5.428002	2.402288	-0.284076	H	-2.753187	-5.9168	0.172491
N	9.937606	2.631894	0.090484	C	1.438561	-1.818236	-2.283234
C	-7.789616	8.617787	0.261115	H	1.698641	-2.581719	-3.022311
C	-7.861119	9.459654	-0.860827	H	2.371323	-1.444535	-1.848533
C	-8.395668	10.735188	-0.660611	H	0.983048	-0.984556	-2.827126
H	-8.467489	11.407891	-1.511135	C	7.979839	3.601184	-0.306841
C	-8.843783	11.167578	0.59394	C	-7.986422	6.159302	-0.238483
C	-8.753184	10.282559	1.675527	H	-9.054085	6.205255	-0.383313
H	-9.104587	10.60096	2.653399	C	0.867489	2.157603	-2.283966
C	-8.228175	8.994415	1.54105	H	0.375657	1.347159	-2.831389
C	4.073321	1.796505	-0.275836	H	1.399634	2.767176	-3.020157
C	-1.793657	-1.461694	1.722909	H	0.075537	2.776889	-1.850226
H	-1.166829	-0.75077	2.271201	C	-2.288805	-0.336431	-2.282657
H	-2.219424	-2.150069	2.459011	H	-1.342849	-0.351905	-2.833907
H	-2.618949	-0.889412	1.286754	H	-3.086614	-0.187656	-3.016222
H	-2.420193	-1.331482	-1.845384	C	-4.092545	-10.931548	-2.240166
C	-3.590018	-11.041392	0.262202	H	-4.419517	-9.88451	-2.272136
C	-3.729023	-11.58615	1.549162	H	-4.68531	-11.480804	-2.975144
C	-4.592743	-12.676238	1.683654	H	-3.048324	-10.956861	-2.574176
H	-4.722422	-13.118127	2.668053	C	-2.989641	-11.031719	2.745144
C	-5.289749	-13.214317	0.594289	H	-3.284567	-9.998519	2.968394
C	-5.112753	-12.62874	-0.66554	H	-1.90331	-11.035398	2.595526
H	-5.649635	-13.033111	-1.519547	H	-3.200664	-11.629666	3.634621
C	-4.263021	-11.537554	-0.866119	C	15.583943	1.815237	0.767991
C	9.342386	3.8255	-0.229112	H	15.78718	0.765095	1.014429
H	9.9193	4.724724	-0.376033	H	15.987529	2.425322	1.581435
C	-0.868476	-8.699749	-0.303013	H	16.139667	2.049058	-0.144999
C	-1.355293	-9.991871	-0.224305	C	11.50792	1.858461	-2.224217
H	-0.863302	-10.941483	-0.36313	H	10.769114	1.047136	-2.232249
C	0.498626	-6.74191	-0.573271	H	11.000473	2.764903	-2.575752
H	1.460455	-6.279003	-0.762431	H	12.276038	1.606618	-2.958949
C	6.833674	4.389719	-0.593472	C	-6.189797	-14.412433	0.769698
H	6.963963	5.444887	-0.806704	H	-5.622368	-15.343446	0.643444
C	12.126672	2.04873	-0.858493	H	-6.997105	-14.419849	0.031432

C	13.498603	1.868214	-0.663439	C	-4.092545	-10.931548	-2.240166
H	14.112055	1.587903	-1.515615	H	-4.419517	-9.88451	-2.272136
C	14.103302	2.042542	0.5878	H	-4.68531	-11.480804	-2.975144
C	13.297798	2.415135	1.671255	H	-3.048324	-10.956861	-2.574176
H	13.754206	2.562504	2.646481	C	-2.989641	-11.031719	2.745144
C	11.920187	2.611301	1.541673	H	-3.284567	-9.998519	2.968394
C	11.368542	2.417185	0.264824	H	-1.90331	-11.035398	2.595526
C	0.389319	-8.101552	-0.581736	H	-3.200664	-11.629666	3.634621
H	1.239776	-8.742176	-0.787007	C	15.583943	1.815237	0.767991
C	11.081096	3.017681	2.731219	H	15.78718	0.765095	1.014429
H	10.310873	2.271848	2.964856	H	15.987529	2.425322	1.581435
H	10.569554	3.973813	2.567298	H	16.139667	2.049058	-0.144999
H	11.707322	3.12906	3.61932	C	11.50792	1.858461	-2.224217
C	-9.392624	12.560657	0.779891	H	10.769114	1.047136	-2.232249
H	-8.5892	13.261235	1.041683	H	11.000473	2.764903	-2.575752
H	-10.131887	12.596484	1.585585	H	12.276038	1.606618	-2.958949
H	-9.863602	12.931756	-0.135181	C	-6.189797	-14.412433	0.769698
C	-8.149665	8.063073	2.728853	H	-5.622368	-15.343446	0.643444
H	-8.721873	7.141469	2.567461	H	-6.997105	-14.419849	0.031432
H	-8.553468	8.547651	3.620685	H	-6.636294	-14.436156	1.768281
H	-7.116649	7.76998	2.954621	H	-4.041579	-8.269224	0.440382
C	-7.392038	9.023396	-2.229754	H	-5.160325	7.629587	0.451612
H	-6.320509	8.787155	-2.242154	H	9.191896	0.643391	0.460454
H	-7.558805	9.817671	-2.96089				
H	-7.926232	8.133118	-2.583035				

Table S4. Cartesians coordinates of calculated ($[Ag_3(\mathbf{1})_2](PF_6)_3$) at the UB3LYP/ LANL2DZ, 6-31G*.

Atom	X	Y	Z	Atom	X	Y	Z
Ag	4.520697	7.42717	-0.137306	H	-1.128243	-0.720587	1.099327
Ag	-8.815099	0.000762	-0.00011	H	-2.828989	-1.101074	0.839299
C	0.7861	-4.27045	3.406109	H	-1.902499	-1.959912	2.075361
N	2.87264	-9.546974	1.744611	C	1.764477	-1.086196	1.570411
N	2.199216	-7.591119	2.32788	H	1.113962	-0.284142	1.210844
C	1.097286	-1.976343	2.601672	H	2.080667	-1.670395	0.699709
C	-2.178156	1.413994	4.624075	H	2.656567	-0.59972	1.982597
N	5.515384	5.813236	2.422868	C	-3.759931	0.602386	2.482545
C	-2.484361	0.0557	2.631034	H	-4.341826	0.301706	1.615896
C	0.276067	-1.462384	3.641416	C	0.125791	-6.678714	3.915935
C	1.30175	-3.352443	2.480536	H	-0.70801	-6.307186	4.498677
H	1.86355	-3.710022	1.621966	C	3.131541	-8.225698	1.545867
C	0.954022	2.363447	2.893228	C	-4.288602	1.538653	3.382696
C	-1.629751	0.505465	3.678936	C	1.00417	-5.732828	3.259757
C	1.046761	1.183207	3.692982	C	0.308323	-8.022888	3.802074

C	2.000157	3.289379	2.873379	H	-0.348392	-8.729665	4.297688
H	1.871016	4.189175	2.278041	N	-9.764793	2.620844	1.434624
C	2.232461	1.014655	4.465567	C	0.035424	-3.750391	4.469503
C	-0.240199	2.686768	2.012831	H	-0.340746	-4.413498	5.241825
H	-0.557124	1.835076	1.40378	C	-0.248076	-2.386348	4.583933
H	0.005105	3.505288	1.328354	C	2.026906	-6.225713	2.496016
H	-1.110408	2.995036	2.600439	H	2.764253	-5.614892	1.992891
N	-7.788988	2.137819	2.129036	C	1.366194	-8.51807	2.991114
C	3.257876	1.96358	4.41016	C	5.296886	4.126591	4.605226
H	4.152544	1.773729	4.994	H	5.168883	3.501379	5.480182
C	-3.484222	1.894838	4.473254	C	-5.630299	2.143182	3.173336
H	-3.87021	2.562655	5.237463	C	-8.788445	1.683023	1.30634
C	4.443492	4.936946	2.495321	B	-0.097587	0.080401	3.702186
H	3.775408	4.974188	1.645677	C	5.780191	6.731648	1.436815
C	4.300148	4.083453	3.555262	C	-6.560683	1.542588	2.369847
N	6.971101	7.271917	1.811113	H	-6.424896	0.585455	1.884895
C	3.581621	-10.638945	1.109143	C	-1.41201	1.849668	5.856213
C	4.696673	-11.191283	1.760295	H	-1.462256	1.08168	6.639415
C	5.315926	-12.290165	1.156773	H	-1.832256	2.766536	6.280833
H	6.177428	-12.735526	1.648186	H	-0.355057	2.029033	5.644761
C	4.852389	-12.838675	-0.044409	C	6.527331	5.809384	3.40742
C	3.743305	-12.247166	-0.660554	C	1.818434	-9.757215	2.610868
H	3.37014	-12.660388	-1.594503	H	1.479787	-10.746815	2.872916
C	3.083073	-11.1485	-0.1018	C	2.455034	-0.160479	5.400349
C	3.176261	3.112923	3.614575	H	1.580543	-0.368925	6.023504
C	-2.060708	-0.982479	1.609788	H	3.292133	0.044402	6.074573
H	2.686892	-1.081028	4.85521	H	2.037878	-9.497299	-1.046179
C	-1.093414	-1.94123	5.760741	C	5.216061	-10.633712	3.064829
H	-0.576491	-1.199425	6.381352	H	5.578358	-9.605348	2.947863
H	-1.33845	-2.787655	6.409099	H	6.045163	-11.240179	3.438047
H	-2.034074	-1.486994	5.433418	H	4.440343	-10.615747	3.839208
C	-11.037627	2.575358	0.74402	C	-11.980683	1.265518	2.71602
C	-11.150309	3.207186	-0.505829	H	-11.26843	0.432605	2.67911
C	-12.399374	3.178567	-1.132995	H	-12.943048	0.868774	3.049021
H	-12.50883	3.663915	-2.099872	H	-11.623351	1.961566	3.483989
C	-13.510062	2.558992	-0.547562	C	-9.97686	3.902211	-1.156562
C	-13.346542	1.9411	0.69723	H	-9.142329	3.212151	-1.33058
H	-14.198503	1.45486	1.165914	H	-9.592631	4.719587	-0.534569
C	-12.120343	1.936488	1.369602	H	-10.268795	4.327213	-2.120342
C	7.448324	6.739012	2.992178	C	10.009192	11.246353	-1.01763
H	8.379164	7.059912	3.43178	H	11.031058	11.264544	-0.61762
C	-8.146374	3.354339	2.749335	H	9.595069	12.252117	-0.897638
C	-9.411626	3.63999	2.296941	H	10.086663	11.032787	-2.088876

H	-10.070273	4.467123	2.508456	C	8.679393	6.415271	-0.365841
C	-5.980152	3.403682	3.794296	H	8.995393	5.800538	0.485488
H	-5.246973	3.907606	4.412088	H	7.733976	5.99672	-0.731206
C	6.380489	4.947135	4.529014	H	9.425977	6.299086	-1.155729
H	7.12957	4.972966	5.312986	C	-14.858006	2.588356	-1.227739
C	8.536277	7.86974	0.018037	H	-15.408191	3.500757	-0.963902
C	9.259891	8.858016	-0.654559	H	-15.479022	1.738294	-0.928175
H	9.921582	8.559863	-1.464342	H	-14.759431	2.574624	-2.317982
C	9.172401	10.21111	-0.304486	C	3.132972	8.225191	-1.545914
C	8.31791	10.571621	0.742373	C	-8.78872	-1.681567	-1.306476
H	8.239463	11.617282	1.028858	Ag	4.519441	-7.427906	0.137298
C	7.564624	9.626632	1.447206	N	2.874275	9.546509	-1.744629
C	7.691266	8.282461	1.06305	N	2.200558	7.590769	-2.327954
C	-7.197694	3.983187	3.602792	N	-7.789294	-2.136575	-2.129095
H	-7.456932	4.926704	4.070794	N	-9.765147	-2.619324	-1.434623
C	6.650407	10.055484	2.571305	C	5.779101	-6.732602	-1.436783
H	6.868739	9.525496	3.505316	C	3.583424	10.638336	-1.109104
H	5.598021	9.86473	2.328462	C	1.820098	9.756932	-2.610877
H	6.757015	11.125949	2.763693	C	2.02804	6.225395	-2.496124
C	5.508485	-14.060982	-0.641391	C	1.367673	8.517867	-2.991158
H	5.388242	-14.093245	-1.728889	C	-6.560932	-1.541489	-2.369983
H	5.061398	-14.97885	-0.238425	C	-8.146783	-3.35316	-2.749208
H	6.57842	-14.097258	-0.412122	C	-11.037951	-2.573606	-0.743975
C	1.874098	-10.549259	-0.782247	C	-9.412061	-3.638636	-2.296773
H	0.986124	-10.583778	-0.13988	N	5.514445	-5.814134	-2.422835
H	1.640377	-11.093678	-1.700944	N	6.969968	-7.272991	-1.81103
C	4.698719	11.190382	-1.760077	H	1.641865	11.093555	1.70069
C	3.084821	11.148017	0.101769	H	2.039095	9.497071	1.046009
H	1.481602	10.746591	-2.872901	C	1.302437	3.352226	-2.480718
C	1.005237	5.732683	-3.259891	C	0.036135	3.750433	-4.469646
H	2.765272	5.614451	-1.992981	H	-0.706831	6.307345	-4.498827
C	0.309744	8.022865	-3.802151	C	-3.484466	-1.89434	-4.473285
C	-5.630592	-2.142292	-3.173366	C	-3.760049	-0.601658	-2.482707
H	-6.42506	-0.584298	-1.885168	H	-5.247421	-3.906928	-4.411861
C	-7.198156	-3.982213	-3.602573	H	-12.509142	-3.661587	2.100138
C	-11.150646	-3.205267	0.505947	C	-13.510305	-2.556733	0.54775
C	-12.120625	-1.934668	-1.369584	H	-9.142361	-3.210662	1.329981
H	-10.070776	-4.465746	-2.508166	H	-9.59366	-4.718356	0.535025
C	4.442676	-4.937697	-2.495318	H	-10.269061	-4.324734	2.120809
C	6.526437	-5.810394	-3.407341	H	-14.198697	-1.452722	-1.165837
C	7.447306	-6.74013	-2.992067	H	-11.267683	-0.43197	-2.679817
C	7.689975	-8.283641	-1.062957	H	-12.943055	-0.866189	-3.04865
C	5.318145	12.289122	-1.156463	H	-11.62494	-1.960626	-3.484244

C	5.218335	10.632556	-3.064409	C	3.175748	-3.113451	-3.614586
C	3.745245	12.246508	0.66063	C	5.296249	-4.127441	-4.60518
C	1.8756	10.549068	0.782037	H	7.128845	-4.974048	-5.312886
C	0.786921	4.270343	-3.406266	C	9.258523	-8.859422	0.654645
C	0.127018	6.678723	-3.916059	C	8.678445	-6.41658	0.365855
H	-0.346866	8.729752	-4.297746	C	8.316226	-10.572899	-0.742229
C	-4.288821	-1.537944	-3.382769	C	6.648773	-10.056546	-2.571131
C	-5.98056	-3.402845	-3.794151	C	5.510895	14.059868	0.641745
H	-7.457472	-4.925776	-4.070438	C	1.097719	1.976171	-2.601862
C	-12.399679	-3.176386	1.133189	H	1.864338	3.709691	-1.62217
C	-9.977277	-3.900429	1.156676	H	-0.339937	4.413614	-5.241951
C	-13.346775	-1.939021	-0.697144	C	-0.247607	2.386436	-4.5841
C	-11.980963	-1.26402	-2.71616	C	-2.178336	-1.413692	-4.624125
H	3.774555	-4.974872	-1.645702	H	-3.870535	-2.562173	-5.237438
C	4.299483	-4.084161	-3.555246	C	-2.484396	-0.055154	-2.631225
C	6.379744	-4.948124	-4.528935	H	-4.341921	-0.300808	-1.6161
H	8.378119	-7.061145	-3.431642	C	-14.858229	-2.585792	1.22798
C	8.53507	-7.871037	-0.017973	C	1.999692	-3.289575	-2.873228
C	7.563093	-9.627803	-1.447074	C	3.257458	-1.964247	-4.410362
H	6.179828	12.734275	-1.64775	H	5.168373	-3.502226	-5.480149
C	4.85457	12.837741	0.044648	H	9.920275	-8.561364	1.464412
H	5.582087	9.604775	-2.946756	C	9.170794	-10.212507	0.304614
H	6.046505	11.239836	-3.438378	H	8.994791	-5.801976	-0.48544
H	4.44238	10.612934	-3.838495	H	7.733047	-5.997777	0.730975
H	3.372053	12.659822	1.594527	H	9.424879	-6.300527	1.155905
H	0.987733	10.583785	0.139533	H	8.237594	-11.618554	-1.028687
H	6.866905	-9.526355	-3.505073	H	2.65602	0.598284	-1.983085
H	5.596397	-9.865969	-2.328101	H	-0.5759	1.200083	-6.381894
H	6.755481	-11.126964	-2.763733	H	-1.33839	2.788068	-6.408954
H	5.390413	14.092201	1.729215	H	-2.033451	1.486822	-5.433642
H	5.064186	14.977862	0.238644	H	-1.461148	-1.081199	-6.639003
H	6.580896	14.095812	0.412722	H	-1.833252	-2.7658	-6.281396
C	0.276375	1.462369	-3.641604	H	-0.355498	-2.030289	-5.644291
C	1.764681	1.085853	-1.570604	H	-1.128274	0.72109	-1.099498
C	-1.092991	1.941487	-5.760937	H	-2.828973	1.101923	-0.83968
C	-1.629828	-0.505143	-3.679053	H	-1.902215	1.960429	-2.075771
C	-1.412153	-1.849618	-5.85615	C	1.046561	-1.183373	-3.693071
C	-2.060642	0.983086	-1.610082	C	-0.24048	-2.686406	-2.012538
H	-15.409523	-3.497028	0.962435	C	2.454874	0.159819	-5.400765
H	-15.478277	-1.734434	0.930068	H	11.028953	-11.267065	0.616901
H	-14.759556	-2.574219	2.318231	H	9.592494	-12.253438	0.898687
C	0.953711	-2.363474	-2.893118	H	10.085909	-11.033722	2.088781
H	1.870448	-4.189244	-2.277722	H	-0.55688	-1.834636	-1.403293

C	2.232204	-1.01515	-4.465802	H	0.004605	-3.505112	-1.328203
H	4.152082	-1.774624	-4.994338	H	-1.11094	-2.994205	-2.59999
C	10.007426	-11.247893	1.017734	H	1.580418	0.368171	-6.024006
B	-0.097587	-0.080343	-3.702309	H	3.292002	-0.045194	-6.074912
H	1.113548	0.284628	-1.21027	H	2.686718	1.080451	-4.855766
H	2.08194	1.670138	-0.700351				

Table S5. Cartesians coordinates of calculated ($[Au_3(\mathbf{1})_2](PF_6)_3$) at the UB3LYP/ LANL2DZ, 6-31G*.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.830495	4.284154	3.36246	C	-2.219428	-1.007051	4.440704
N	-2.933742	9.540134	1.634544	C	0.287946	-2.677534	2.022214
N	-2.253906	7.585839	2.239284	H	0.607304	-1.828906	1.410369
C	-1.114669	1.981267	2.573365	H	0.054754	-3.502661	1.341566
C	2.204419	-1.355816	4.61414	H	1.153113	-2.976525	2.621946
N	-5.450656	-5.830445	2.367646	N	7.801234	-2.048073	2.078915
C	2.490265	-0.004983	2.613121	C	-3.240737	-1.959694	4.375083
C	-0.287777	1.483396	3.616598	H	-4.141482	-1.770309	4.949267
C	-1.335067	3.354004	2.442893	C	3.515607	-1.822738	4.462839
H	-1.901672	3.698228	1.582209	H	3.910312	-2.482411	5.229663
C	-0.917816	-2.354328	2.886761	C	-4.375316	-4.959607	2.460343
C	1.643154	-0.459519	3.664983	H	-3.674142	-5.025958	1.640274
C	-1.025766	-1.170488	3.679695	C	-4.270148	-4.080498	3.50419
C	-1.959874	-3.28458	2.857538	N	-6.898861	-7.295784	1.73219
H	-1.818922	-4.184751	2.265802	C	-3.631259	10.63019	0.980777
C	-4.763	11.178708	1.60425	H	0.389239	-1.982158	5.641766
C	-5.361171	12.284798	0.992009	C	-6.501173	-5.797071	3.308768
H	-6.234605	12.729081	1.462698	C	-1.903744	9.758064	2.525611
C	-4.863256	12.840205	-0.191716	H	-1.580965	10.751202	2.793788
C	-3.740456	12.248085	-0.782712	C	-2.456279	0.167304	5.372983
H	-3.342167	12.664676	-1.704707	H	-1.584235	0.387954	5.995198
C	-3.098819	11.144215	-0.213851	H	-3.290421	-0.046708	6.048074
C	-3.146873	-3.109809	3.581807	H	-2.7003	1.083663	4.826021
C	2.052921	1.02288	1.587214	C	1.072073	1.991765	5.73509
H	1.120217	0.749979	1.083189	H	0.562617	1.248196	6.359768
H	2.816531	1.142815	0.812349	H	1.306344	2.845167	6.378233
H	1.888856	2.00202	2.047274	H	2.018452	1.546318	5.412151
C	-1.771738	1.077133	1.548028	C	11.026352	-2.502509	0.624793
H	-1.114303	0.276399	1.198719	C	11.101287	-3.168614	-0.610172
H	-2.089113	1.650934	0.670928	C	12.333535	-3.166614	-1.269488
H	-2.661922	0.588328	1.961646	H	12.414475	-3.677997	-2.22566

C	3.771592	-0.537709	2.464595	C	13.463521	-2.540313	-0.729237
H	4.347716	-0.233965	1.595342	C	13.335579	-1.885428	0.500279
C	-0.209809	6.701433	3.876945	H	14.202515	-1.392676	0.933322
H	0.614997	6.342255	4.479555	C	12.126552	-1.85044	1.202972
C	-3.169518	8.215354	1.434868	C	-7.413863	-6.728796	2.879565
C	4.31288	-1.463715	3.367979	H	-8.364468	-7.030578	3.289104
C	-1.062644	5.743533	3.204936	C	8.178446	-3.25387	2.70569
C	-0.404718	8.043047	3.755327	C	9.436769	-3.539193	2.232798
H	0.232066	8.75893	4.263592	H	10.103178	-4.360653	2.441612
N	9.771576	-2.531839	1.350915	C	6.029637	-3.305449	3.78603
C	-0.076063	3.779123	4.430594	H	5.310964	-3.807399	4.422128
H	0.291378	4.450241	5.19997	C	-6.392403	-4.910621	4.415111
C	0.223555	2.419325	4.554097	H	-7.172006	-4.91441	5.169093
C	-2.073143	6.221883	2.415381	C	-8.408	-7.91212	-0.101076
H	-2.792823	5.604123	1.896167	C	-9.130046	-8.903955	-0.770102
C	-1.448528	8.523878	2.918799	H	-9.759204	-8.614876	-1.60854
C	-5.307037	-4.095189	4.5152	C	-9.080946	-10.248486	-0.381679
H	-5.210707	-3.451656	5.380593	C	-8.264657	-10.597953	0.699073
C	5.65909	-2.056757	3.153721	H	-8.21365	-11.637389	1.012969
C	8.785492	-1.604263	1.233726	C	-7.514735	-9.649481	1.402579
B	0.105663	-0.054382	3.68654	C	-7.606347	-8.314101	0.981111
C	-5.688834	-6.77323	1.398729	C	7.248955	-3.877703	3.583329
C	6.572657	-1.457072	2.330352	H	7.523556	-4.812605	4.059646
H	6.424266	-0.508016	1.834281	C	-6.636957	-10.065047	2.559836
C	1.445305	-1.793396	5.849889	H	-6.877095	-9.516999	3.478116
H	1.491188	-1.022148	6.630151	H	-5.577127	-9.88629	2.341579
H	1.873966	-2.705281	6.276836	H	-6.757779	-11.131009	2.768126
C	-5.497314	14.068979	-0.799058	C	6.552863	1.513567	-2.332754
H	-5.396702	14.077806	-1.889163	C	8.13789	3.331318	-2.696164
H	-5.017081	14.981352	-0.422615	C	10.995942	2.593026	-0.623721
H	-6.561195	14.138866	-0.551172	C	9.393181	3.627625	-2.2218
C	-1.879201	10.539337	-0.869192	N	-5.506381	5.783307	-2.361038
H	-1.008227	10.552396	-0.203132	N	-6.965186	7.23701	-1.723158
H	-1.613845	11.093776	-1.773164	C	-4.68057	-11.211364	-1.606994
H	-2.052519	9.494121	-1.153286	C	-3.009359	-11.174302	0.204602
C	-5.329049	10.604396	2.881358	H	-1.500847	-10.763048	-2.802567
H	-5.746823	9.603716	2.716836	C	-1.021635	-5.751227	-3.210634
H	-6.129742	11.240923	3.266498	H	-2.750166	-5.626236	-1.898204
H	-4.568014	10.514021	3.664801	C	-0.347004	-8.045166	-3.763986
C	12.02407	-1.121569	2.522114	C	5.632138	2.108793	-3.151326
H	11.425181	-0.207416	2.426142	H	6.415451	0.559403	-1.843314
H	13.016333	-0.83177	2.877311	C	7.200921	3.950625	-3.569058
H	11.557171	-1.737199	3.299013	C	11.064917	3.23349	0.624667

C	9.904347	-3.864956	-1.214383	C	12.102916	1.967128	-1.217998
H	9.07609	-3.166587	-1.385503	H	10.049681	4.458541	-2.4245
H	9.524978	-4.66279	-0.564537	C	-4.423306	4.922447	-2.456161
H	10.167451	-4.316509	-2.174373	C	-6.55945	5.739453	-3.298833
C	-9.916719	-11.286199	-1.092397	C	-7.478816	6.663924	-2.868142
H	-10.945304	-11.287151	-0.709477	C	-7.678407	8.25103	-0.971709
H	-9.515967	-12.294366	-0.948909	C	-5.270548	-12.322589	-0.996174
H	-9.973786	-11.089309	-2.168048	C	-5.254372	-10.635672	-2.879989
C	-8.502347	-6.467096	-0.531805	C	-3.643077	-12.28337	0.7723
H	-8.813423	-5.815805	0.29377	C	-1.79004	-10.565618	0.857025
H	-7.538468	-6.090849	-0.895539	C	-0.801567	-4.289937	-3.36767
H	-9.232312	-6.354411	-1.337588	C	-0.162756	-6.701988	-3.885052
C	14.793549	-2.6005	-1.441829	H	0.294193	-8.755721	-4.274178
H	15.334432	-3.51936	-1.18121	C	4.292201	1.502834	-3.368057
H	15.436033	-1.757875	-1.167831	C	5.988135	3.365853	-3.775336
H	14.668129	-2.597384	-2.529455	H	7.46464	4.891889	-4.038958
C	-3.10539	-8.240471	-1.437725	C	12.298786	3.231872	1.281712
C	8.764555	1.678015	-1.236773	C	9.861041	3.902967	1.245092
N	-2.860097	-9.563256	-1.639182	C	13.312364	1.999874	-0.516658
N	-2.196352	-7.603374	-2.24361	C	12.003961	1.274215	-2.556545
N	7.774812	2.116687	-2.077963	H	-3.720048	4.99689	-1.638588
N	9.73978	2.617826	-1.347422	C	-4.31329	4.042989	-3.499193
C	-5.749762	6.725248	-1.392639	C	-6.446129	4.852444	-4.404268
C	-3.549156	-10.659099	-0.986176	H	-8.433222	6.956935	-3.275197
C	-1.830416	-9.772617	-2.532654	C	-8.473166	7.844749	0.11392
C	-2.02667	-6.237976	-2.419227	C	-7.598152	9.586408	-1.395518
C	-1.385313	-8.534674	-2.925634	H	-6.143499	-12.769867	-1.464902
C	-4.765038	-12.879394	0.183692	H	-9.824172	8.539787	1.625143
H	-5.674882	-9.6369	-2.710941	C	-9.162575	10.176449	0.393278
H	-6.0545	-11.273967	-3.263377	H	-8.864786	5.744835	-0.275731
H	-4.497058	-10.540521	-3.666491	H	-7.586696	6.031252	0.907517
H	-3.23904	-12.700815	1.691408	H	-9.280501	6.28304	1.356572
H	-0.920153	-10.577807	0.189498	H	-8.310453	11.56966	-1.006454
H	-1.521909	-11.118285	1.761259	H	-6.968595	9.457005	-3.473671
H	-1.965019	-9.52038	1.13994	H	-5.665834	9.833875	-2.342844
C	-1.312656	-3.364632	-2.446845	H	-6.855301	11.071834	-2.764567
C	-0.05255	-3.777919	-4.436323	H	-5.283993	-14.126273	1.878831
H	0.657904	-6.335987	-4.489205	H	-4.907642	-15.022133	0.406725
C	3.492232	1.856291	-4.462776	H	-6.455013	-14.1875	0.546571
C	3.759627	0.569883	-2.466758	C	-0.282631	-1.484549	-3.620504
H	5.263369	3.863747	-4.407758	C	-1.767385	-1.092431	-1.549596
H	12.375746	3.724109	2.248193	C	1.079343	-1.979831	-5.740513
C	13.434712	2.629999	0.726687	C	1.632367	0.474212	-3.667843

H	9.045929	3.188873	1.414542	C	1.422607	1.8096	-5.850587
H	9.463753	4.701032	0.606393	C	2.055313	-1.008001	-1.592404
H	10.123458	4.348456	2.208108	H	15.306345	3.608292	1.176785
H	14.184026	1.526005	-0.96106	H	15.407525	1.84701	1.162977
H	11.329292	0.410839	-2.510813	H	14.641226	2.686198	2.525761
H	12.985324	0.914484	-2.875806	C	-0.944413	2.347095	-2.887693
H	11.62341	1.942852	-3.337462	H	-1.86128	4.168523	-2.263889
C	-3.181187	3.082775	-3.579301	C	-2.235452	0.989471	-4.441408
C	-5.353646	4.046862	-4.506766	H	-4.164861	1.735528	-4.947096
H	-7.228103	4.848078	-5.155786	C	-10.003444	11.209083	1.105387
C	-9.200262	8.83222	0.783952	B	0.098236	0.056408	-3.689613
C	-8.554919	6.399772	0.547411	H	-1.117759	-0.284333	-1.202777
C	-8.352711	10.530336	-0.690888	H	-2.075623	-1.669196	-0.671176
C	-6.727582	10.006628	-2.55654	H	-2.664263	-0.613639	-1.96056
C	-5.390215	-14.113558	0.789307	H	0.562373	-1.241303	-6.365035
C	-1.103935	-1.990015	-2.576598	H	1.321814	-2.83087	-6.383761
H	-1.875151	-3.714122	-1.585582	H	2.0214	-1.525076	-5.417889
H	0.319802	-4.445383	-5.206529	H	1.471639	1.038037	-6.630327
C	0.235505	-2.415569	-4.559167	H	1.845651	2.723546	-6.278695
C	2.185659	1.377159	-4.61547	H	0.365774	1.992577	-5.641091
H	3.881294	2.521104	-5.228082	H	1.121455	-0.743196	-1.086169
C	2.48332	0.0255	-2.616561	H	2.821086	-1.123993	-0.81909
H	4.338554	0.270247	-1.597932	H	1.89778	-1.987215	-2.054496
C	14.765399	2.68965	1.438086	C	-1.042578	1.162877	-3.681413
C	-1.994868	3.267736	-2.856366	C	0.259556	2.680512	-2.024577
C	-3.265338	1.932673	-4.373641	C	-2.462749	-0.185889	-5.374825
H	-5.254431	3.403107	-5.371655	H	-11.032474	11.204308	0.723683
H	-9.608652	12.219588	0.961769	H	-3.298519	0.022094	-6.049794
H	-10.058058	11.011475	2.181021	H	-2.699545	-1.104694	-4.828774
H	0.586563	1.834676	-1.412926	Au	-4.426585	-7.446799	-0.077245
H	0.020433	3.503895	-1.343879	Au	-4.488456	7.410449	0.078762
H	1.121566	2.986257	-2.625433	Au	8.767795	0.034978	-0.004061
H	-1.588957	-0.399002	-5.997179				

6. F^- binding investigations

In order to determine the bind ratio between $[Au_3(\mathbf{1})_2](PF_6)_3$ and TBAF, the analysis of UV-vis absorption spectroscopic data was carried out using a nonlinear least-squares curve fitting procedure performed with the online software Bindfit (http://supramolecular.org/) with a 1:2 global fitting modelS6 (Nelder-Mead method) [S10,S11]. A solution of $[Au_3(\mathbf{1})_2](PF_6)_3$ (3 mL, 1×10^{-5} M in CH_3CN) was placed in the colorimetric dish and was titrated with incremental amounts of fluoride anions by addition 2.5 μL of solution of *n*-Bu_4NF in CH_3CN (3×10^{-3} M), which represents 4 equivalents of $[Au_3(\mathbf{1})_2](PF_6)_3$. The emission at 349 nm was monitored.

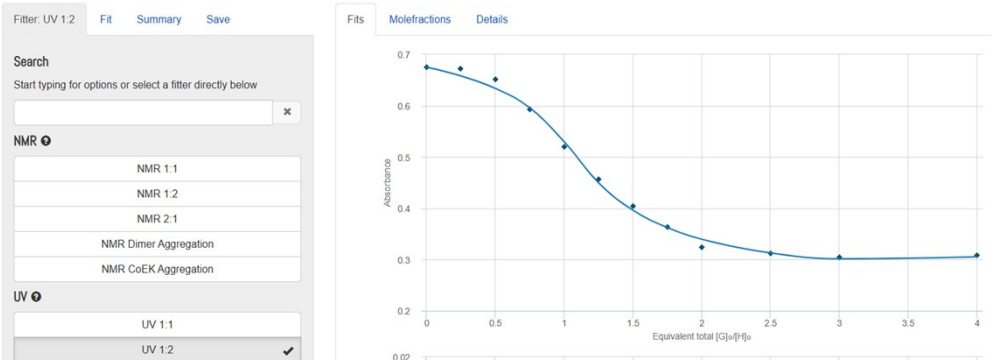


Fig. S27 Fitted binding isotherm of $[Au_3(\mathbf{1})_2](PF_6)_3$ with TBAF showing the change in the chemical shift for the UV-vis absorption signal at 349 ppm upon addition of fluoride and the fitted isotherm obtained using a 1:2 binding model.

Job plot of $[Au_3(1)_2](PF_6)_3$ with fluoride ions

Maintaining the total concentration of $[Au_3(\mathbf{1})_2](PF_6)_3$ and fluoride anions at 1×10^{-5} M, a series of solutions of $[Au_3(\mathbf{1})_2](PF_6)_3$ and fluoride anions in varying proportions was sampled. A full set of fluorescence spectra was measured monitoring fluorescence intensity at λ_{em}= 478 nm (λ_{ex} = 330 nm).

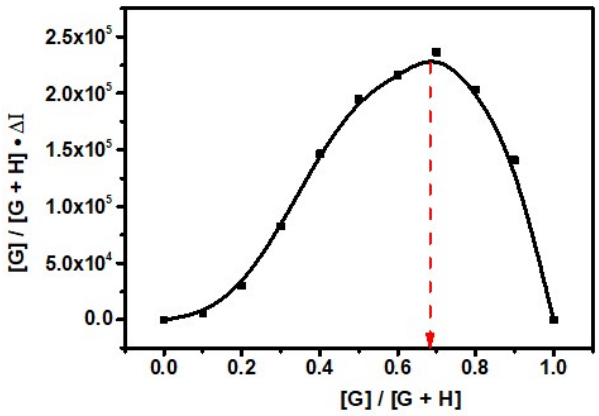


Fig. S28 Job plot of $[Au_3(\mathbf{1})_2](PF_6)_3$ with TBAF in CH_3CN at 298 K. G: TBAF; H: $[Au_3(\mathbf{1})_2](PF_6)_3$.

7. References

(1) F. Rauch, P. Endres, A. Friedrich, D. Sieh, M. Hähnel, I. Krummenacher, H. Braunschweig, M. Finze, L. Ji and T. B. Marder, *Chem. – Eur. J.,* 2020, **26**, 12951–12963.

(2) N. Mihara, T. K. Ronson and J. R. Nitschke, *Angew. Chem., Int. Ed.,* 2019, **58**, 12497–12501.

(3) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *Appl. Cryst.*, 2009, **42**, 339–341.

(4) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59–75.

(5) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.

(6) R. B. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M.

Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(7) P. Hohenberg, W. Kohn, *Phys. Rev. B.*, 1964, **136**, B864–B871.

(8) W. Kohn, L. Sham, *J. Phys. Rev.*, 1965, **140**, A1133–A1138.

(9) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

(10) P. Thordarson, *Chem. Soc. Rev.*, 2011, 40, 1305–1323.

(11) M. Kazem-Rostami, A. Orte, A. M. Ortuño, A. H. G. David, I. Roy, D. Miguel, A. Garci, C. M. Cruz, C. L. Stern, J. M. Cuerva, J. F. Stoddart, *J. Am. Chem. Soc.*, 2022, **144**, 9380–9389.