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Process-Tracing Study on the Post-Assembly Modification of Poly-NHC-Based Metallosupramolecular Cylinders with Tunable Aggregation-Induced Emission

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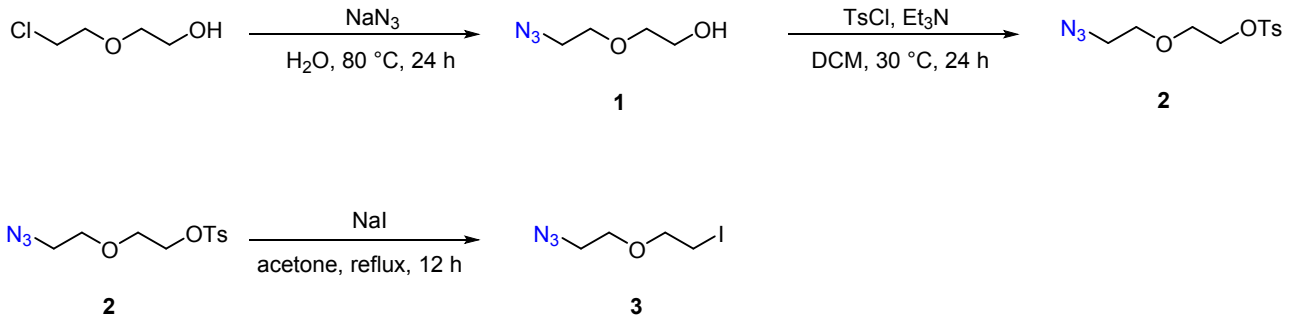
Contents

1. General description of synthetic procedures

^{1}H, $^{13}C\{^{1}H\}$ and 2D NMR spectra were recorded on Bruker AVANCE III 400. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. Mass spectra were obtained with a Bruker microTOF-Q II mass spectrometer (Bruker Daltonics Corp., USA) in the electrospray ionization (ESI) mode. Compounds 2,4,6-tris[4-(1H-imidazol-1-yl)phenyl]-1,3,5-triazine, 2,4,6-tris[4-(1H-imidazol-1-yl)phenyl]-1,3,5-benzene, were synthesized according to published procedures.[1] Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification.

2. Synthesis of 1-azido-2-(2-iodoethoxy)ethane

Scheme S1. Synthesis of 1-azido-2-(2-iodoethoxy)ethane.



2.1. Synthesis of 2-(2-azidoethoxy)ethan-1-ol (1). A sample of 2-(2-chloroethoxy)ethan-1-ol (10 mL, 94.7 mmol) was dissolved in H_2O (60 mL) and sodium azide (15.4 g, 236.8 mmol, 2.5 eq) was added. The reaction mixture was stirred at 80 ºC for 24 h and then poured into sodium hydroxide (5%, 100 mL) and extracted with diethyl ether (100 mL x 3). The organic layer was dried over Na_2SO_4 and evaporated to dryness to afford **1** (7.505 g, 57.2 mmol, 60%) as a clear oil. The analytical data of **1** were in complete agreement with literature data.[2]

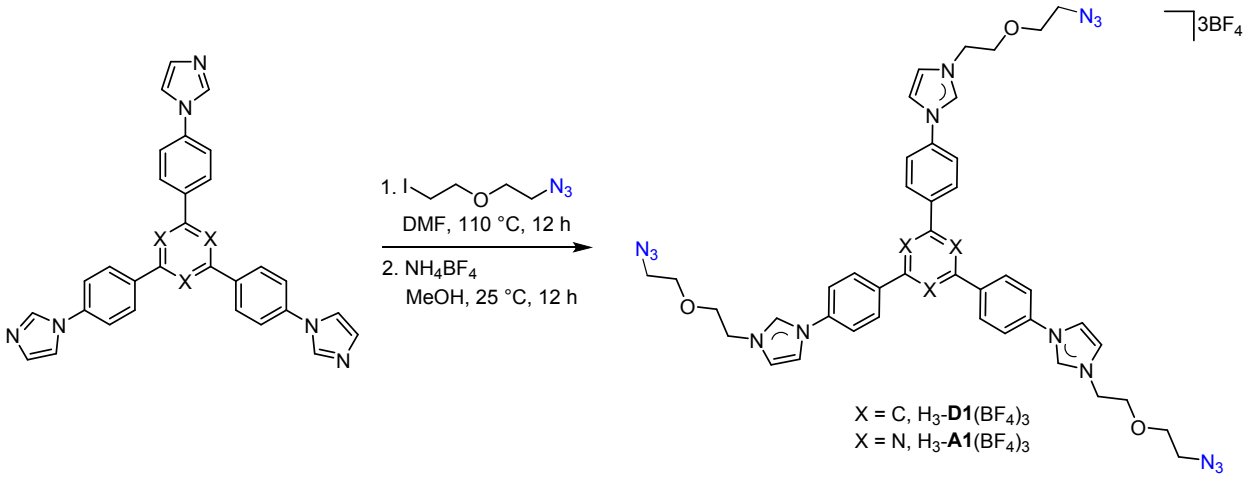
2.2. Synthesis of 2-(2-azidoethoxy)ethyl 4-methylbenzenesulfonate (2). A sample of 2-(2-azidoethoxy)ethan-1-ol (3.952 g, 30.1 mmol) in CH_2Cl_2 (80 mL) was added Et_3N (8.5 mL, 60.7 mmol) at room temperature. Then *p*-TsCl (8.621 g, 45.2 mmol) was added and this solution stirred for 24 h. The solution was washed with H_2O (100 mL) dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/ petroleum ether 1:10) affording the desired linker **2**

(7.646 g, 26.8 mmol, 89%) as a clear oil. The analytical data of **2** were in complete agreement with literature data.[3]

2.3. Synthesis of 1-azido-2-(2-iodoethoxy)ethane (3). A sample of 2-(2-azidoethoxy)ethan-1-ol (3.074 g, 10 mmol) in acetone (80 mL) was added NaI (4.497 g, 30 mmol). The reaction mixture was stirred and refluxed for 12 h. The solution was cooled down to room temperature, evaporated to dryness. The target compound was extracted with dichloromethane (200 mL) and washed with brine (2 x 100 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to dryness to afford **3** (2.610 g, 57.2 mmol, 60%) as an orange oil (2.350 g, 9.7 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (t, J = 6.8 Hz, 2H), 3.62 (t, J = 4.8 Hz, 2H), 3.35 (t, J = 4.8 Hz, 2H), 3.21 (t, J = 6.8 Hz, 2H).

3. Synthesis of trisimidazolium tris-NHC precursors

Scheme S2. Synthesis of the trisimidazolium salts H_3-**D1**$(BF_4)_3$ and H_3-**A1**$(BF_4)_3$.



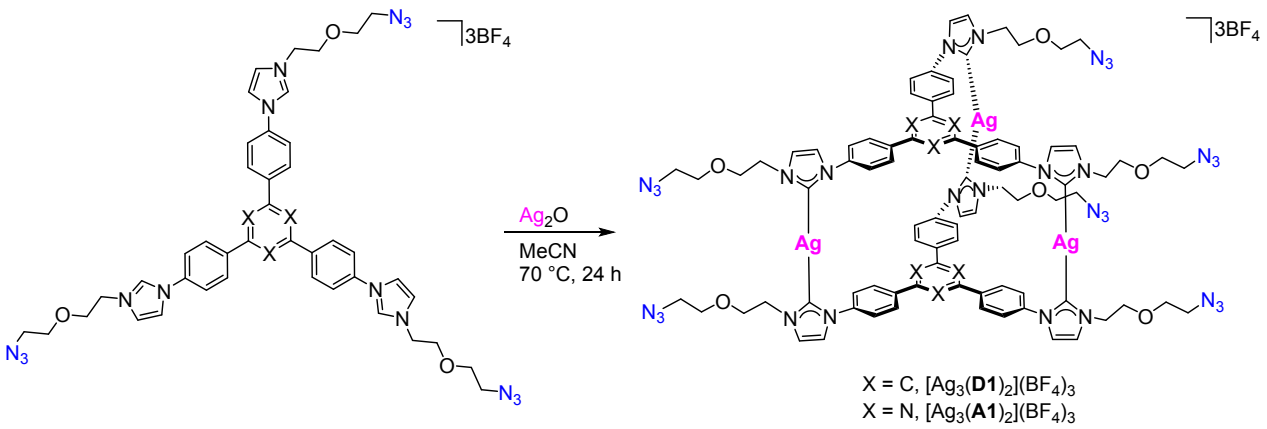
3.1. Synthesis of H_3-D1$(BF_4)_3$. A sample of 2,4,6-tris[4-(1H-imidazol-1-yl)phenyl]-1,3,5-benzene (0.505 g, 1.0 mmol) and an excess of 1-azido-2-(2-iodoethoxy)ethane (1.2 g, 5.0 mmol) were dissolved in 3 mL of DMF and the reaction mixture was heated to 110 °C for 12 h. After the reaction was cooled to room temperature, 40 mL ethyl acetate was then added to the mixture. During this time, a white compound precipitated. The precipitate was then removed from the solution by vacuum filtration, washed with ethyl acetate and dried *in vacuo* to give H_3-**D1**$(Br)_3$ as a white solid. The obtained solid was transferred to a bottle containing 10 mL methanol. To this was added a solution of NH_4BF_4 (0.420 g, 4.0 mmol) in methanol (35 mL). The mixture was stirred at 25 °C for 24 h. Over this period, the

tetrafluoroborate salt H_3-**D1**$(BF_4)_3$ precipitated as a white solid. The solid was collected by filtration, washed with methanol, and dried *in vacuo*. Yield: 0.781 g (0.71 mmol, 71%, over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.91 (s, 3H, imidazolium-H), 8.46 (s, 3H, imidazolium-H), 8.29 (d, J = 8.2 Hz, 6H, Ar-H), 8.18 (s, 3H, Ar-H), 8.07 (s, 3H, imidazolium-H), 7.94 (d, J = 8.2 Hz, 6H, Ar-H), 4.51 (t, *J* = 5.0 Hz, 6H), 3.96 (t, *J* = 5.0 Hz, 6H), 3.70 (t, *J* = 4.8 Hz, 6H), 3.42 (t, *J* = 4.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 140.9, 140.1, 135.6, 134.3, 129.0, 125.4, 123.6, 122.1, 121.1, 69.3, 67.6, 49.9, 49.3. ESI-MS (positive ions): *m* / *z* = 466.7103 (calcd for $[H_3$-**D1**$(BF_4)]^{2+}$ 466.7045), *m* / *z* = 282.1416 (calcd for $[H_3$-**D1**$]^{3+}$ 282.1349).

3.2. Synthesis of H_3-A1$(BF_4)_3$. A sample of 2,4,6-tris[4-(1H-imidazol-1-yl)phenyl]-1,3,5-triazine (0.508 g, 1.0 mmol) and an excess of 1-azido-2-(2-iodoethoxy)ethane (1.2 g, 5.0 mmol) were dissolved in 3 mL of DMF and the reaction mixture was heated to 110 °C for 12 h. After the reaction was cooled to room temperature, 40 mL ethyl acetate was then added to the mixture. During this time, a yellowish compound precipitated. The precipitate was then removed from the solution by vacuum filtration, washed with ethyl acetate and dried *in vacuo* to give H_3-**A1**$(Br)_3$ as a yellowish solid. The obtained solid was transferred to a bottle containing 10 mL methanol. To this was added a solution of NH_4BF_4 (0.420 g, 4.0 mmol) in methanol (35 mL). The mixture was stirred at 25 °C for 24 h. Over this period, the tetrafluoroborate salt H_3-**A1**$(BF_4)_3$ precipitated as a white solid. The solid was collected by filtration, washed with methanol, and dried *in vacuo*. Yield: 0.987 g (0.89 mmol, 89%, over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.02 (s, 3H, imidazolium-H), 9.09 (d, J = 8.0 Hz, 6H, Ar-H), 8.55 (s, 3H, imidazolium-H), 8.11 (s, 3H, imidazolium-H), 8.09 (d, J = 8.0 Hz, 6H, Ar-H), 4.58–4.43 (m, 12H), 4.03–3.90 (m, 12H), 3.76–3.64 (m, 12H), 3.51–3.39 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 170.2, 138.1, 136.1, 136.0, 130.8, 123.8, 122.1, 121.0, 69.3, 67.6, 49.9, 49.4. ESI-MS (positive ions): *m* / *z* = 468.2033 (calcd for $[H_3$-**A1**$(BF_4)]^{2+}$ 468.1974), *m* / *z* = 283.1373 (calcd for $[H_3$-**A1**$]^{3+}$ 283.1302).

4. Synthesis of the trisilver assemblies $[Ag_3(L)_2](BF_4)_3$ (L = D1, A1)

Scheme S3. Synthesis of trisilver assemblies $[Ag_3(D1)_2](BF_4)_3$ and $[Ag_3(A1)_2](BF_4)_3$



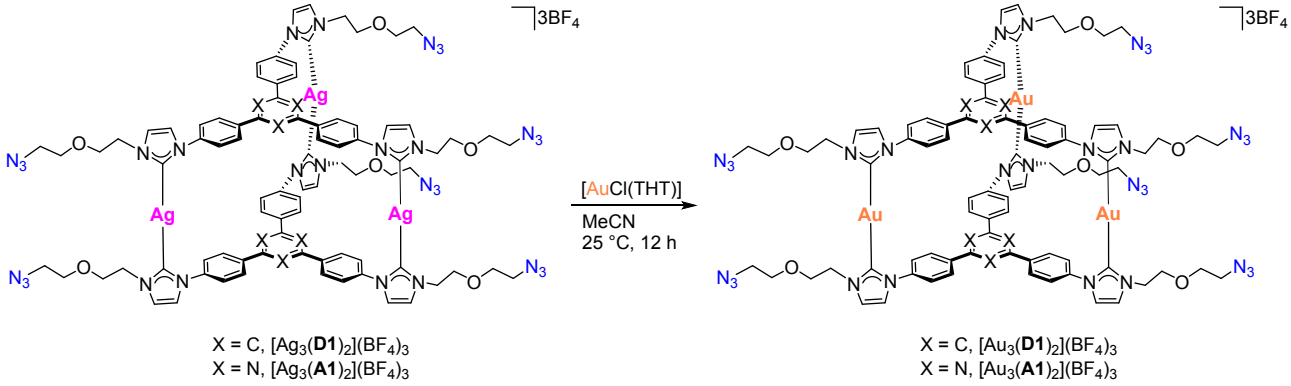
4.1. Synthesis of $[Ag_3(D1)_2](BF_4)_3$. To a mixture of H_3-**D1**$(BF_4)_3$ (0.332 g, 0.3 mmol) and Ag_2O (0.278 g, 1.2 mmol) was added 40 mL of acetonitrile. The reaction mixture was then heated to 70 °C for 24 h under exclusion of light. After cooling of the reaction mixture to ambient temperature, the resulting suspension was filtered through a pad of Celite to give a reddish brown solution. The filtrate was concentrated to 2 mL, and diethyl ether (40 mL) was added. The cylinder-like complex $[Ag_3(\mathbf{D1})_2](BF_4)_3$ precipitated as reddish brown solid. The solid was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.538 g, (0.237 mmol, 79%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.01 (s, 6H, imidazolylidine-H), 7.82 (s, 6H, Ar-H), 7.79 (d, J = 8.0 Hz, 12H, Ar-H), 7.75 (d, J = 8.0 Hz, 12H, Ar-H), 7.64 (s, 6H, imidazolylidine-H), 4.63–4.55 (m, 12H), 4.05–3.99 (m, 12H), 3.76–3.68 (m, 12H), 3.47–3.43 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 179.1, 171.4, 138.9, 138.7, 138.5, 127.2, 123.5, 122.8, 122.0, 69.7, 69.3, 51.7, 50.1. ESI-MS (positive ions): *m* / *z* = 1049.2413 (calcd for $[Ag_3(\mathbf{D1})_2(BF_4)]^{2+}$ 1049.2415), *m* / *z* = 670.4994 (calcd for $[Ag_3(\mathbf{D1})_2]^{3+}$ 670.4931).

4.2. Synthesis of $[Ag_3(A1)_2](BF_4)_3$. To a mixture of H_3-**A1**$(BF_4)_3$ (0.333 g, 0.3 mmol) and Ag_2O (0.278 g, 1.2 mmol) was added 40 mL of acetonitrile. The reaction mixture was then heated to 70 °C for 24 h under exclusion of light. After cooling of the reaction mixture to ambient temperature, the resulting suspension was filtered through a pad of Celite to give a reddish brown solution. The filtrate was concentrated to 2 mL, and diethyl ether (40 mL) was added. The cylinder-like complex $[Ag_3(\mathbf{A1})_2](BF_4)_3$ precipitated as reddish brown solid.

The solid was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.492 g, (0.216 mmol, 72%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.34 (d, J = 8.0 Hz, 12H, Ar-H), 8.12 (s, 6H, imidazolylidine-H), 7.95 (d, J = 8.0 Hz, 12H, Ar-H), 7.89 (s, 6H, imidazolylidine-H), 4.70–4.55 (m, 12H), 4.12–3.97 (m, 12H), 3.80–3.69 (m, 12H), 3.50–3.44 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 169.2, 142.7, 134.2, 129.1, 123.7, 122.7, 121.6, 69.6, 67.3, 51.8, 50.1. ESI-MS (positive ions): m / z = 672.4932 (calcd for $[Ag_3(\mathbf{A1})_2]^{3+}$ 672.4836).

5. Synthesis of the trigold assemblies $[Au_3(L)_2](BF_4)_3$ (L = D1, A1)

Scheme S4. Synthesis of trigold assemblies $[Au_3(D1)_2](BF_4)_3$ and $[Au_3(A1)_2](BF_4)_3$



5.1. Synthesis of $[Au_3(D1)_2](BF_4)_3$. A solution of $[Ag_3(\mathbf{D1})_2](BF_4)_3$ (0.136 g, 0.060 mmol) in acetonitrile (30 mL) was added solid [AuCl(THT)] (0.062 g, 0.192 mmol). Immediately after the addition the mixture turned from light reddish to black. The reaction mixture was stirred at ambient temperature for 12 h and was then slowly filtered through a pad of Celite until a clear filtrate was obtained. The filtrate was concentrated to 2 mL, and diethyl ether (40 mL) was added to give $[Au_3(\mathbf{D1})_2](BF_4)_3$ a dark solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo.* Yield: 0.142 g (0.056 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.00 (s, 6H, imidazolylidine-H), 7.86 (s, 6H, Ar-H), 7.84 (d, J = 8.0 Hz, 12H, Ar-H), 7.76 (d, J = 8.0 Hz, 12H, Ar-H), 7.71 (s, 6H, imidazolylidine-H), 4.70–4.60 (m, 12H), 4.11–4.02 (m, 12H), 3.77–3.68 (m, 12H), 3.48–3.40 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 181.3, 171.0, 138.7, 138.4, 138.0, 126.9, 124.4, 123.6, 122.7, 69.4, 69.3, 51.1, 50.1. ESI-MS (positive ions): m / z = 1182.3371 (calcd for $[Au_3(\mathbf{D1})_2(BF_4)]^{2+}$ 1182.3344), m / z = 759.5606 (calcd for $[Au_3(\mathbf{D1})_2]^{3+}$ 759.5557).

5.2. Synthesis of $[Au_3(A1)_2](BF_4)_3$. A solution of $[Ag_3(\mathbf{A1})_2](BF_4)_3$ (0.342 g, 0.150 mmol) in acetonitrile (30 mL) was added solid [AuCl(THT)] (0.154 g, 0.480 mmol). Immediately after the addition the mixture turned from light reddish to black. The reaction mixture was stirred at ambient temperature for 12 h and was then slowly filtered through a pad of Celite until a clear filtrate was obtained. The filtrate was concentrated to 2 mL, and diethyl ether (40 mL) was added to give $[Au_3(\mathbf{A1})_2](BF_4)_3$ a dark solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo.* Yield: 0.228 g (0.132 mmol, 88%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.37 (d, J = 8.0 Hz, 12H, Ar-H), 8.12 (s, 6H, imidazolylidine-H), 7.97 (d, J = 8.0 Hz, 12H, Ar-H), 7.93 (s, 6H, imidazolylidine-H), 4.75–4.65 (m, 12H), 4.14–4.04 (m, 12H), 3.80–3.71 (m, 12H), 3.52–3.41 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 181.3, 169.2, 141.7, 134.4, 128.7, 123.6, 122.1, 69.3, 51.2, 50.1. ESI-MS (positive ions): m / z = 1185.3175 (calcd for $[Au_3(\mathbf{A1})_2BF_4]^{2+}$ 1185.3201). m / z = 761.5561 (calcd for $[Au_3(\mathbf{A1})_2]^{3+}$ 761.5462).

6. Postassembly modification of $[Au_3(D1)_2](BF_4)_3$ and $[Au_3(A1)_2](BF_4)_3$

6.1 Clickable modification of $[Au_3(D1)_2](BF_4)_3$ with phenylacetylene. $[Au_3(\mathbf{D1})_2](BF_4)_3$ (127 mg, 0.05 mmol) was dissolved in acetonitrile (25 mL), to which phenylacetylene (102 mg, 0.5 mmol) and $[Cu(CH_3CN)_4]BF_4$ (16 mg, 0.05 mmol) was added. The reaction was monitored by ESI-MS. The reaction mixture was stirred at 70 °C for 21 d. The resulting mixture was then concentrated to 5 mL, and ethyl acetate (40 mL) was added to give $[Au_3(\mathbf{D2})_2](BF_4)_3$ a brown solid, which was collected by filtration, washed with ethyl acetate, and dried *in vacuo.* Yield: 0.121 g (0.038 mmol, 77%).

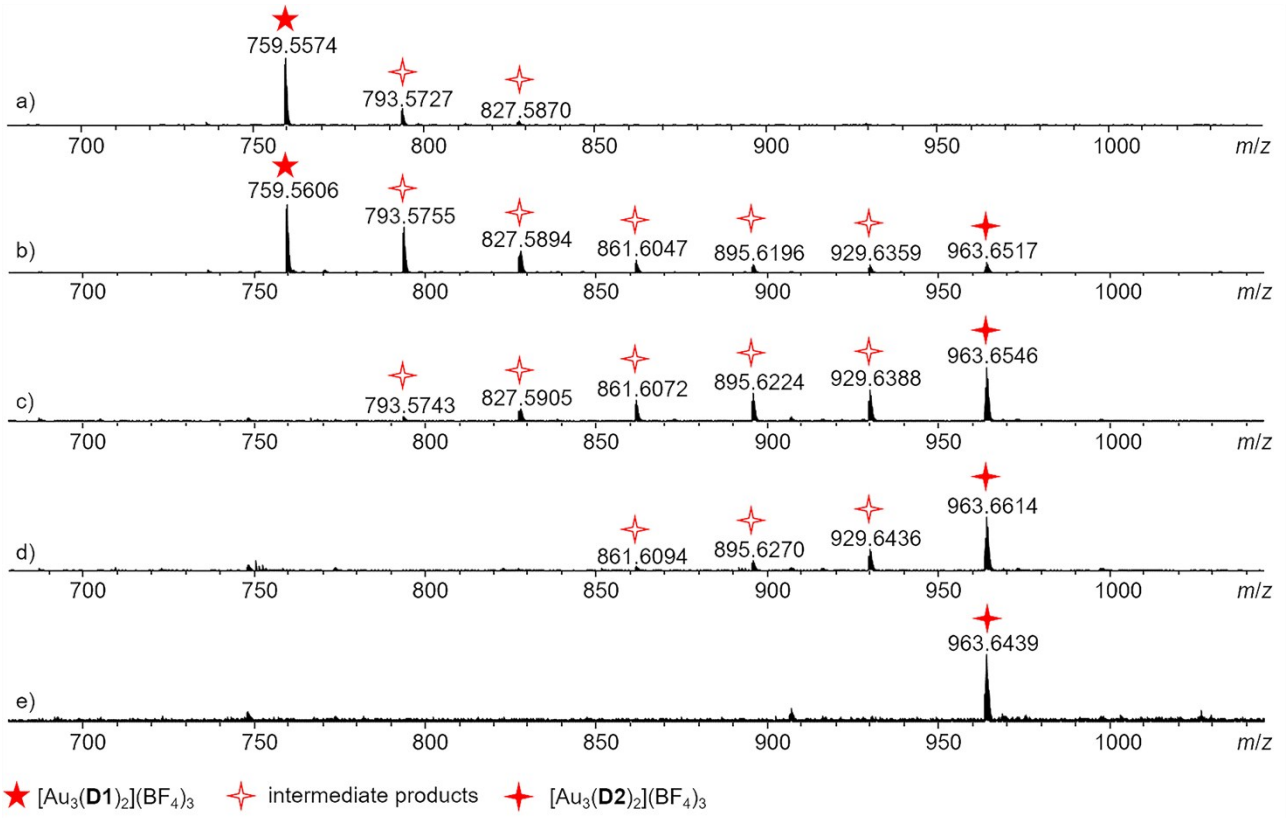


Figure S1. ESI-MS-based process tracing of the PAM products of $[Au_3(\mathbf{D1})_2](BF_4)_3$ with phenylacetylene over various intervals: a) 12 h, b) 3 d, c) 10 d, d) 15 d, e) 21 d.

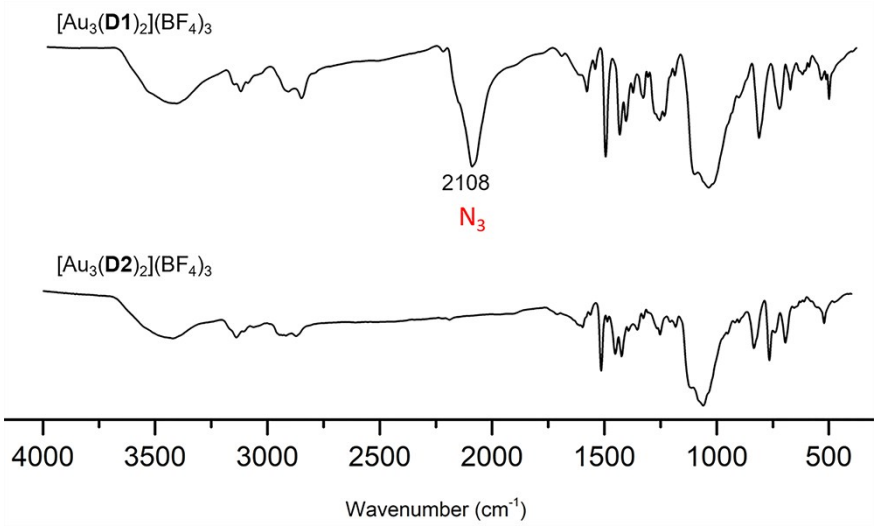


Figure S2. IR spectra of $[Au_3(\mathbf{D1})_2](BF_4)_3$ and $[Au_3(\mathbf{D2})_2](BF_4)_3$.

6.2 Clickable modification of $[Au_3(D1)_2](BF_4)_3$ with (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene. $[Au_3(\mathbf{D1})_2](BF_4)_3$ (127 mg, 0.05 mmol) was dissolved in acetonitrile (25 mL), to which (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene (178 mg, 0.5 mmol) and $[Cu(CH_3CN)_4]BF_4$ (16 mg, 0.05 mmol) was added. The reaction was monitored by ESI-MS. The reaction mixture was stirred at 70 °C for 22 d. The resulting mixture was then concentrated to 5 mL, and ethyl acetate (40 mL) was added to give $[Au_3(\mathbf{D3})_2](BF_4)_3$ a gray solid, which was collected by filtration, washed with ethyl acetate, and dried *in vacuo.* Yield: 0.175 g (0.037 mmol, 75%).

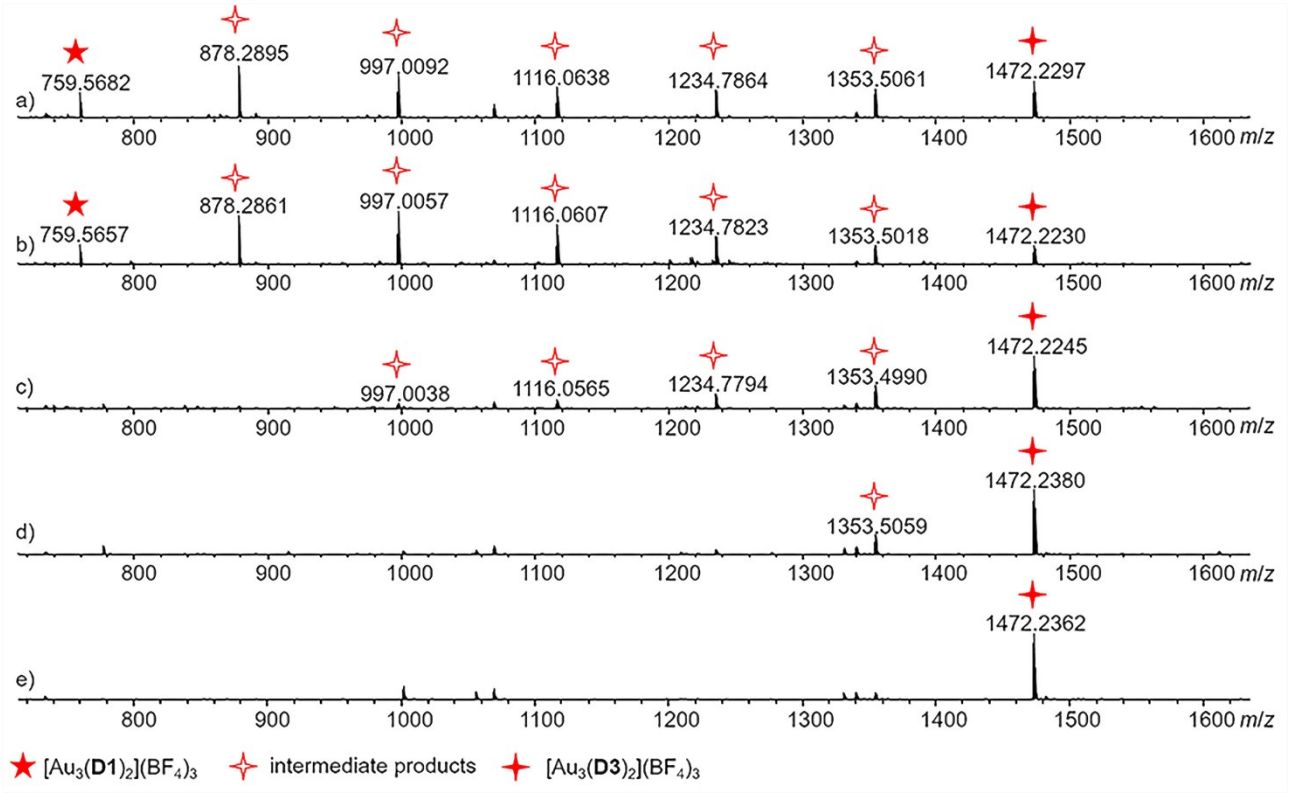


Figure S3. ESI-MS-based process tracing of the PAM products of $[Au_3(\mathbf{D1})_2](BF_4)_3$ with (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene over various intervals: a) 1 d), b) 2 d, c) 7 d, d) 17 d, e) 22 d.

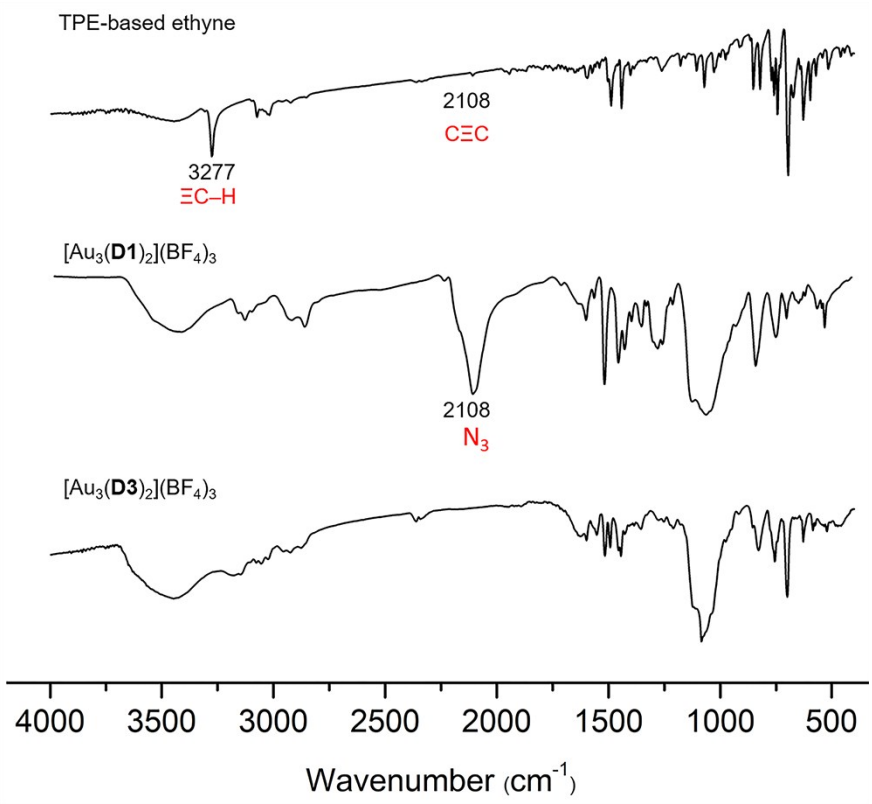


Figure S4. IR spectra of TPE-based alkyne, $[Au_3(\mathbf{D1})_2](BF_4)_3$ and $[Au_3(\mathbf{D3})_2](BF_4)_3$.

6.3 Clickable modification of $[Au_3(A1)_2](BF_4)_3$ with phenylacetylene. $[Au_3(\mathbf{A1})_2](BF_4)_3$ (127 mg, 0.05 mmol) was dissolved in acetonitrile (25 mL), to which phenylacetylene (102 mg, 0.5 mmol) and $[Cu(CH_3CN)_4]BF_4$ (16 mg, 0.05 mmol) was added. The reaction was monitored by ESI-MS. The reaction mixture was stirred at 70 °C for 22 d. The resulting mixture was then concentrated to 5 mL, and ethyl acetate (40 mL) was added to give $[Au_3(\mathbf{A2})_2](BF_4)_3$ a brown solid, which was collected by filtration, washed with ethyl acetate, and dried *in vacuo.* Yield: 0.132 g (0.042 mmol, 84%).

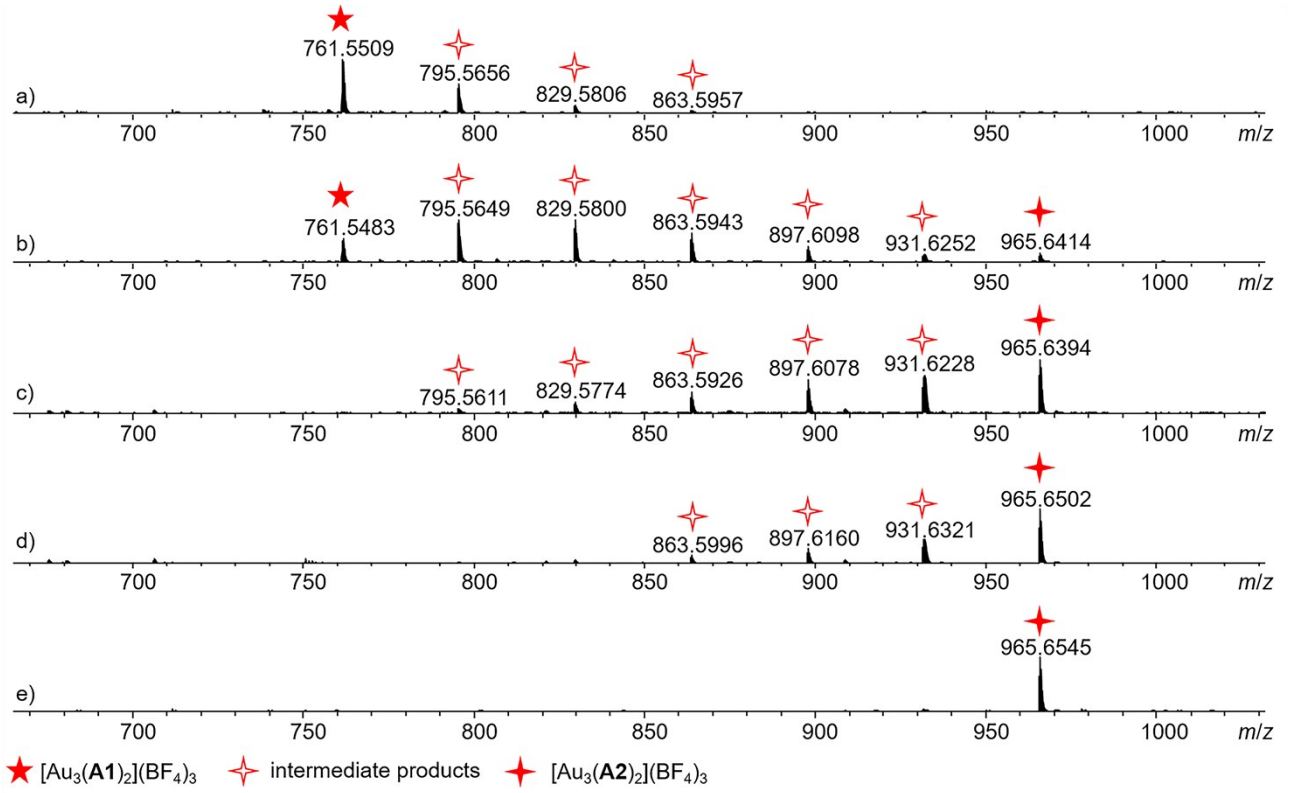


Figure S5. ESI-MS-based process tracing of the PAM products of $[Au_3(\mathbf{A1})_2](BF_4)_3$ with phenylacetylene over various intervals: a) 1 d, b) 2 d, c) 3 d, d) 5 d, e) 22 d.

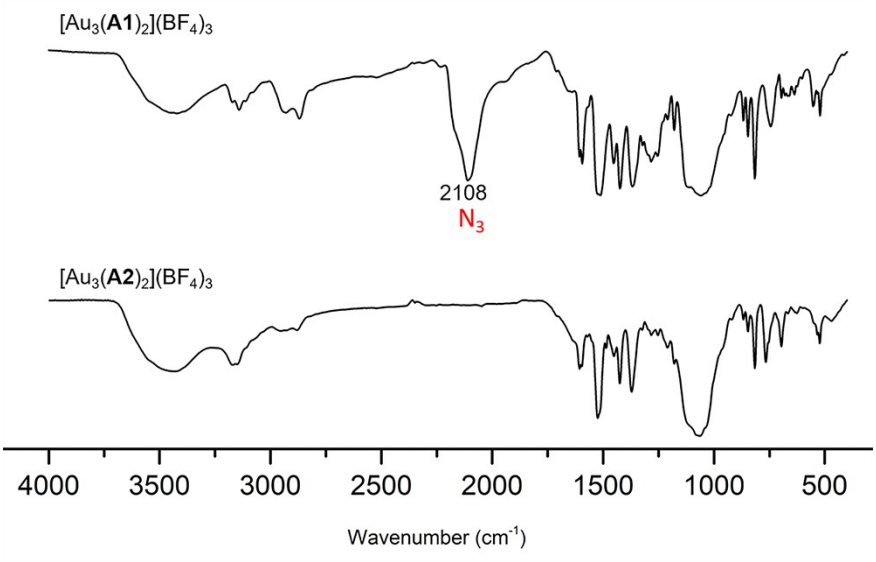


Figure S6. IR spectra of $[Au_3(\mathbf{A1})_2](BF_4)_3$ and $[Au_3(\mathbf{A2})_2](BF_4)_3$.

6.4 Clickable modification of $[Au_3(A1)_2](BF_4)_3$ with (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene. $[Au_3(\mathbf{A1})_2](BF_4)_3$ (127 mg, 0.05 mmol) was dissolved in acetonitrile (25 mL), to which (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene (178 mg, 0.5 mmol) and $[Cu(CH_3CN)_4]BF_4$ (16 mg, 0.05 mmol) was added. The reaction was monitored by ESI-MS. The reaction mixture was stirred at 70 °C for 22 d. The resulting mixture was then concentrated to 5 mL, and ethyl acetate (40 mL) was added to give $[Au_3(\mathbf{A3})_2](BF_4)_3$ a gray solid, which was collected by filtration, washed with ethyl acetate, and dried *in vacuo.* Yield: 0.182 g (0.039 mmol, 78%).

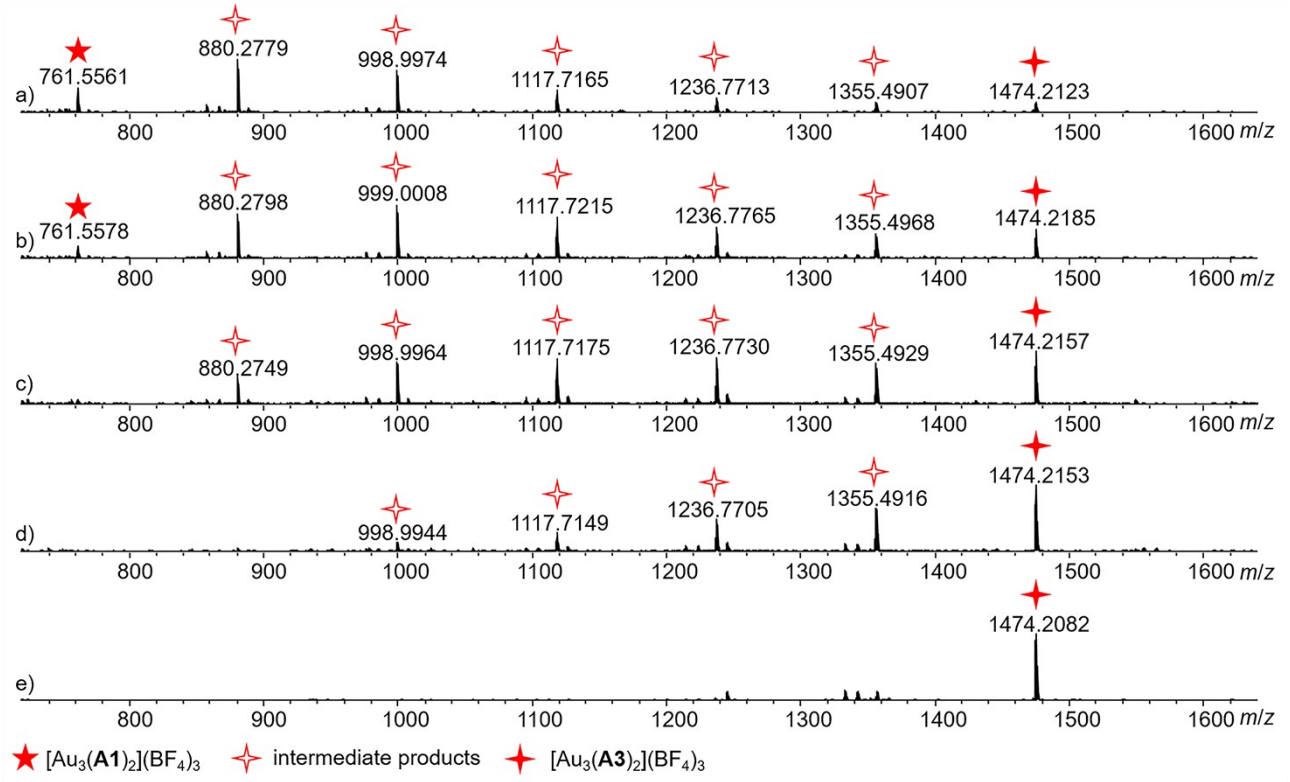


Figure S7. ESI-MS-based process tracing of the PAM products of $[Au_3(\mathbf{A1})_2](BF_4)_3$ with (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene over various intervals: a) 1 d, b) 2 d, c) 3 d, d) 5 d, e) 22 d.

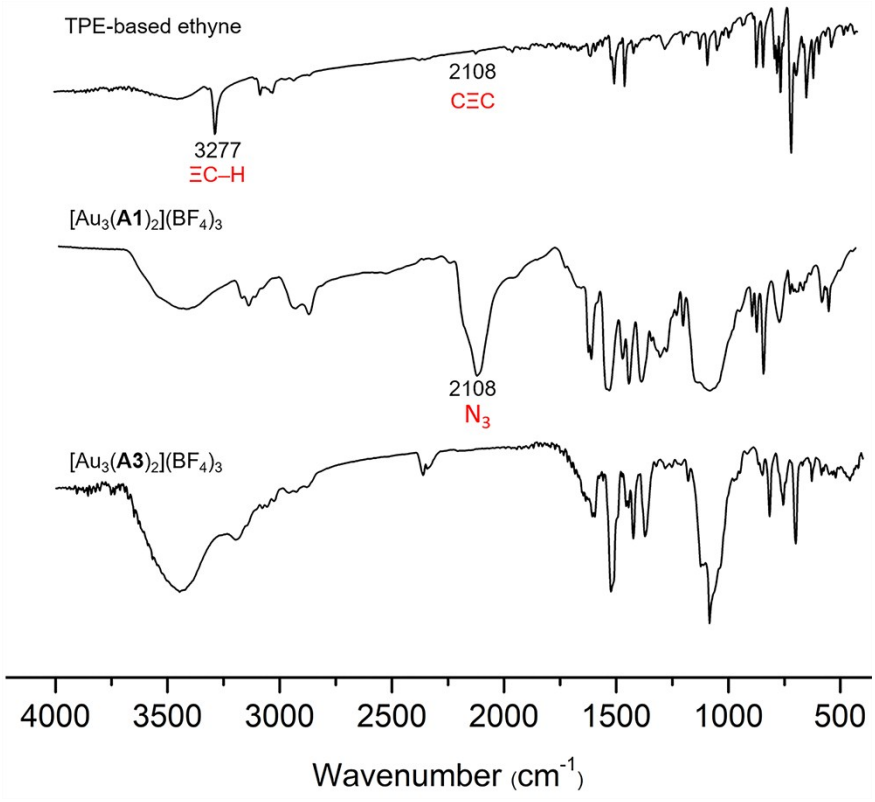


Figure S8. IR spectra of TPE-based alkyne, $[Au_3(\mathbf{A1})_2](BF_4)_3$ and $[Au_3(\mathbf{A3})_2](BF_4)_3$.

7. Aggregation-induced emission study of $[Au_3(D3)_2](BF_4)_3$ and $[Au_3(A3)_2](BF_4)_3$

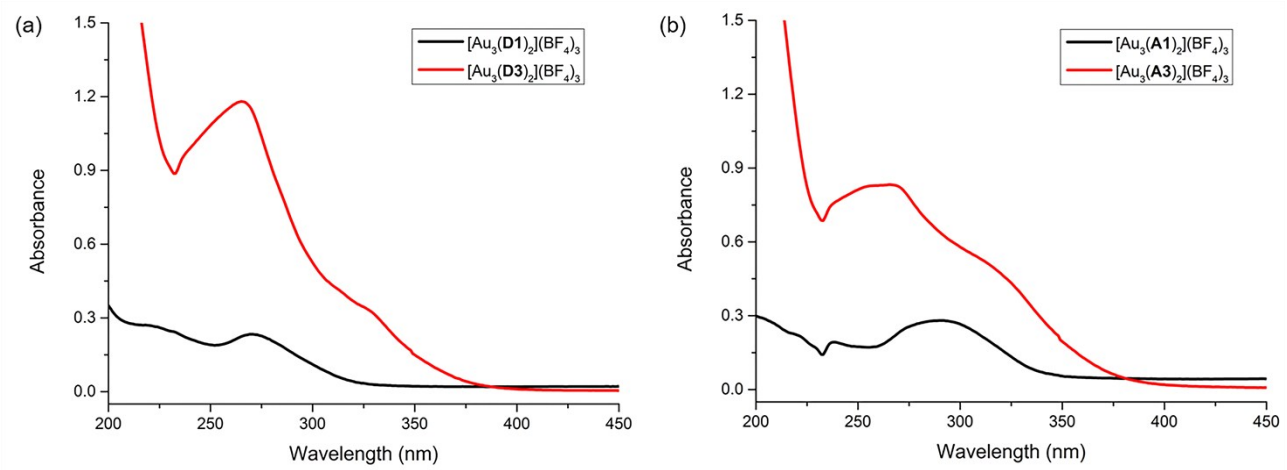


Figure S9. UV/Vis absorption spectra (water fraction = 90%, 6.7 μM) of $[Au_3(\mathbf{D1})_2](BF_4)_3$ and $[Au_3(\mathbf{D3})_2](BF_4)_3$ (a) ; $[Au_3(\mathbf{A1})_2](BF_4)_3$ and $[Au_3(\mathbf{A3})_2](BF_4)_3$ (b).

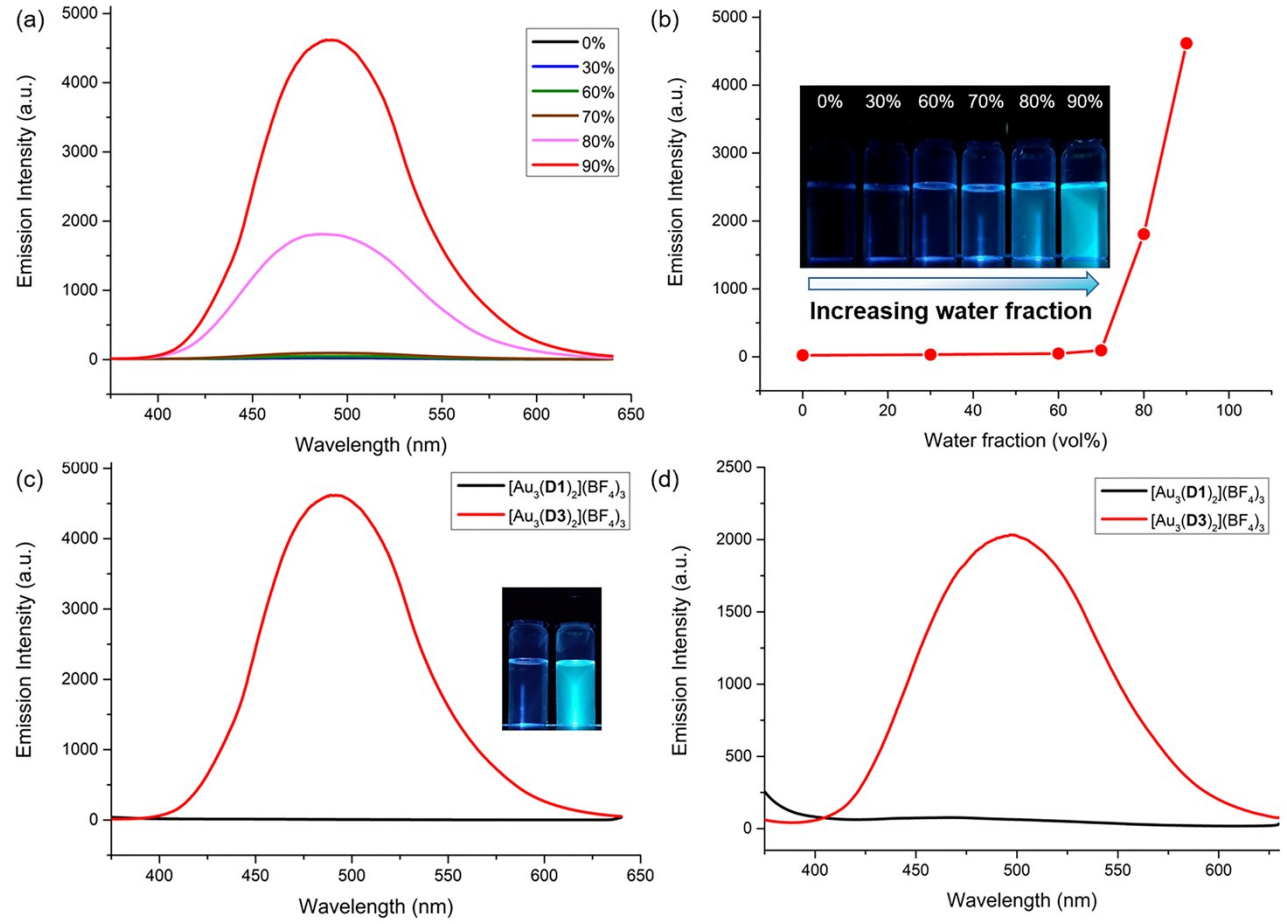


Figure S10. Emission spectrum and plot of maximum emission intensity and wavelength of $[Au_3(\mathbf{D3})_2](BF_4)_3$ (a,b). The inset photographs show the CH_3CN solution of $[Au_3(\mathbf{D3})_2](BF_4)_3$ with increasing water content from 0 to 90% under 365 nm UV light.

Emission spectrum of $Au_3(\mathbf{D1})_2](BF_4)_3$ and $Au_3(\mathbf{D3})_2](BF_4)_3$ in MeCN/H_2O (10/90) mixture (λ_{ex} = 325 nm, c = 6.7 μM) (c) and solid state (d).

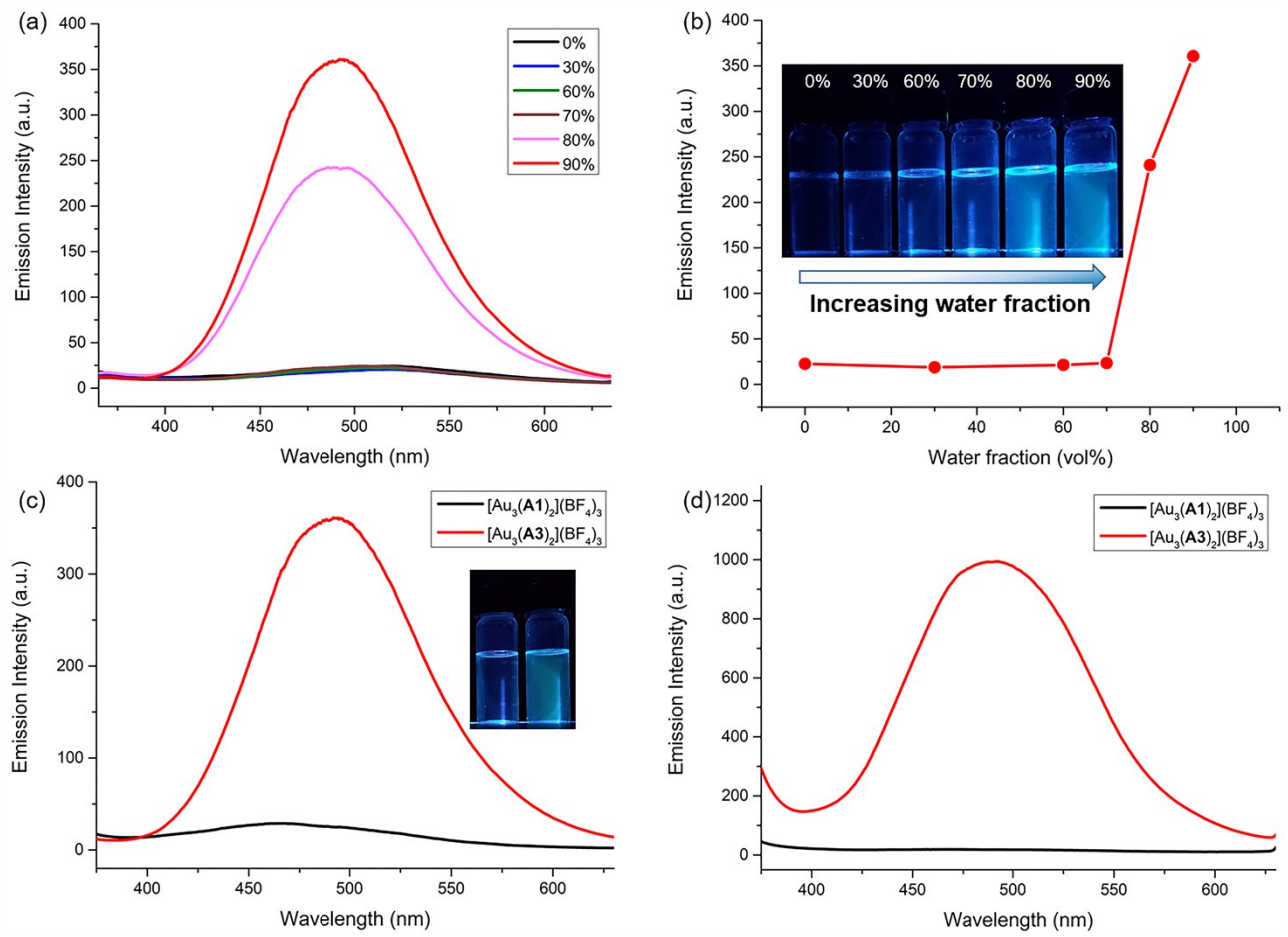


Figure S11. Emission spectrum and plot of maximum emission intensity and wavelength of $[Au_3(\mathbf{A3})_2](BF_4)_3$ (a,b). The inset photographs show the CH_3CN solution of $[Au_3(\mathbf{A3})_2](BF_4)_3$ with increasing water content from 0 to 90% under 365 nm UV light. Emission spectrum of $Au_3(\mathbf{A1})_2](BF_4)_3$ and $Au_3(\mathbf{A3})_2](BF_4)_3$ in MeCN/H_2O (10/90) mixture (λ_{ex} = 325 nm, c = 6.7 μM) (c) and solid state (d).

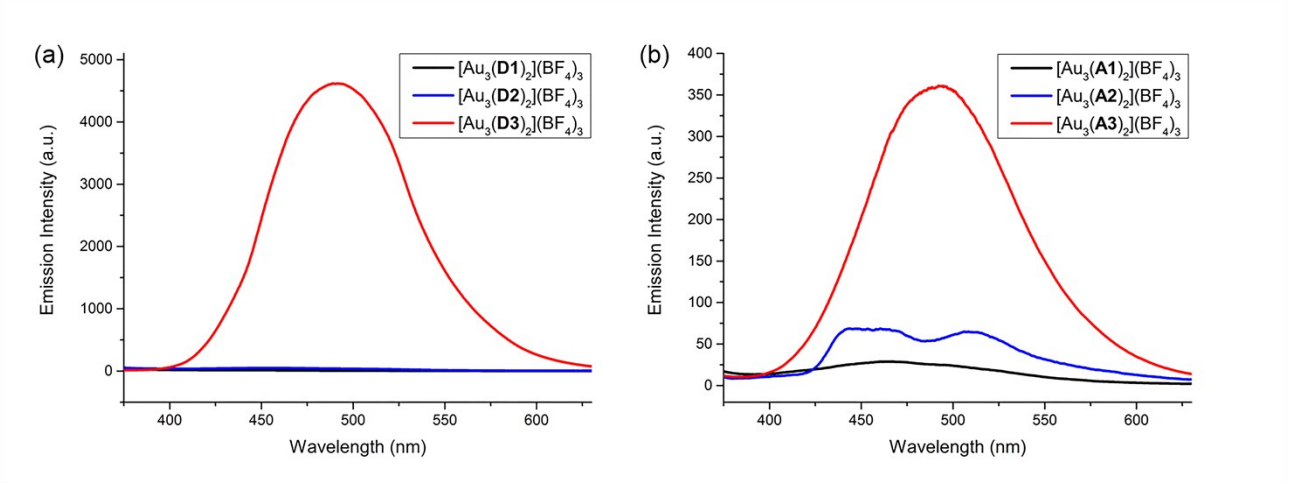


Figure S12. Emission spectra of Au_3(**D1**)$_2$]$(BF_4)_3$, Au_3(**D2**)$_2$]$(BF_4)_3$, Au_3(**D3**)$_2$]$(BF_4)_3$ (a) and Au_3(**A1**)$_2$]$(BF_4)_3$, Au_3(**A2**)$_2$]$(BF_4)_3$, Au_3(**A3**)$_2$]$(BF_4)_3$ (b) in MeCN/H_2O (10/90) mixture (λ_{ex} = 325 nm, c = 6.7 μM).

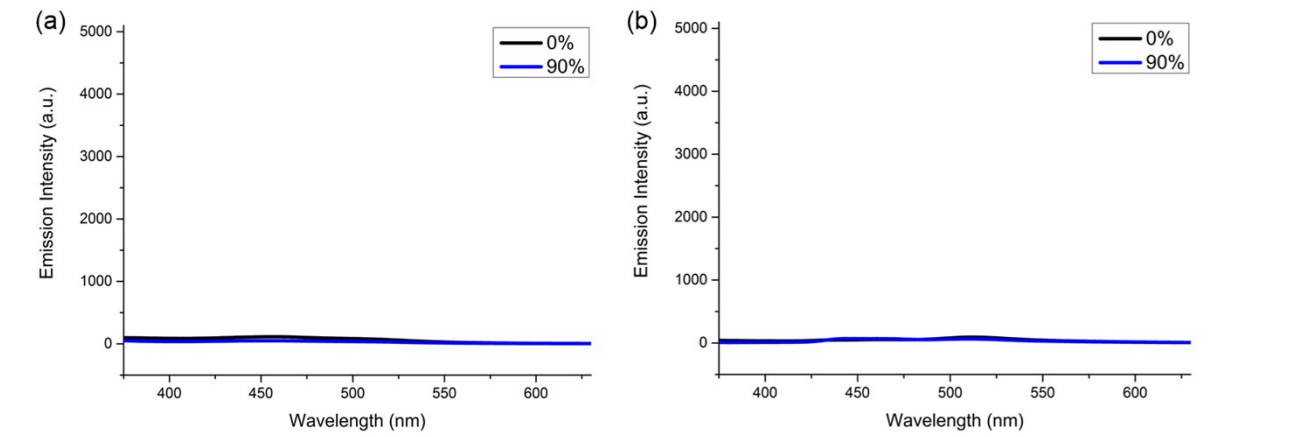


Figure S13. Emission spectrum of Au_3(**D2**)$_2$]$(BF_4)_3$ (a), and Au_3(**A2**)$_2$]$(BF_4)_3$ (b) in MeCN and MeCN/H_2O (10/90) mixture (λ_{ex} = 325 nm, c = 6.7 μM).

8. References

1 (a) Y.-S. Wang, T. Feng, Y.-Y. Wang, F. E. Hahn and Y.-F. Han, *Angew. Chem.*, *Int. Ed.*, 2018, **57**, 15767–15771; (b) L.-Y. Sun, N. Sinha, T. Yan, Y.-S. Wang, T. T. Y. Tan, L. Yu, Y.-F. Hahn and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2018, ***57***, 5161–5165; (c) A. Rit, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2010, **132**, 4572–4573.

2 J. Sinha, R. Sahoo and A. Kumar, *Macromolecules*, 2009, **42**, 2015–2022.

9. Selected NMR and MS spectra for new compounds

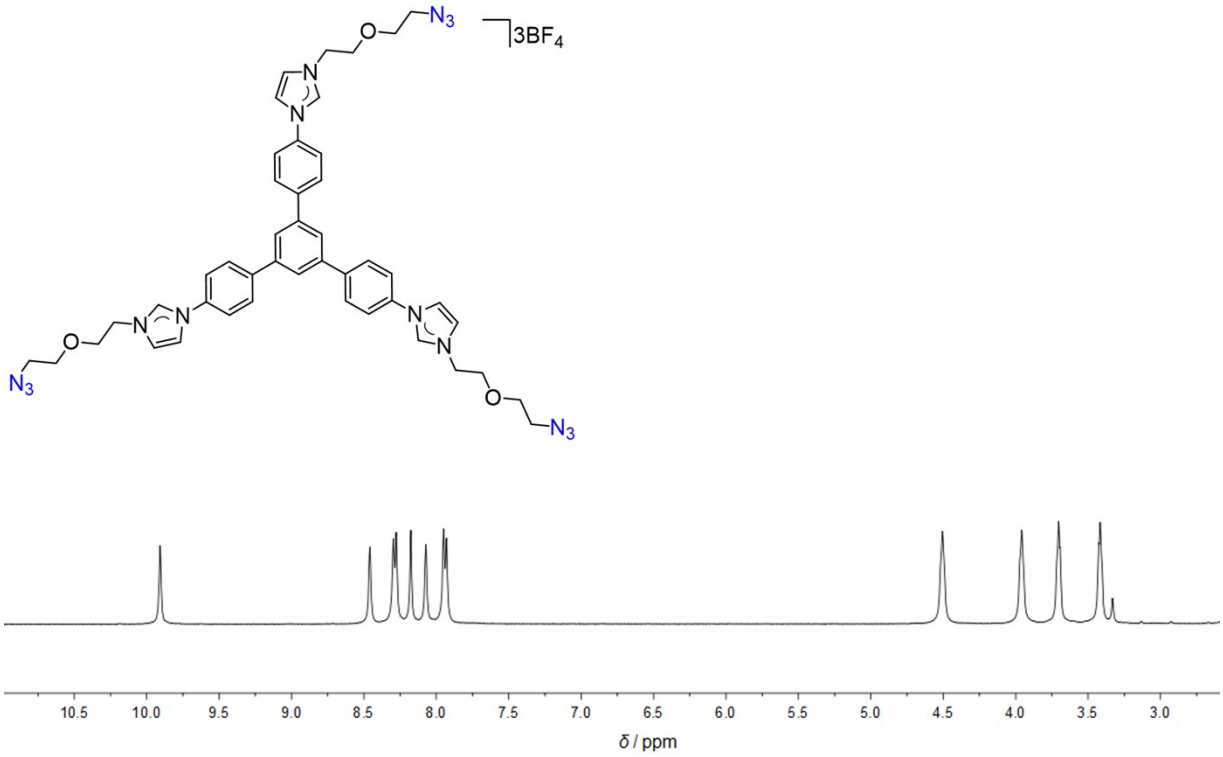


Figure S14. ^{1}H NMR spectrum of H_3-**D1**$(BF_4)_3$ (400 MHz, DMSO-d_6).

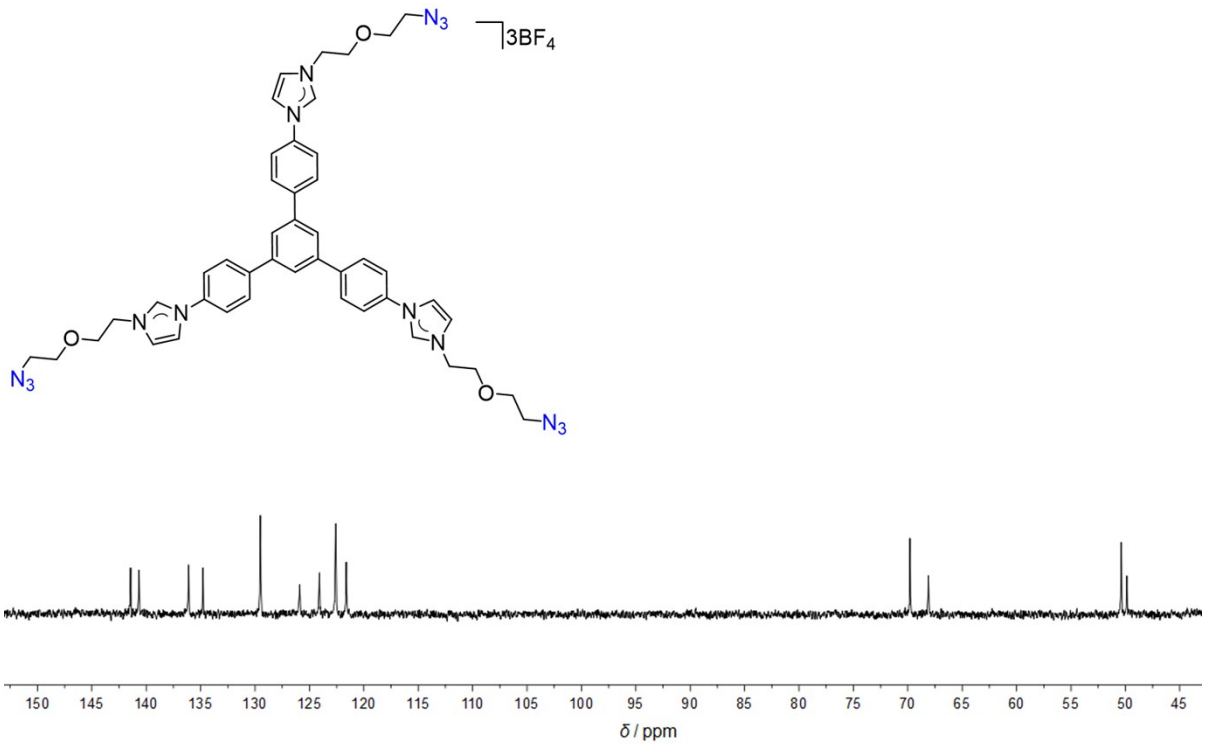


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of H_3-**D1**$(BF_4)_3$ (100 MHz, DMSO-d_6).

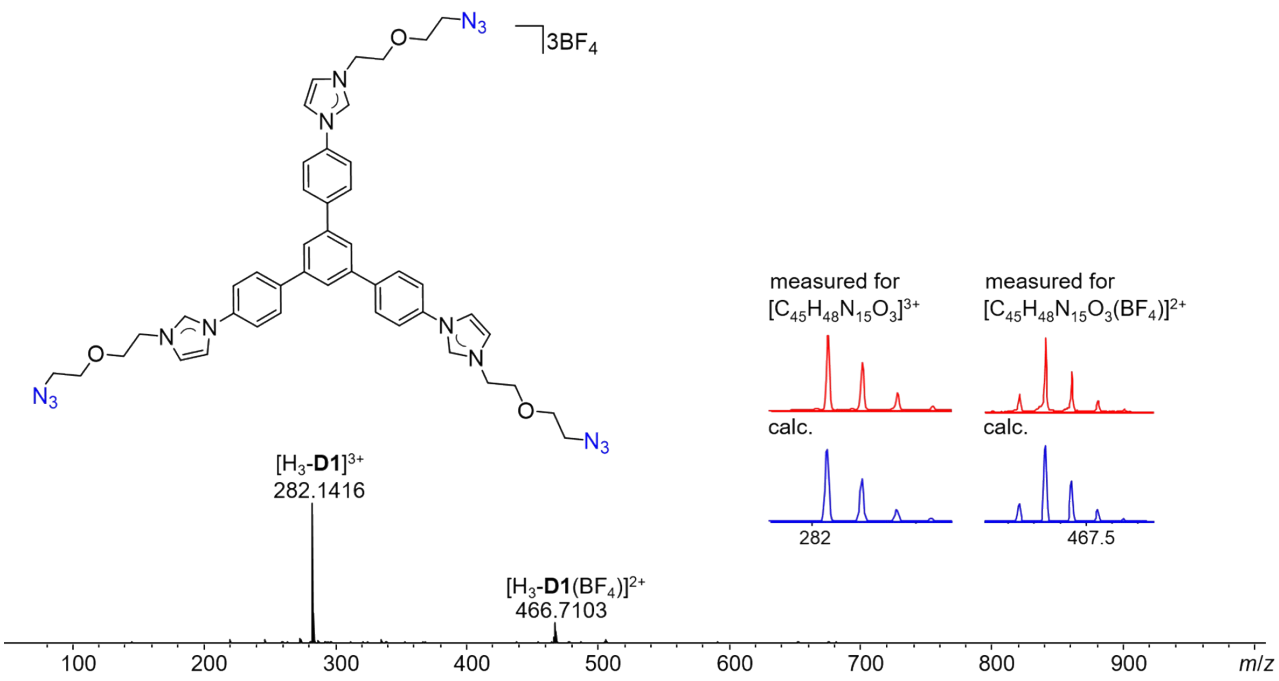


Figure S16. HR-ESI mass spectrum (positive ions) of H_3-**D1**$(BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

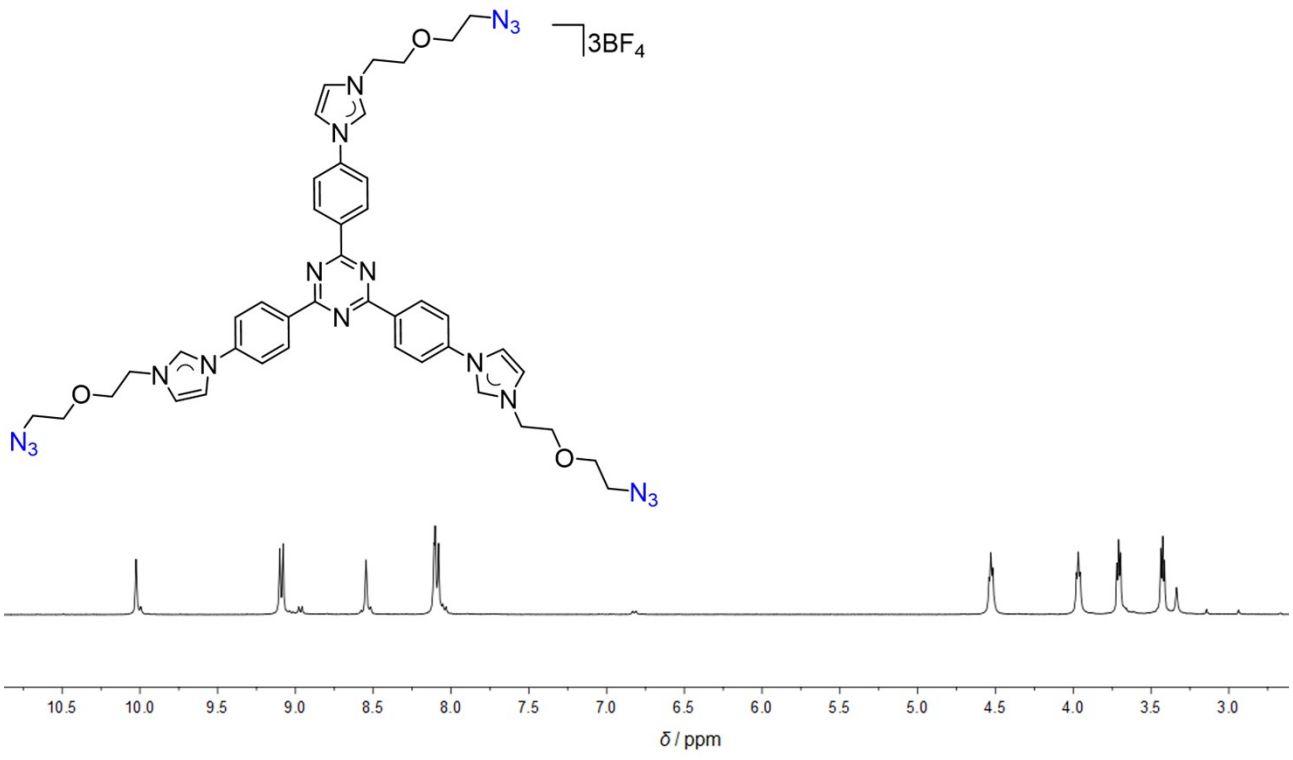


Figure S17. ^{1}H NMR spectrum of H_3-**A1**$(BF_4)_3$ (400 MHz, DMSO-d_6).

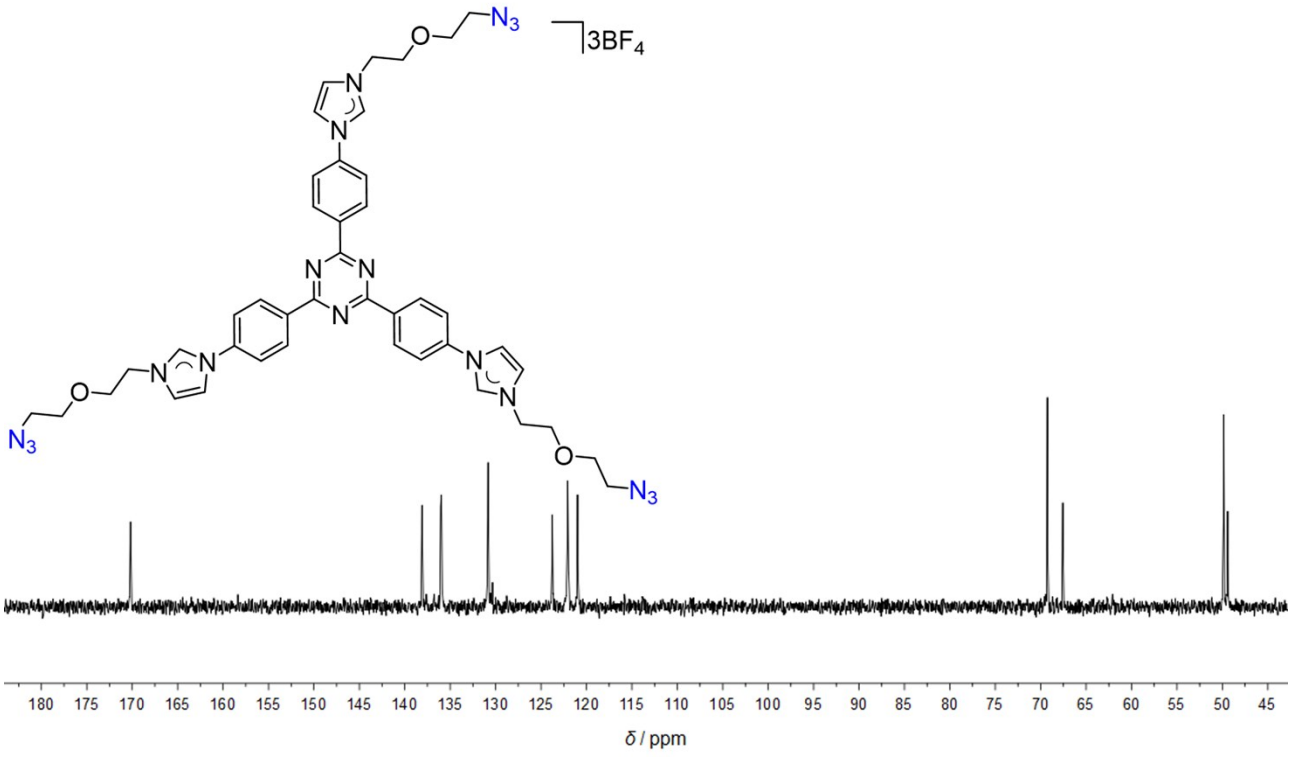


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of H_3-**A1**$(BF_4)_3$ (100 MHz, DMSO-d_6).

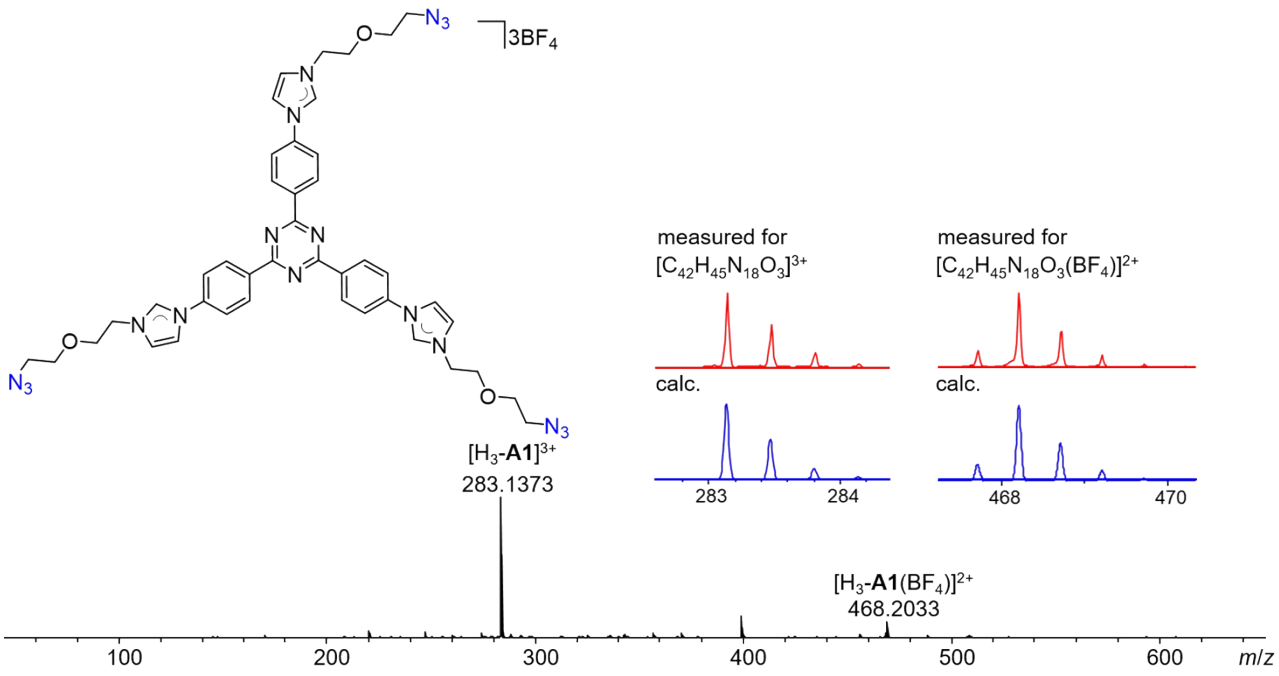


Figure S19. HR-ESI mass spectrum (positive ions) of H_3-**A1**$(BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

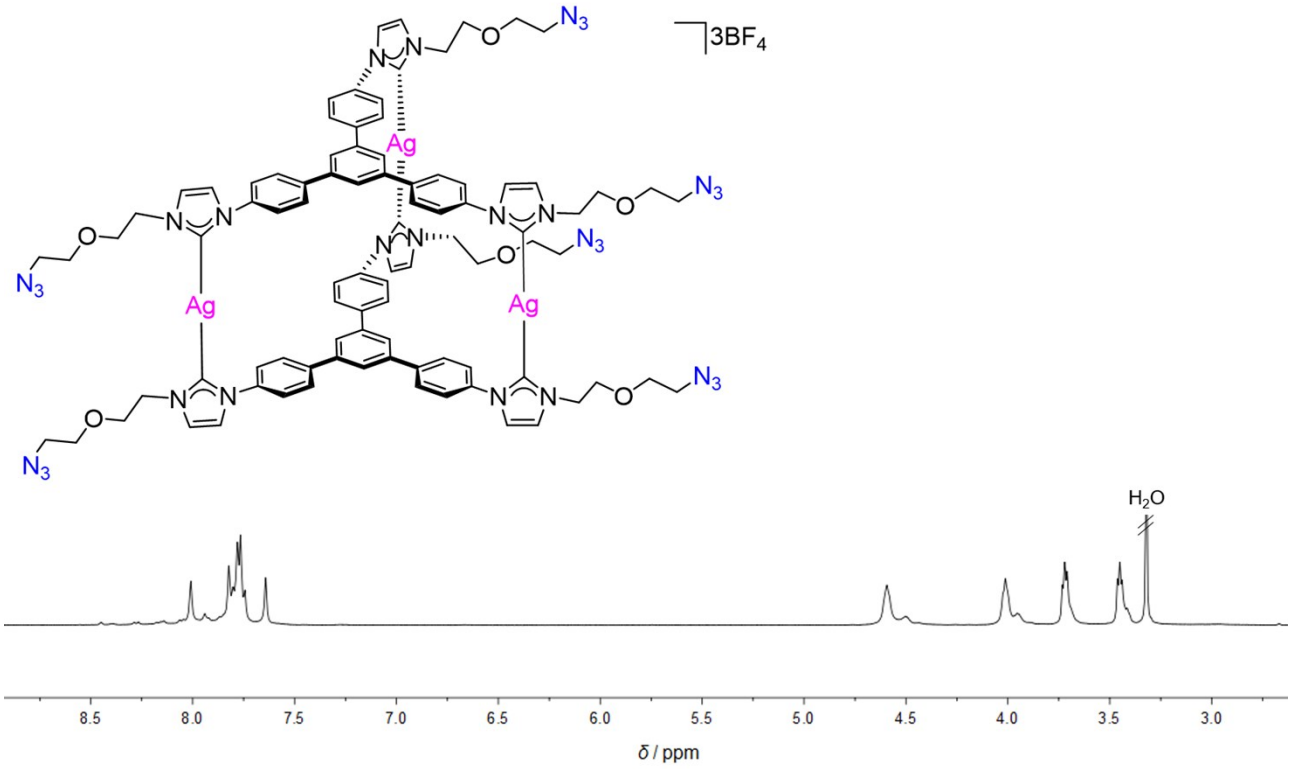


Figure S20. ^{1}H NMR spectrum of $[Ag_3(\mathbf{D1})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

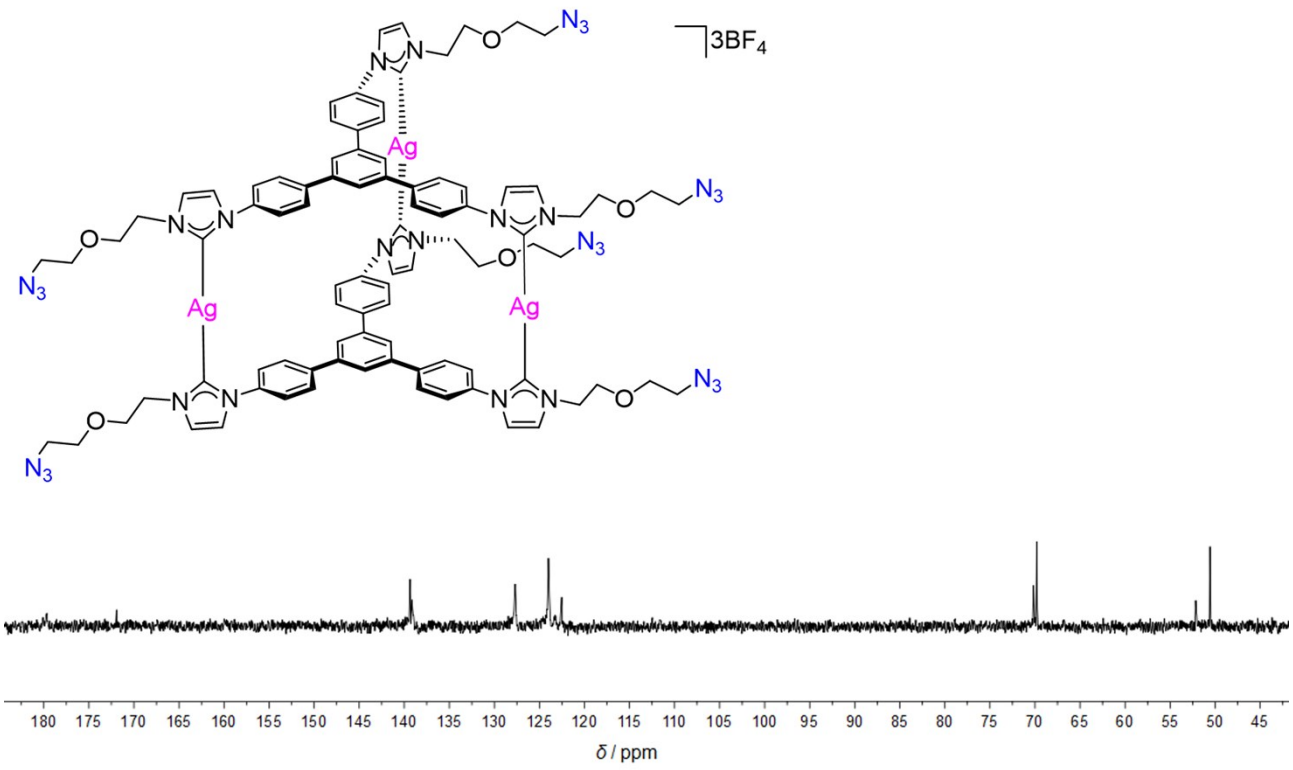


Figure S21. ^{13}C{^{1}H} NMR spectrum of $[Ag_3(\mathbf{D1})_2](BF_4)_3$ (100 MHz, DMSO-d_6).

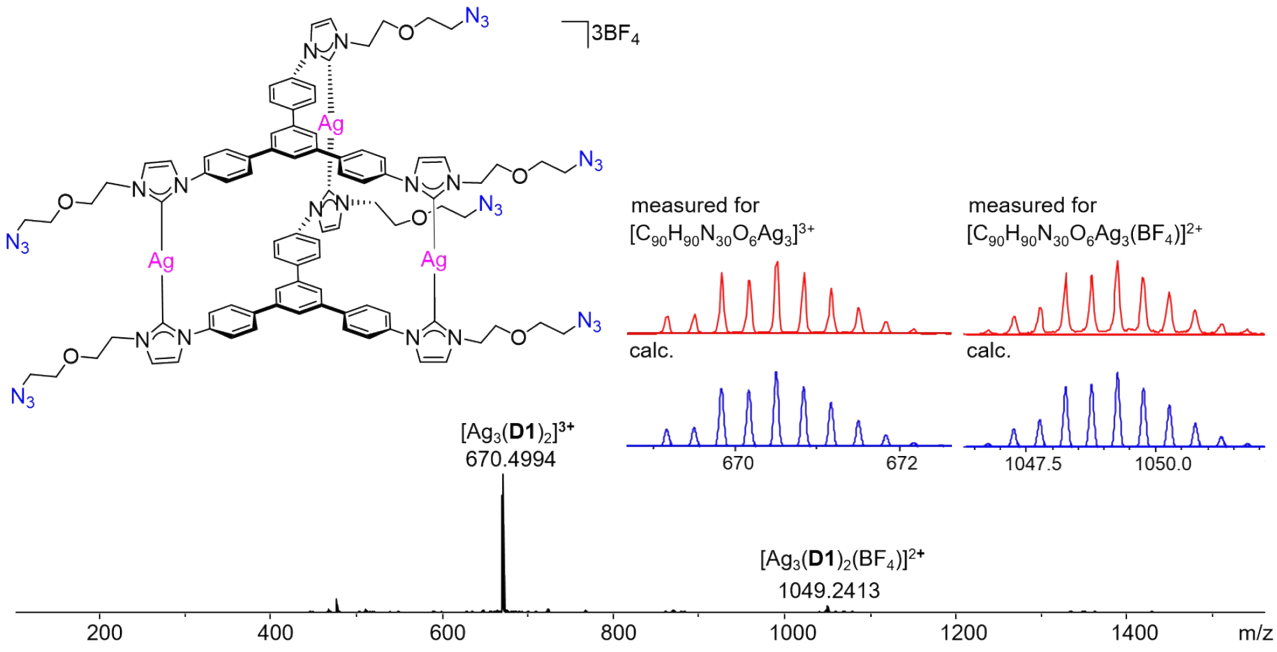


Figure S22. HR-ESI mass spectrum (positive ions) of $[Ag_3(\mathbf{D1})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

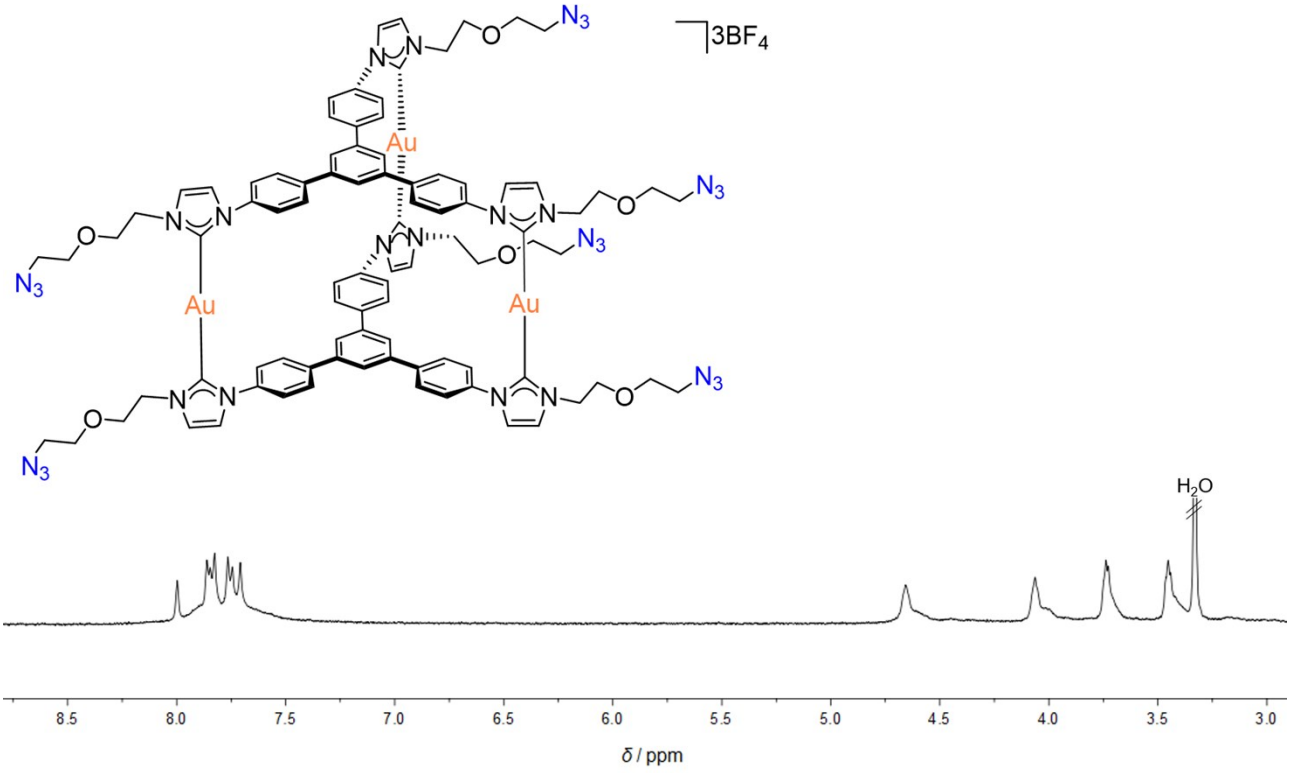


Figure S23. ^{1}H NMR spectrum of $[Au_3(\mathbf{D1})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

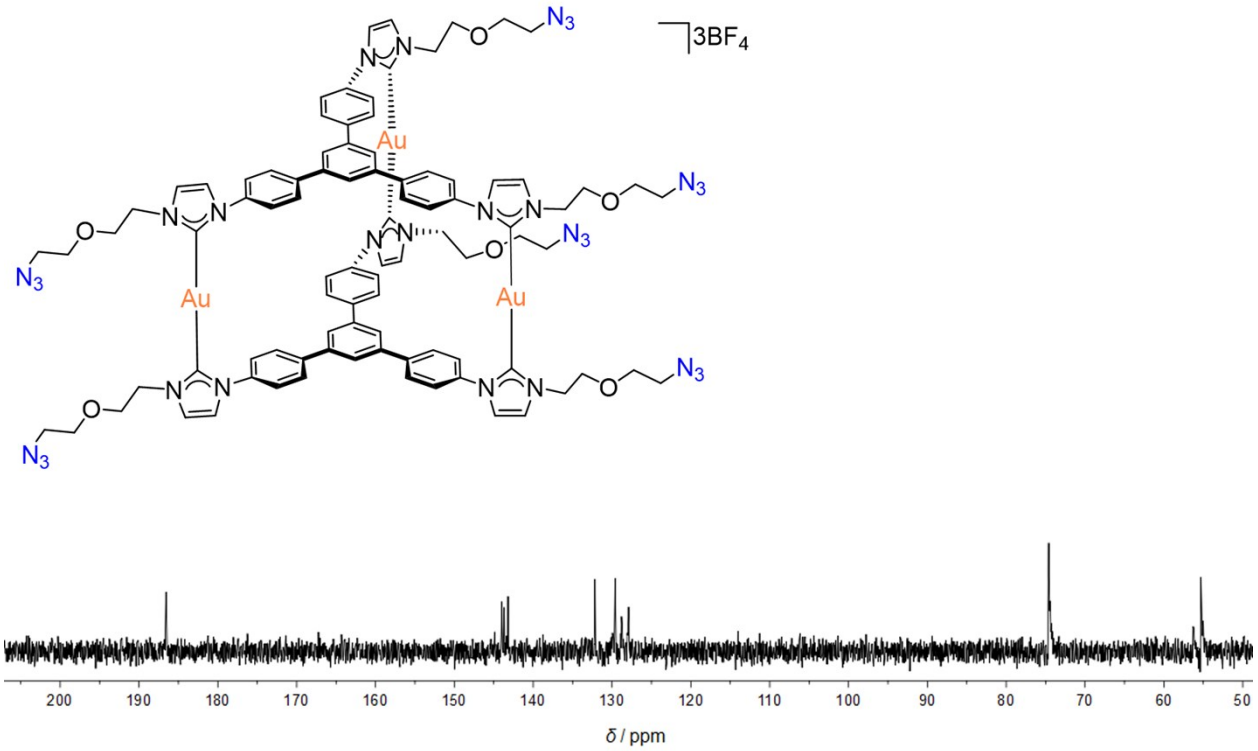


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of $[Au_3(\mathbf{D1})_2](BF_4)_3$ (100 MHz, DMSO-d_6).

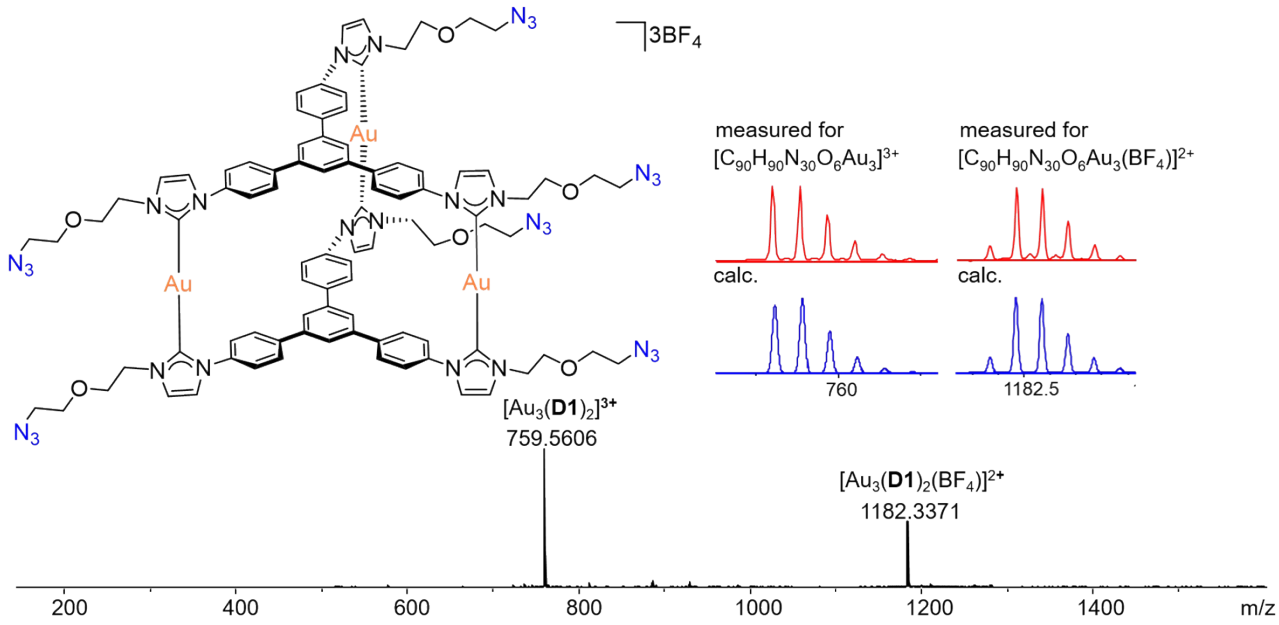


Figure S25. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{D1})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

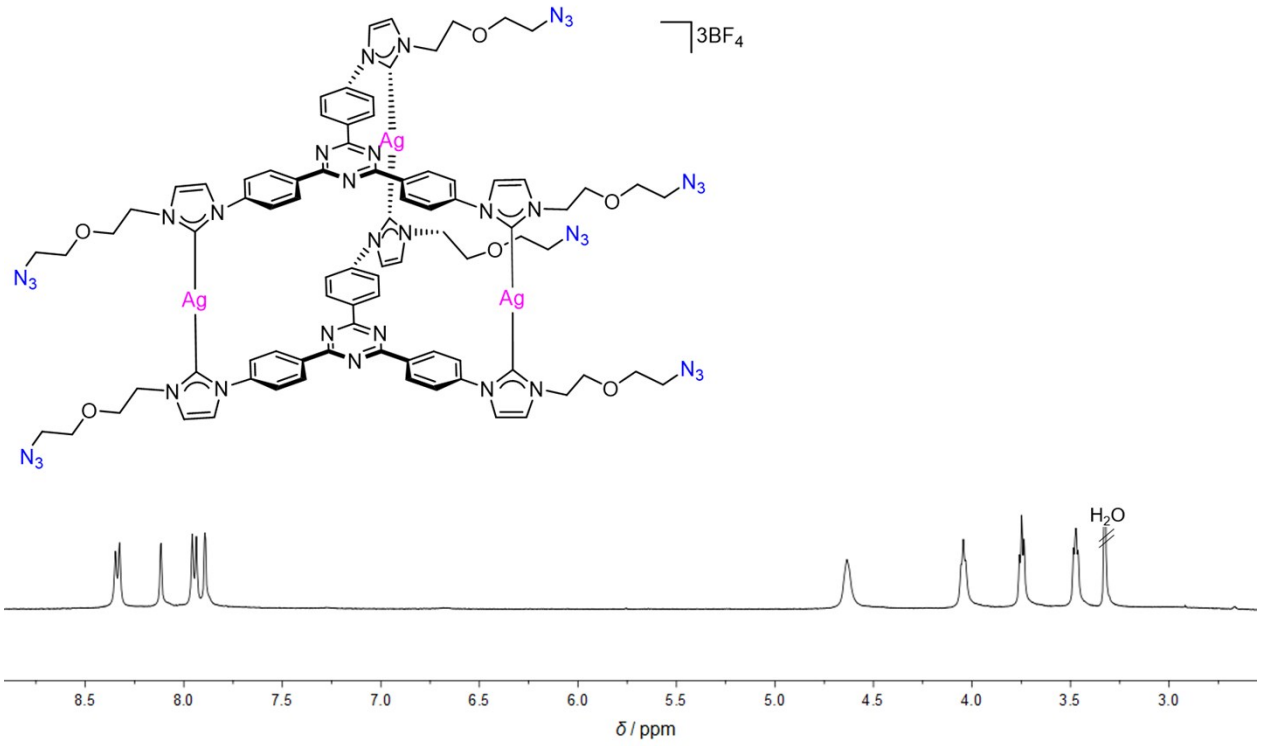


Figure S26. ^{1}H NMR spectrum of $[Ag_3(\mathbf{A1})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

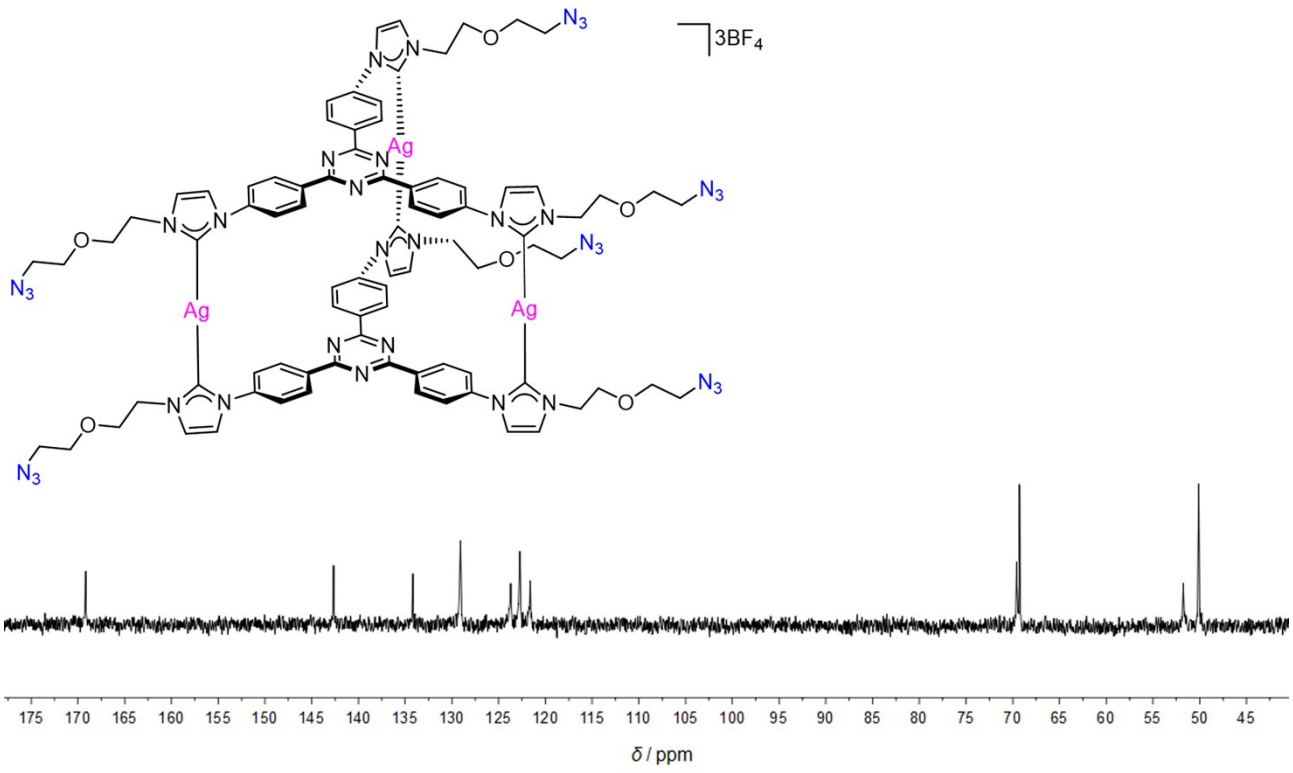


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of $[Ag_3(\mathbf{A1})_2](BF_4)_3$ (100 MHz, DMSO-d_6).

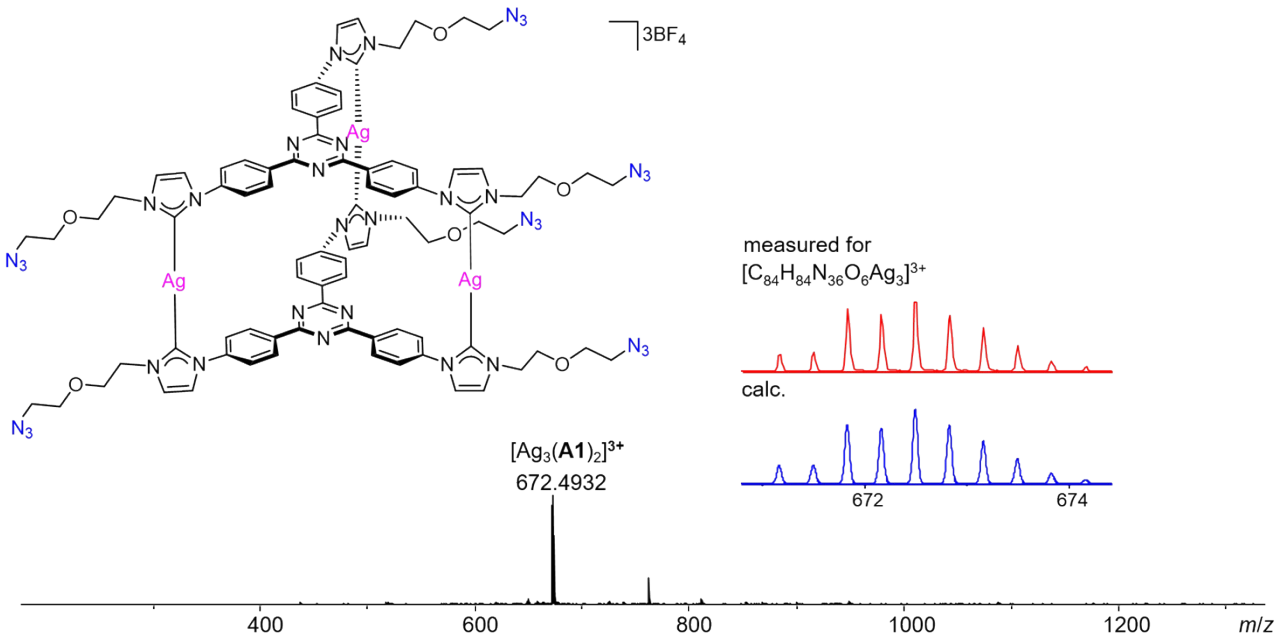


Figure S28. HR-ESI mass spectrum (positive ions) of $[Ag_3(\mathbf{A1})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

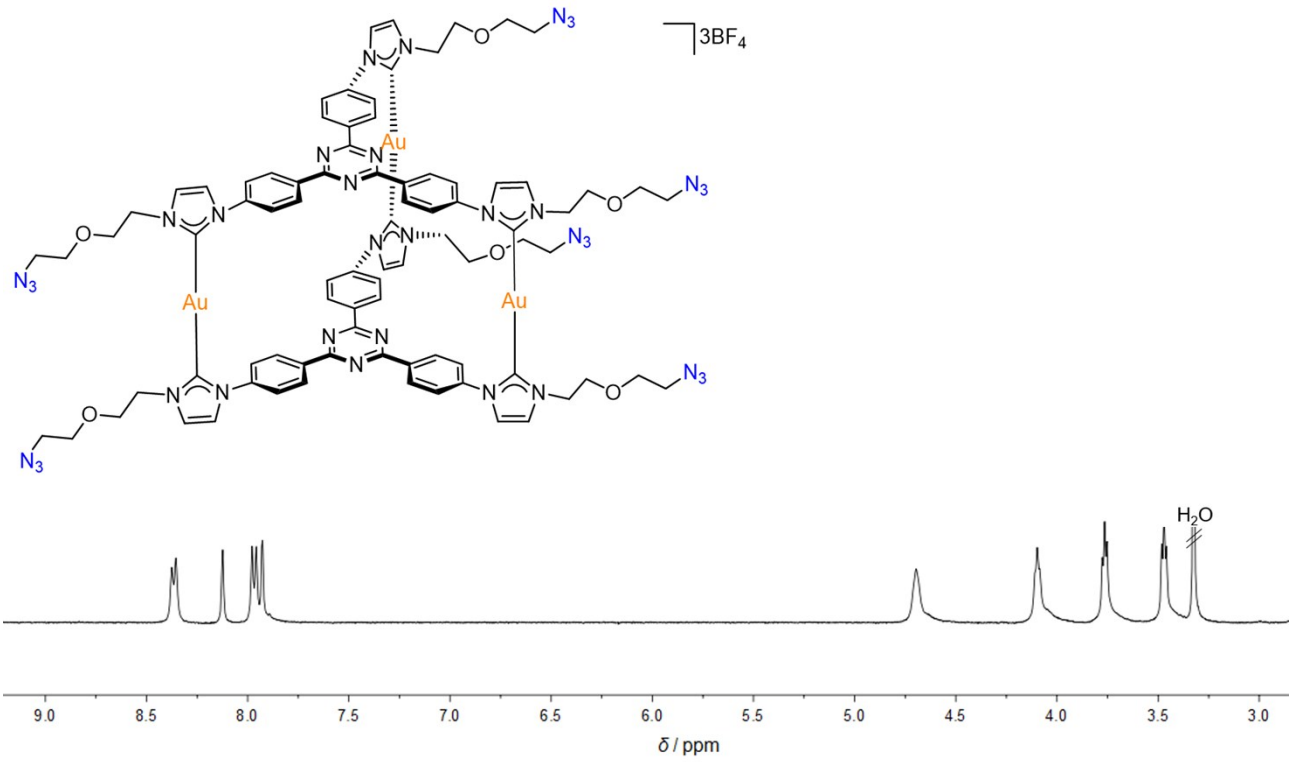


Figure S29. ^{1}H NMR spectrum of $[Au_3(\mathbf{A1})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

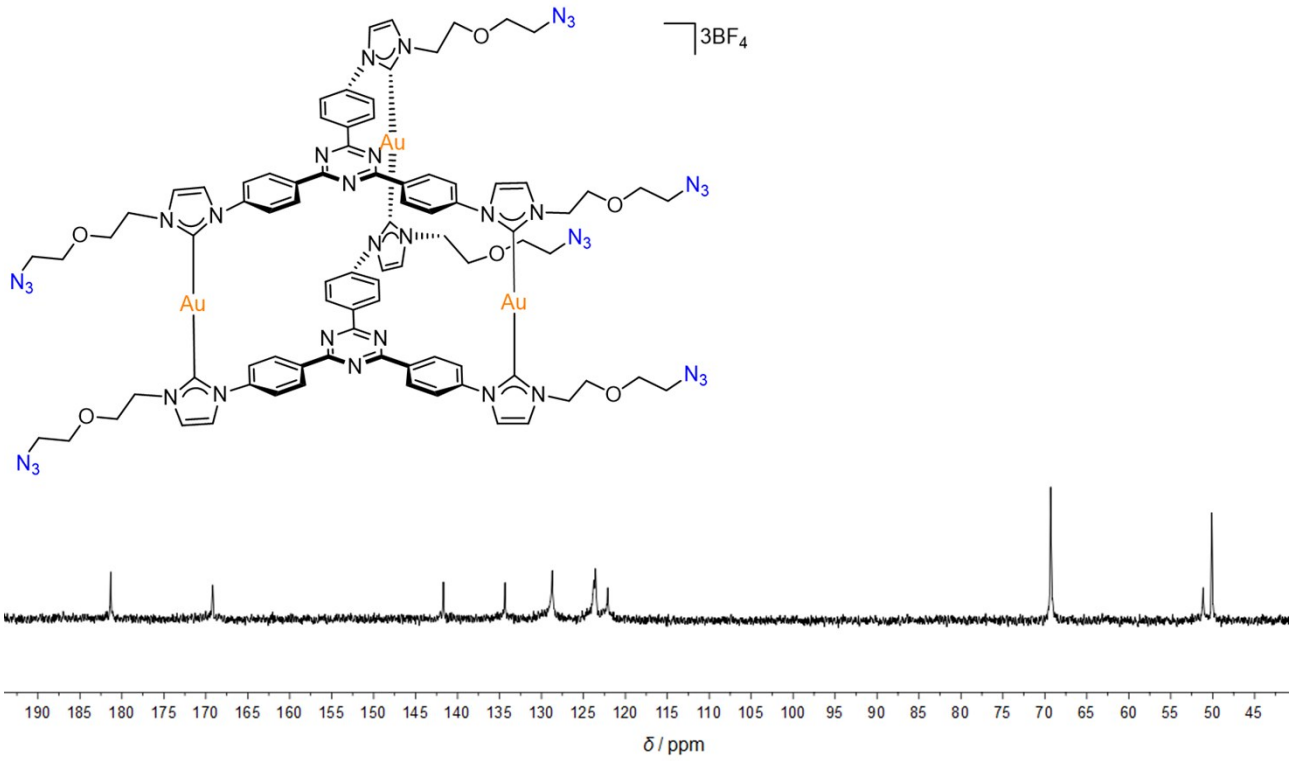


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of $[Au_3(\mathbf{A1})_2](BF_4)_3$ (100 MHz, DMSO-d_6).

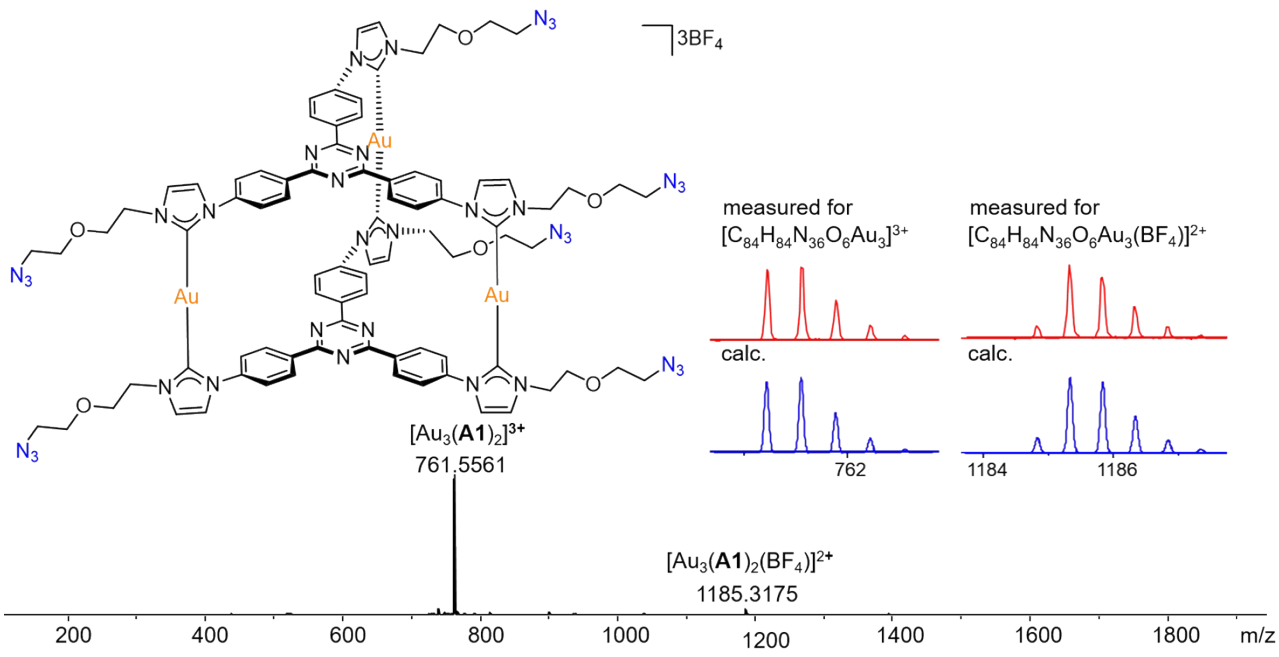


Figure S31. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{A1})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

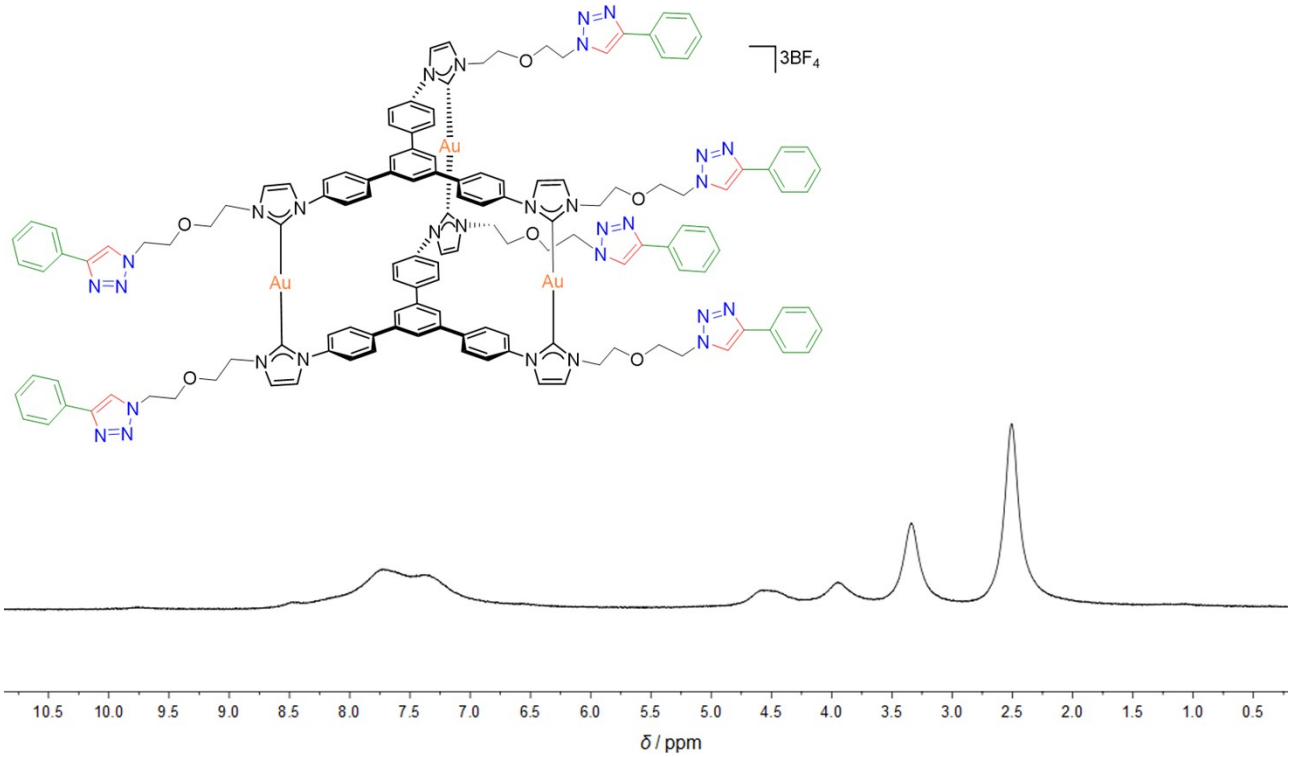


Figure S32. ^{1}H NMR spectrum of $[Au_3(\mathbf{D2})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

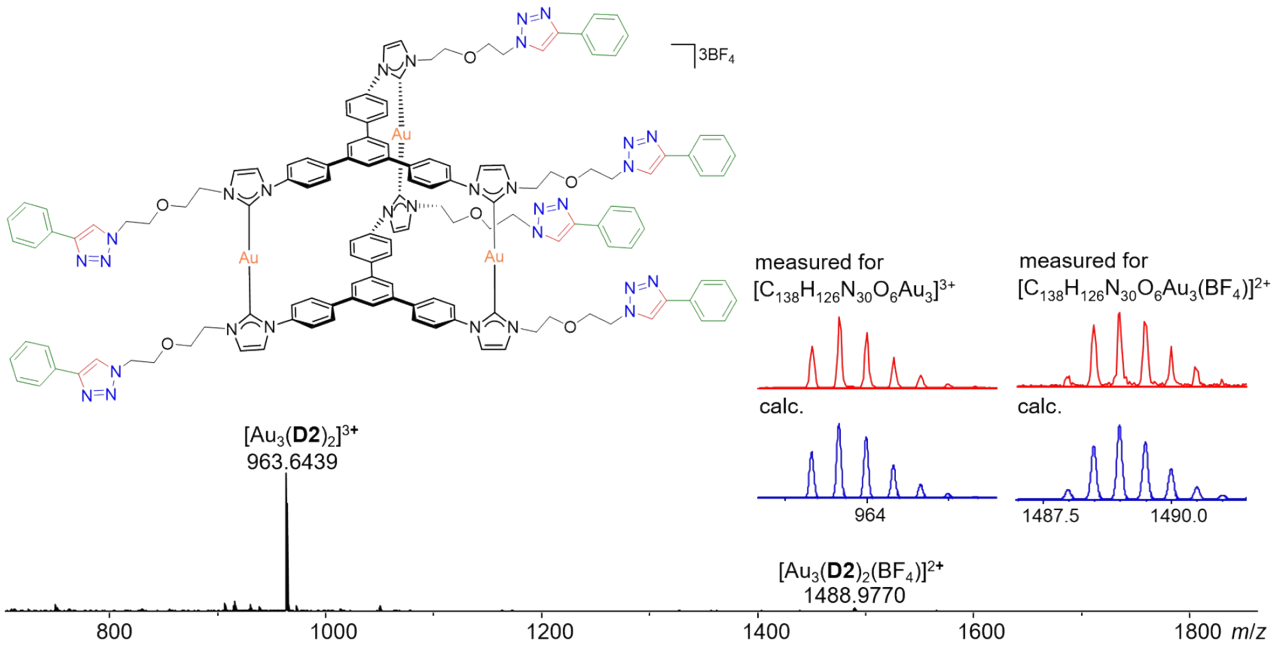


Figure S33. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{D2})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

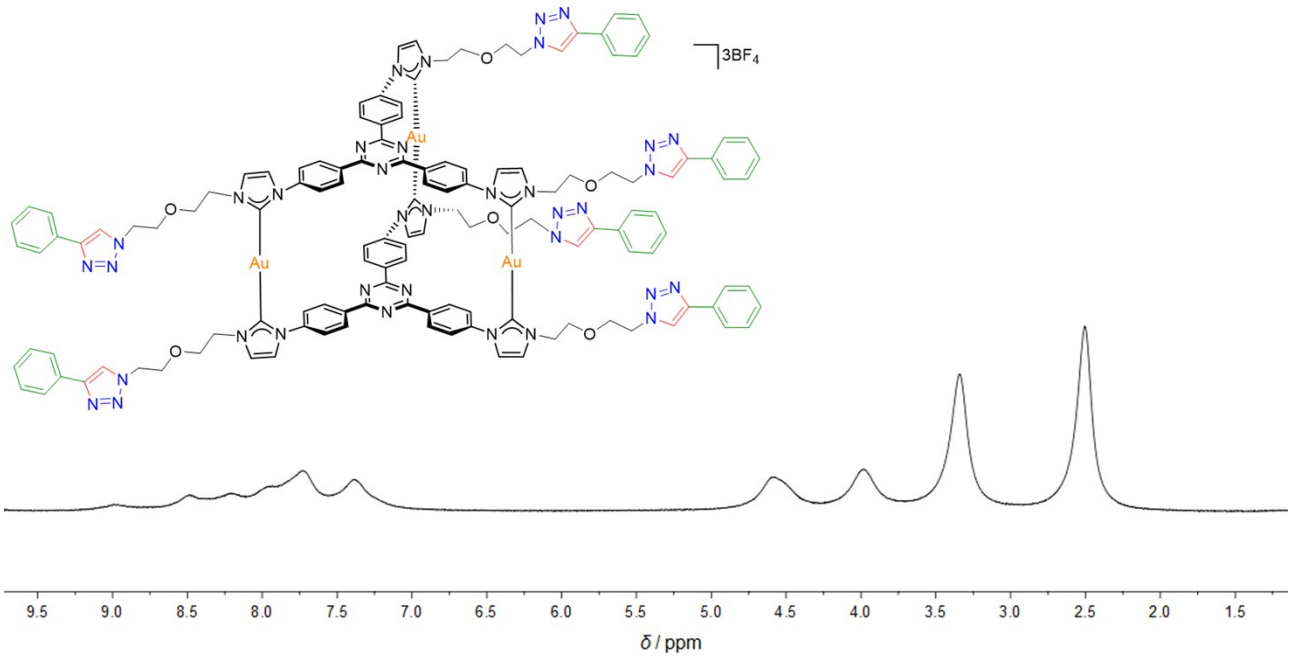


Figure S34. ^{1}H NMR spectrum of $[Au_3(\mathbf{A2})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

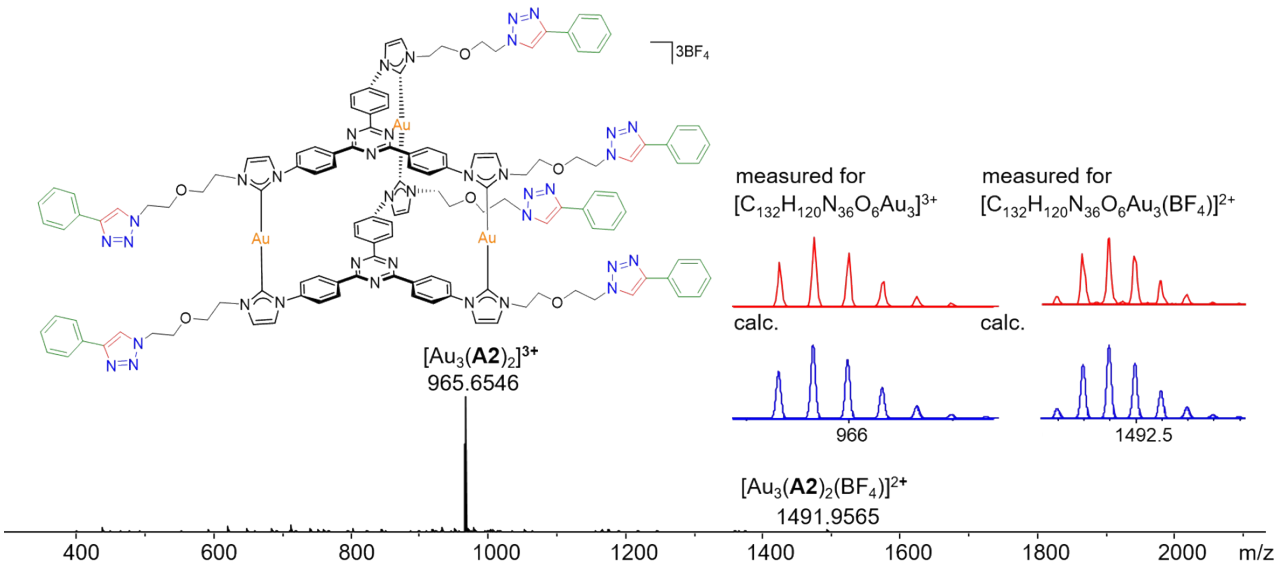


Figure S35. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{A2})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

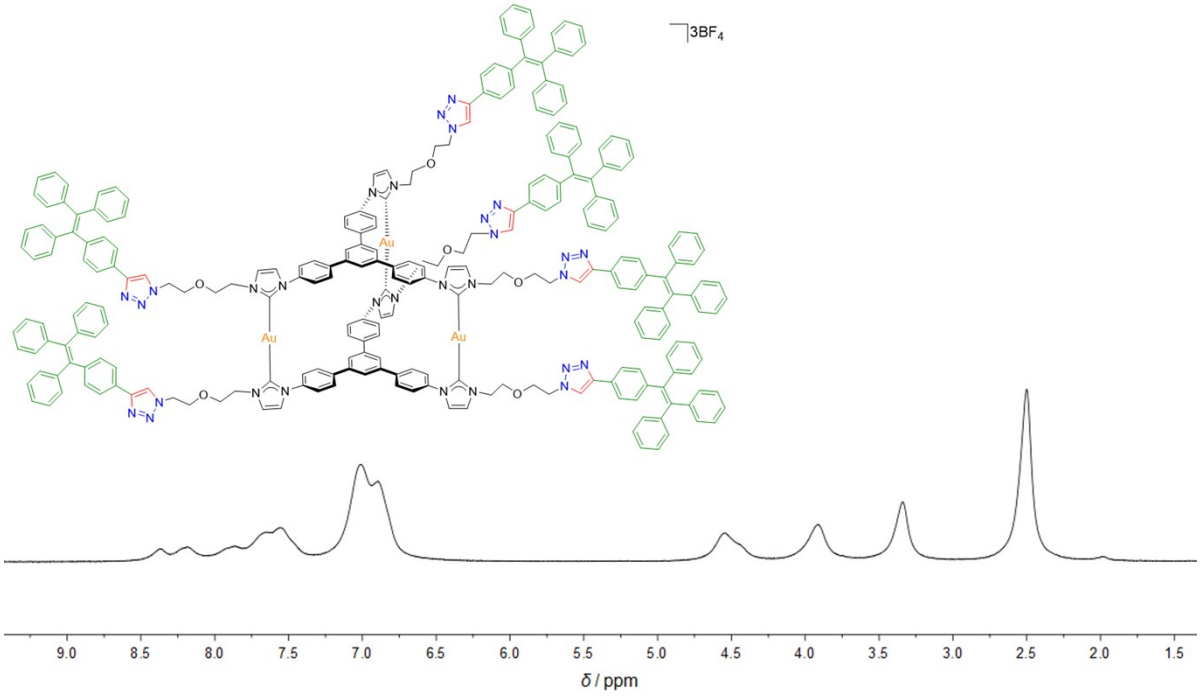


Figure S36. ^{1}H NMR spectrum of $[Au_3(\mathbf{D3})_2](BF_4)_3$ (400 MHz, DMSO-d_6).

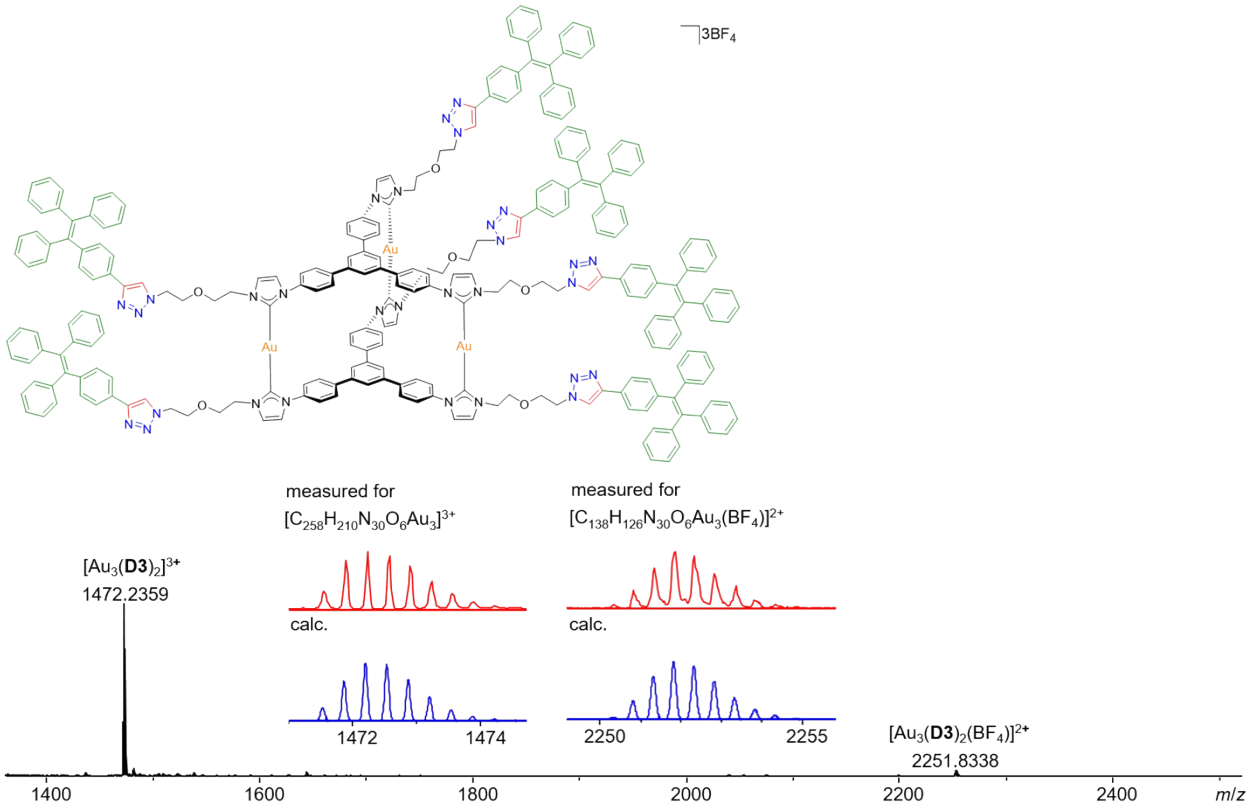


Figure S37. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{D3})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).

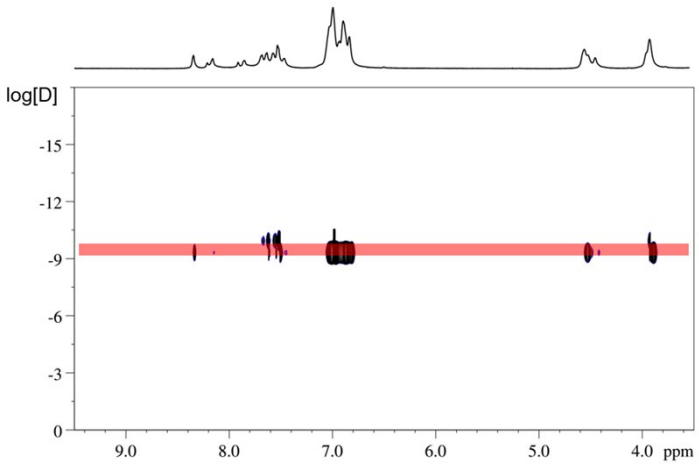


Figure S38. DOSY NMR spectrum of $[Au_3(\mathbf{D3})_2](BF_4)_3$ (400 MHz, DMSO-d_6). *Note:* According to the Diffusion-Ordered NMR spectra, the proton signals assigned to the ligands exhibit the same diffusion coefficient which verify that there is only one assembly structure in solution.

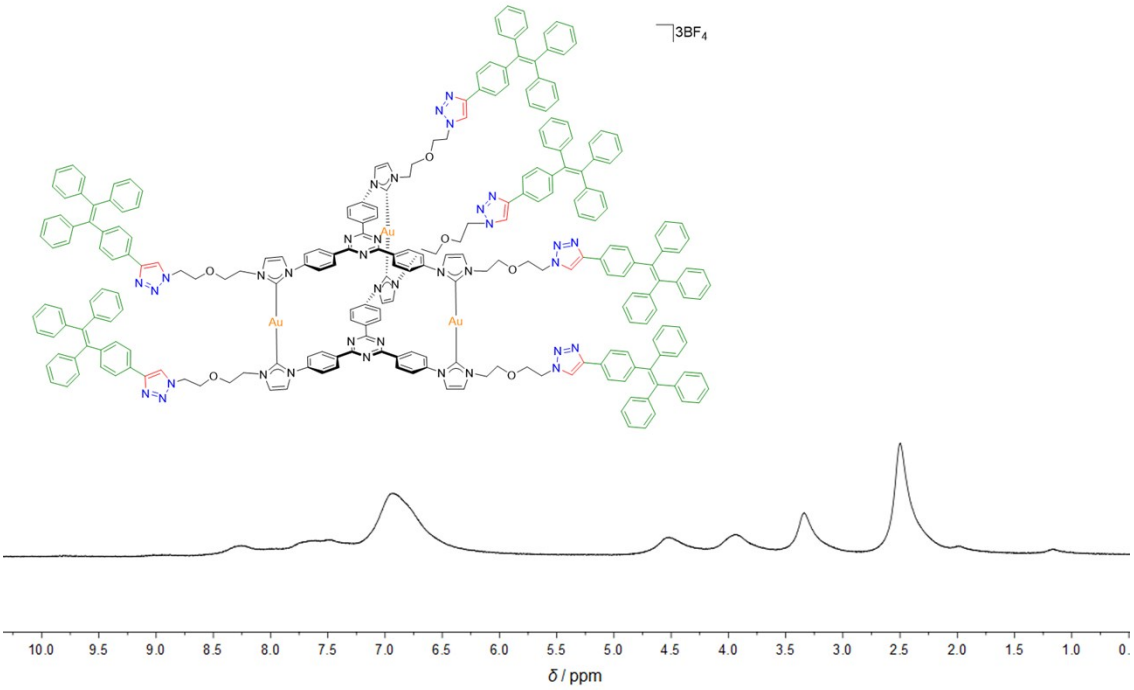


Figure S39. ^{1}H NMR spectrum of $[Au_3(\mathbf{A3})_2](BF_4)_3$ (400 MHz, DMSO-d_6). *Note*: The signals are universally board in the ^{1}H NMR spectra of $[Au_3(\mathbf{A3})_2](BF_4)_3$ due to the tumbling rotation of the pendant TPE moieties.

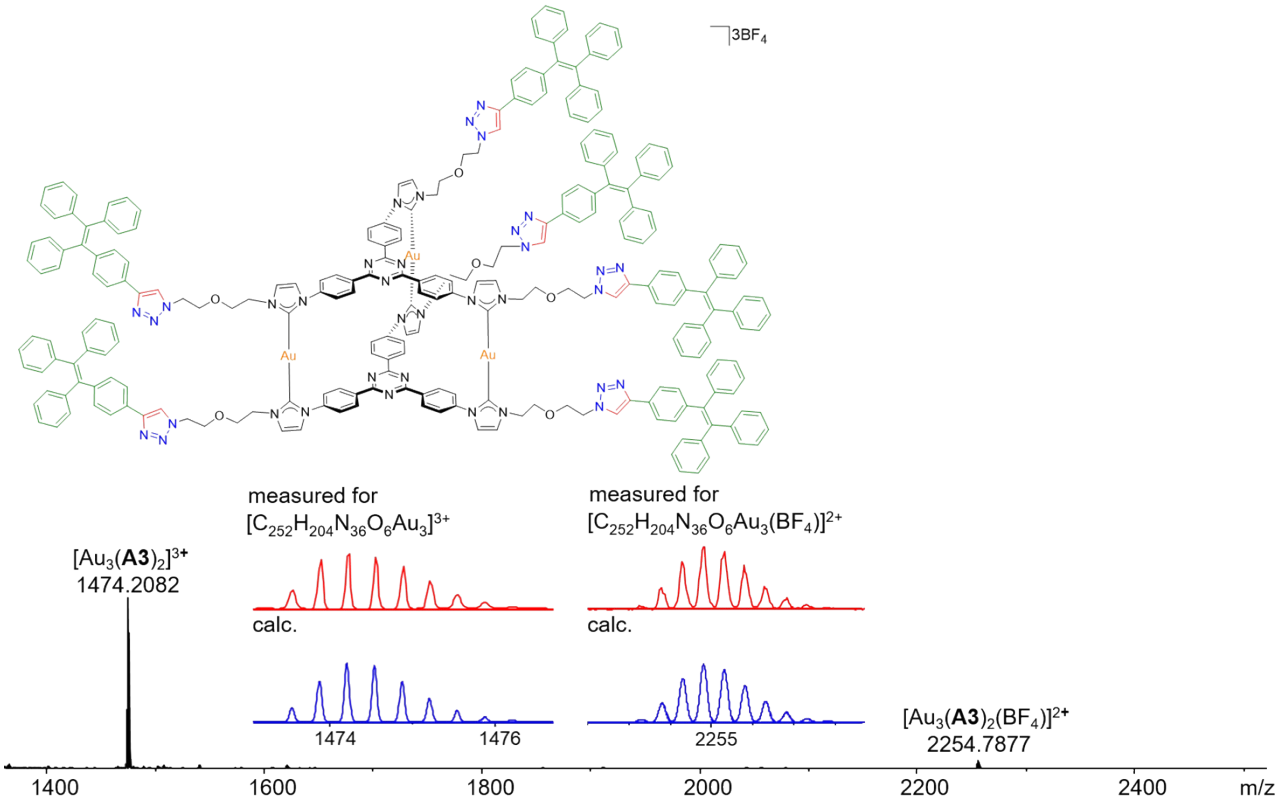


Figure S40. HR-ESI mass spectrum (positive ions) of $[Au_3(\mathbf{A3})_2](BF_4)_3$. Isotope distribution of selected cations is shown as inset (experimentally observed distribution on top and simulated distribution at the bottom).