

Metal-Carbene Template Approach Enables Efficient Synthesis of a Functionalized Cage-Annulated Crown Ether

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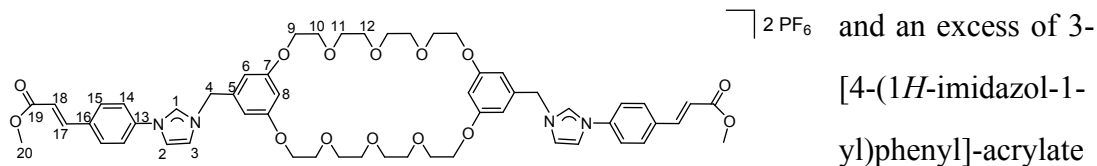
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1. Materials and methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Glassware was dried in an oven at 130 °C before use. Solvents were freshly distilled by standard procedures prior to use. ^1H and $^{13}\text{C}\{^1\text{H}\}$ and 2D NMR spectra were recorded on Bruker AVANCE III 400 or JEOL 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent peaks (^1H NMR: 1.94 ppm for CD_3CN , 2.50 ppm for $\text{DMSO-}d_6$; $^{13}\text{C}\{^1\text{H}\}$ NMR: 1.32 ppm, 118.26 ppm for CD_3CN , 39.52 ppm for $\text{DMSO-}d_6$) as an internal standard. All coupling constants are expressed in Hertz. High-resolution mass spectra were obtained with a Bruker microTOF-Q II mass spectrometer (Bruker Daltonics Corp., USA) in the electrospray ionization (ESI) mode. The UV–Vis spectra were obtained using an Agilent Cary 100 spectrophotometer. Bis(5-bromomethyl-*m*-phenylene)-32-crown-10¹ and 3-[4-(1*H*-imidazol-1-yl)phenyl]-acrylate² were prepared according to literature procedures.

2. Synthesis of compound H₂-1(PF₆)₂.

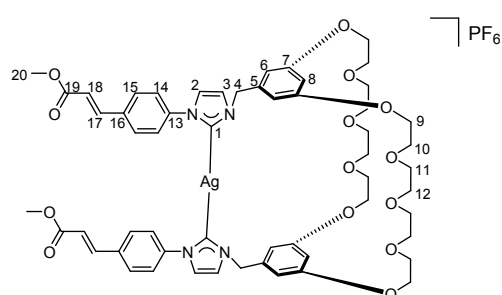
A sample of bis(5-bromomethyl-*m*-phenylene)-32-crown-10 (0.116 g, 0.161 mmol)



(0.147 g, 0.644 mmol) were dissolved in DMF (1 mL) and the reaction mixture was heated to 110 °C for 12 h. After cooling of the reaction mixture to ambient temperature, white precipitate separated out after added ethyl acetate and filtered. The solid was washed with ethyl acetate, and dried in *vacuo*. This solid was dissolved in methanol (1 mL) and NH₄PF₆ (1.320 g, 8.101 mmol in 2 mL of hot water) was added. After stirring for 48 h at ambient temperature, a white solid gradually precipitated out and filtered. The precipitate was washed with water and dried in *vacuo*. Yield: 0.120 g (0.092 mmol, 57%). ¹H NMR (400 MHz, CD₃CN): δ = 8.95 (s, 2H, H1), 7.83 (d, 4H, *J* = 8.5 Hz), 7.76 (t, 2H, *J* = 1.9 Hz), 7.71 (d, 2H, *J* = 16.0 Hz, H17/H18), 7.61 (d, 4H, *J* = 8.5 Hz), 7.57 (t, 2H, *J* = 1.9 Hz), 6.64-6.58 (m, 6H, *due to overlapping of other resonances, one of the olefin proton signals can not well be resolved*), 6.48 (t, 2H, *J* = 2.2 Hz), 5.27 (s, 4H, H4), 4.08-4.03 (m, 8H, belong to H9-H12), 3.77 (s, 6H, H20), 3.76-3.72 (m, 8H, belong to H9-H12), 3.61-3.53 ppm (m, 16H, belong to H9-H12). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ = 167.5, 161.5, 143.1, 137.1, 136.5, 136.2, 135.6, 130.7, 124.2, 123.7, 122.8, 121.2, 108.5, 102.3, 71.3, 71.2, 70.1, 68.7, 54.2, 52.4 ppm. HRMS (ESI, positive ions): *m/z* = 1163. 3685 (calcd for [H₂-1(PF₆)]⁺ 1163.4212), *m/z* = 509.2303 (calcd for [H₂-1]²⁺ 509.2282).

3. Synthesis of compounds [M(1)](PF₆) (M = Ag, Au).

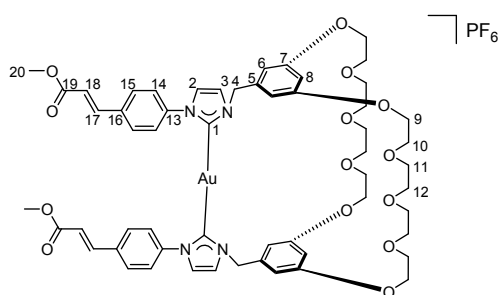
3.1 Synthesis of compound [Ag(1)](PF₆).



A sample of H₂-1(PF₆)₂ (0.046 g, 0.035 mmol) was dissolved in CH₃CN (20 mL) and to this solution was added Ag₂O (0.049 g, 0.211 mmol) under a nitrogen atmosphere. The reaction mixture was heated at 70 °C for

48 h under exclusion of light. Upon cooling to room temperature, a suspension was formed and slowly filtered through a pad of Celite to obtain a clear filtrate. The filtrate was concentrated to 2 mL and diethyl ether (30 mL) was added. This led to the precipitation of a brown solid. The solid was collected by filtration, washed with diethyl ether, and dried in *vacuo* to afford the complex of type [Ag(1)](PF₆). Yield: 0.039 g (0.031 mmol, 89%). ¹H NMR (400 MHz, CD₃CN): δ = 7.59 (d, 2H, *J* = 16.0 Hz, H17), 7.57-7.51 (m, 8H, H14 and H15, partly overlapped), 7.50 (d, 2H, *J* = 1.5 Hz, H2), 7.38 (d, 2H, *J* = 1.5 Hz, H3), 6.48 (d, 2H, *J* = 16.0 Hz, H18), 6.26 (s, 6H, H6 and H8), 5.16 (s, 4H, H4), 3.91-3.84 (m, 8H, belong to H9-H12), 3.78 (s, 6H, H20), 3.74-3.69 (m, 8H, belong to H9-H12), 3.61-3.54 ppm (m, 16H, belong to H9-H12). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ = 181.4 (C1), 167.6 (C19), 161.4 (C7), 143.5 (C17), 141.9 (C13), 139.9 (C5), 135.6 (C16), 130.1 (C15), 125.2 (C14), 124.2 (C3), 123.1 (C2), 120.3 (C18), 107.1 (C6), 100.7 (C8), 71.4, 71.1, 70.2, 68.7 (C9-C12), 56.0 (C4), 52.3 ppm (C20). HRMS (ESI, positive ions): *m/z* = 1125.3244 (calcd for [Ag(1)]⁺ 1125.3465).

3.2 Synthesis of compound [Au(1)](PF₆).

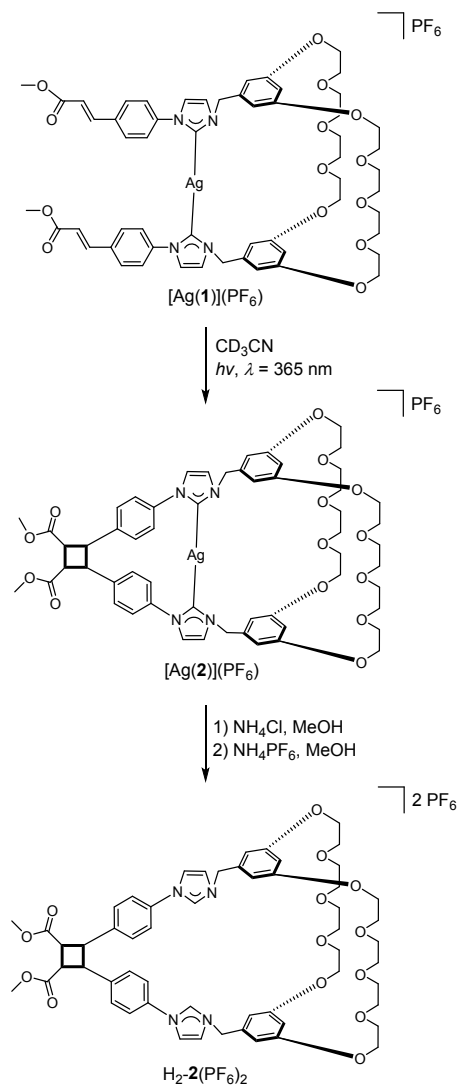


The obtained Ag^I complex [Ag(1)](PF₆) (0.013 g, 0.010 mmol) was dissolved in CH₃CN (5 mL), then solid AuCl(THT) (0.004 g, 0.012 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred for 24 h at ambient temperature

under exclusion of light and was then slowly filtered through a pad of Celite until a clear filtrate was obtained. The filtrate was concentrated to 1 mL and diethyl ether (20 mL) was added to give an off-white solid [Au(1)](PF₆), which was collected by filtration, washed with diethyl ether, and dried in *vacuo*. Yield: 0.010 g (0.007 mmol, 72%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.92 (d, 2H, *J* = 2.0 Hz, H2/H3), 7.84 (d, 2H, *J* = 2.0 Hz, H2/H3), 7.68 (s, 8H, H14 and H15), 7.62 (d, 2H, *J* = 16.0 Hz, H17), 6.62 (d, 2H, *J* = 16.0 Hz, H18), 6.33 (d, 4H, *J* = 2.2 Hz, H6), 6.28 (t, 2H, *J* = 2.2 Hz, H8), 5.27 (s, 4H, H4), 3.81-3.76 (m, 8H, belong to H9-H12), 3.74 (s, 6H, H20), 3.70-

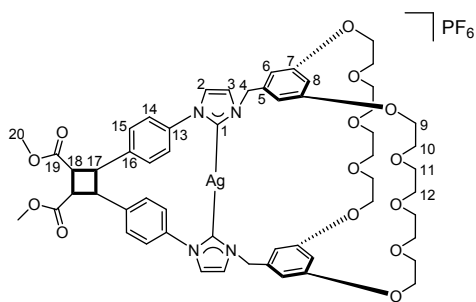
3.64 (m, 8H, belong to H9-H12), 3.57-3.51 ppm (m, 16H, belong to H9-H12). HRMS (ESI, positive ions): $m/z = 1213.4036$ (calcd for $[\text{Au}(\mathbf{1})]^+$ = 1213.4079).

4. [2+2]-Cycloaddition reaction and de-metalation reaction.



Scheme S1 Synthesis of cage $\text{H}_2\text{-}\mathbf{2}(\text{PF}_6)_2$.

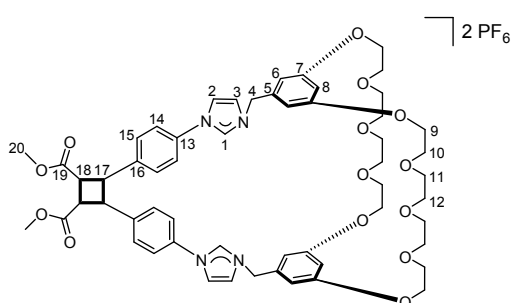
4.1 Synthesis of [Ag(2)](PF₆) by [2+2]-cycloaddition reaction.



A solution of [Ag(1)](PF₆) (0.007 g, 0.006 mmol) in CD₃CN (0.5 mL) in an NMR tube was irradiated with a Philips mercury high-pressure lamp ($\lambda = 365$ nm) at ambient temperature for 13.5 h. Over this time the initially colorless solution turned yellow. The

conversion to [Ag(2)](PF₆) was determined by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CD₃CN): $\delta = 7.42$ (d, 2H, $J = 1.8$ Hz, H3), 7.24 (d, 2H, $J = 1.8$ Hz, H2), 7.22 (d, 4H, $J = 8.5$ Hz, H14), 6.96 (d, 4H, $J = 8.5$ Hz, H15), 6.26 (t, 2H, $J = 2.0$ Hz, H8), 6.16 (d, 4H, $J = 2.0$ Hz, H6), 5.26 (s, 4H, H4), 4.43 (d, 2H, $J = 5.9$ Hz, H17), 4.04 (d, 2H, $J = 5.9$ Hz, H18), 3.92-3.86 (m, 8H, belong to H9-H12), 3.75-3.71 (m, 14H, belong to H9-H12 and H20), 3.60-3.55 ppm (m, 16H, belong to H9-H12). ¹³C{¹H} NMR (100 MHz, CD₃CN): $\delta = 182.4$ (from HMBC, C1), 173.7 (C19), 161.2 (C7), 140.2 (C16), 140.0 (C5), 139.5 (C13), 129.9 (C15), 125.7 (C14), 123.9 (C3), 123.4 (C2), 106.2 (C6), 100.2 (C8), 71.5, 71.0, 70.1, 68.6 (C9-C12), 55.6 (C4), 52.7 (C20), 46.2 (C17), 41.6 ppm (C18). HRMS (ESI, positive ions): $m/z = 1125.3813$ (calcd for [Ag(2)]⁺ 1125.3465).

4.2 Synthesis of H₂-2(PF₆)₂ by de-metalation reaction.



A sample of [Ag(1)](PF₆) (0.050 g, 0.039 mmol) was dissolved in MeOH (20 mL) and NH₄Cl (0.006 g, 0.112 mmol) was added to this solution. A white solid AgCl precipitated immediately. The resulting suspension was filtered through Celite to

obtain a clear solution after stirred for 12 h. The solvent was removed in *vacuo* to give a white solid. The white solid was dissolved in MeOH (10 mL) and a solution of NH₄PF₆ (0.257 g, 1.577 mmol) in water (2 mL) was added. The mixture was stirred at ambient temperature for 12 h. After this period a white solid precipitated, which was

isolated by filtration and dried in *vacuo*. Yield: 0.040 g (0.031 mmol, 78%). ^1H NMR (400 MHz, CD_3CN): δ = 8.70 (t, 2H, J = 1.6 Hz, H1), 7.56-7.52 (m, 4H, H2 and H3), 7.29 (d, 4H, J = 8.6 Hz, H14), 7.22 (d, 4H, J = 8.6 Hz, H15), 6.57 (d, 4H, J = 2.2 Hz, H6), 6.47 (t, 2H, J = 2.2 Hz, H8), 5.21 (s, 4H, H4), 4.50 (d, 2H, J = 6.1 Hz, H17), 4.07-4.01 (m, 10H, belong to H9-H12 and H18, *due to overlapping of other resonances, one of the cyclobutane proton signals can not well be resolved*), 3.77-3.73 (m, 8H, belong to H9-H12), 3.72 (s, 6H, H20), 3.63-3.54 ppm (m, 16H, belong to H9-H12). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): δ = 173.5 (C19), 161.4 (C7), 141.9 (C16), 136.5 (C5), 135.4 (C1), 134.0 (C13), 130.5 (C15), 124.0 (C3), 123.1 (C14), 123.0 (C2), 108.4 (C6), 102.3 (C8), 71.2, 71.1, 70.1, 68.7 (C9-C12), 54.0 (C4), 52.7 (C20), 45.5 (C17), 42.8 ppm (C18). HRMS (ESI, positive ions): m/z = 1163.4559 (calcd for $[\text{H}_2\text{-2}(\text{PF}_6)]^+$ 1163.4212), m/z = 509.2460 (calcd for $[\text{H}_2\text{-2}]^{2+}$ 509.2282).

5. [2+2]-Cycloaddition reaction of carbene complex $[\text{M}(\mathbf{1})](\text{PF}_6)$.

5.1 [2+2]-Cycloaddition reaction of silver(I) carbene complex $[\text{Ag}(\mathbf{1})](\text{PF}_6)$.

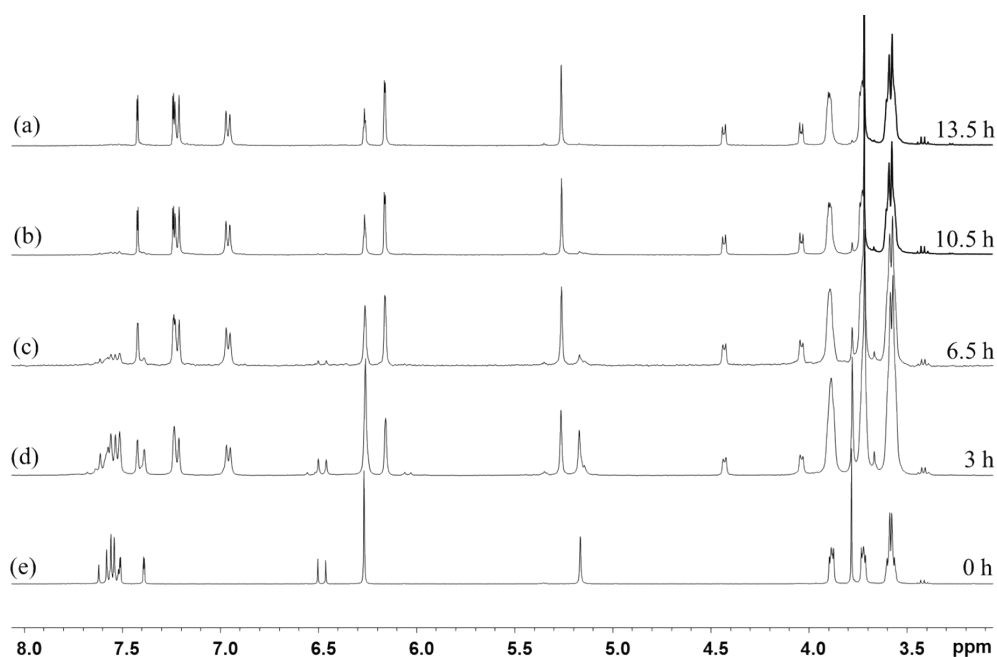


Fig. S1 Section of the ^1H NMR spectra (400 MHz, CD_3CN) showing changes in chemical shifts for the protons of $[\text{Ag}(\mathbf{1})](\text{PF}_6)$ after increasing the photoirradiation time of the solution (λ = 365 nm): (a) 13.5 h; (b) 10.5 h; (c) 6.5 h; (d) 3 h; and (e) $[\text{Ag}(\mathbf{1})](\text{PF}_6)$; c = 0.01 M.

5.2 [2+2]-Cycloaddition reaction of gold(I) carbene complex [Au(1)](PF₆).

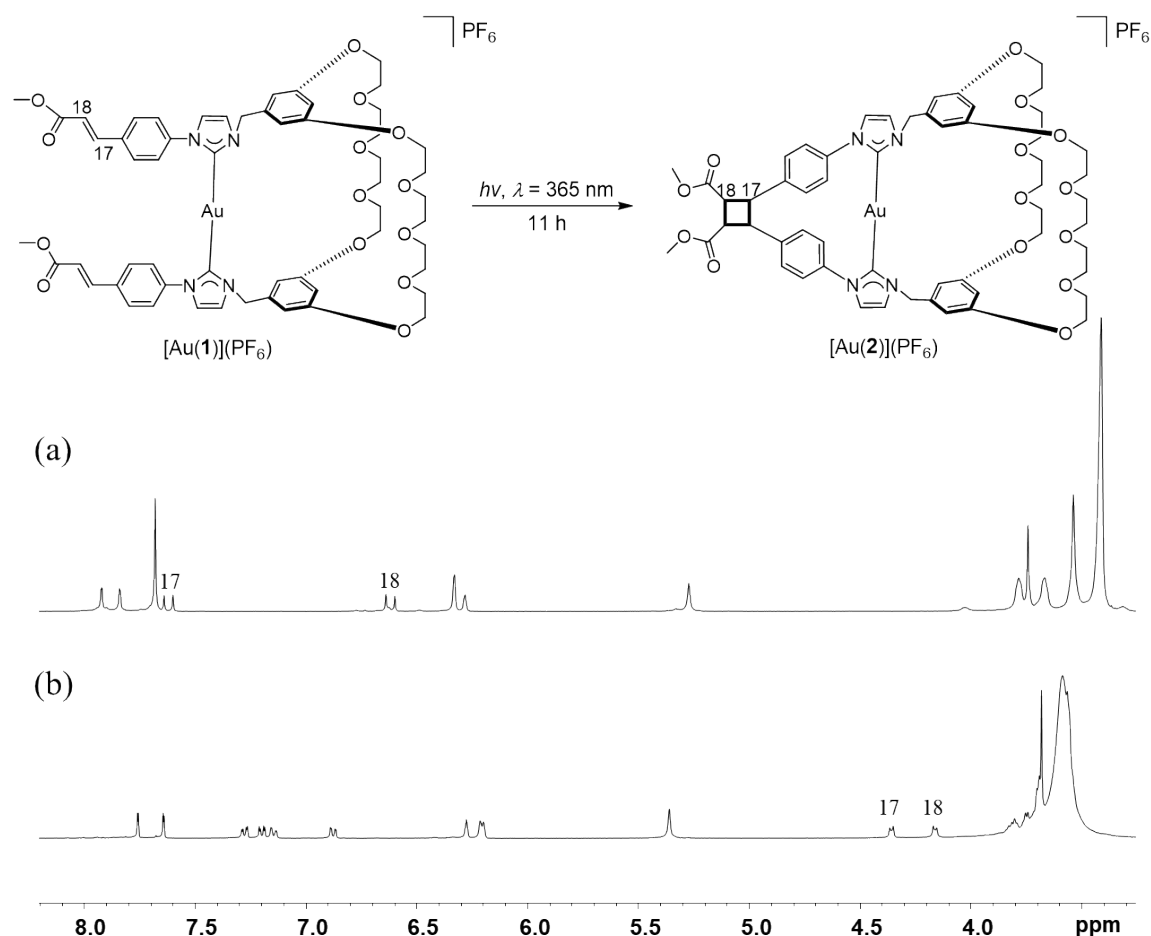


Fig. S2 ¹H NMR spectra (400 MHz, DMSO-*d*₆) of [Au(1)](PF₆) (a) before irradiation and (b) after irradiation at $\lambda = 365$ nm for 11 h. *c* = 0.01 M. The two doublet resonances for the olefin protons H17 and H18 in [Au(1)](PF₆) are disappeared. Instead, the typical upfield shift of the protons H17 and H18 after the [2+2] cycloaddition are observed in [Au(2)](PF₆).

Selected analytical data for [Au(2)](PF₆): ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.76 (d, 2H, *J* = 1.8 Hz), 7.64 (d, 2H, *J* = 1.8 Hz), 7.28 (dd, 2H, *J* = 8.2, 2.4 Hz), 7.20 (dd, 2H, *J* = 8.2, 2.4 Hz), 7.15 (dd, 2H, *J* = 8.4, 2.0 Hz), 6.88 (dd, 2H, *J* = 8.4, 2.0 Hz), 6.27 (t, 2H, *J* = 2.2 Hz, H8), 6.21 (d, 4H, *J* = 6.0 Hz, H6), 5.36 (s, 4H, H4), 4.36 (d, 2H, *J* = 5.8 Hz, H17), 4.16 (d, 2H, *J* = 5.8 Hz, H18), 3.86-3.68 ppm (m, 38H, belong to H9-H12 and H20). HRMS (ESI, positive ions): *m/z* = 1213.3877 (calcd for [Au(2)]⁺ = 1213.4079).

6. NMR spectra and ESI-MS spectra

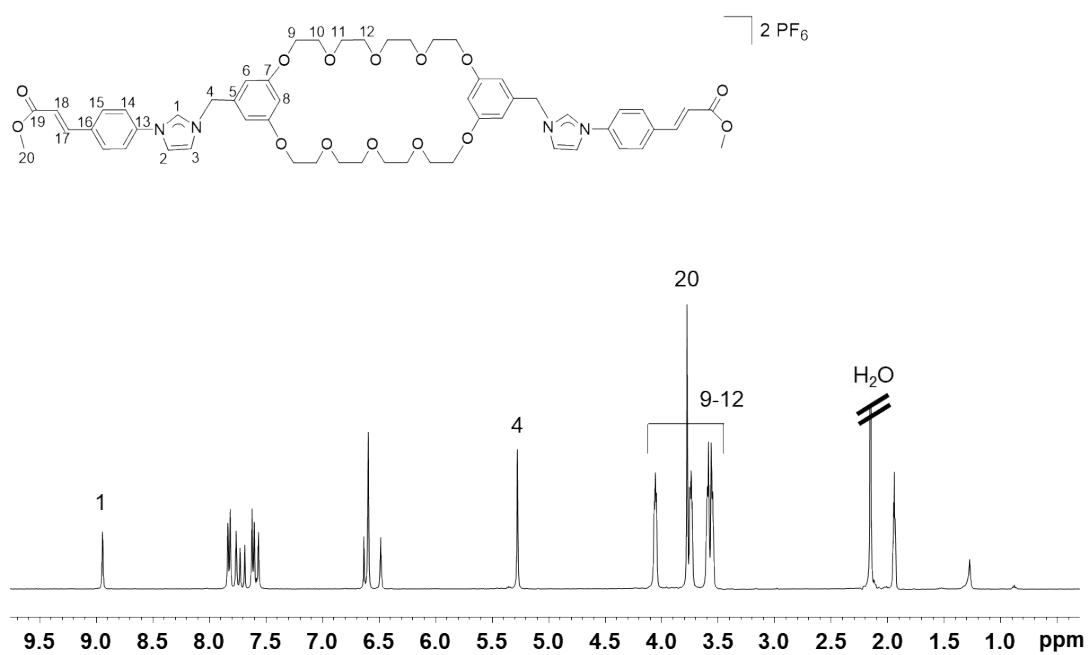


Fig. S3 1H NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $H_2-1(PF_6)$.

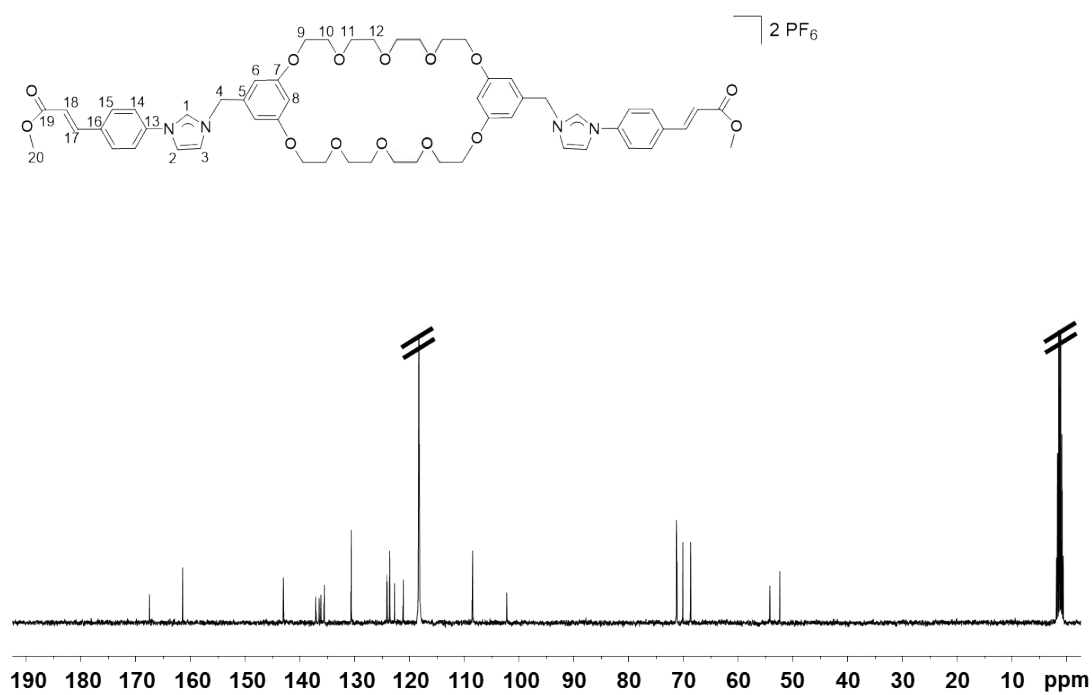


Fig. S4 $^{13}C\{^1H\}$ NMR spectrum (100 MHz, CD_3CN , $c = 0.03$ M) of $H_2-1(PF_6)_2$.

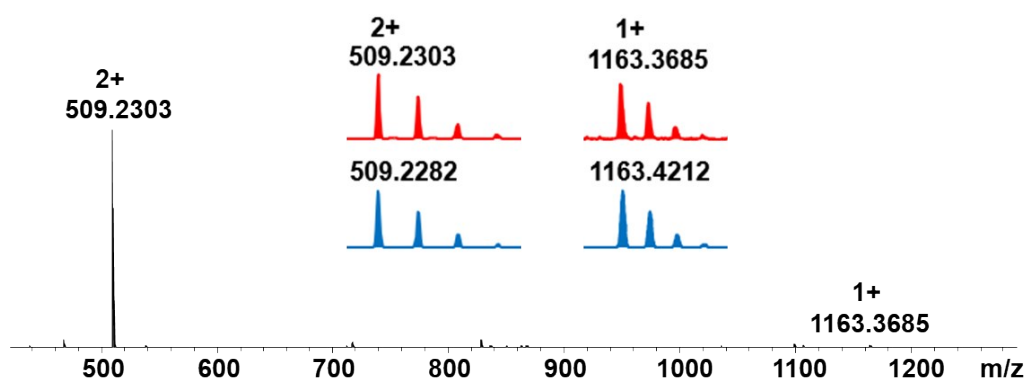


Fig. S5 HR-ESI mass spectrum (positive ions) of $\text{H}_2\text{-1}(\text{PF}_6)_2$ (experimental in red, calculated in blue, PF_6^- counterions).

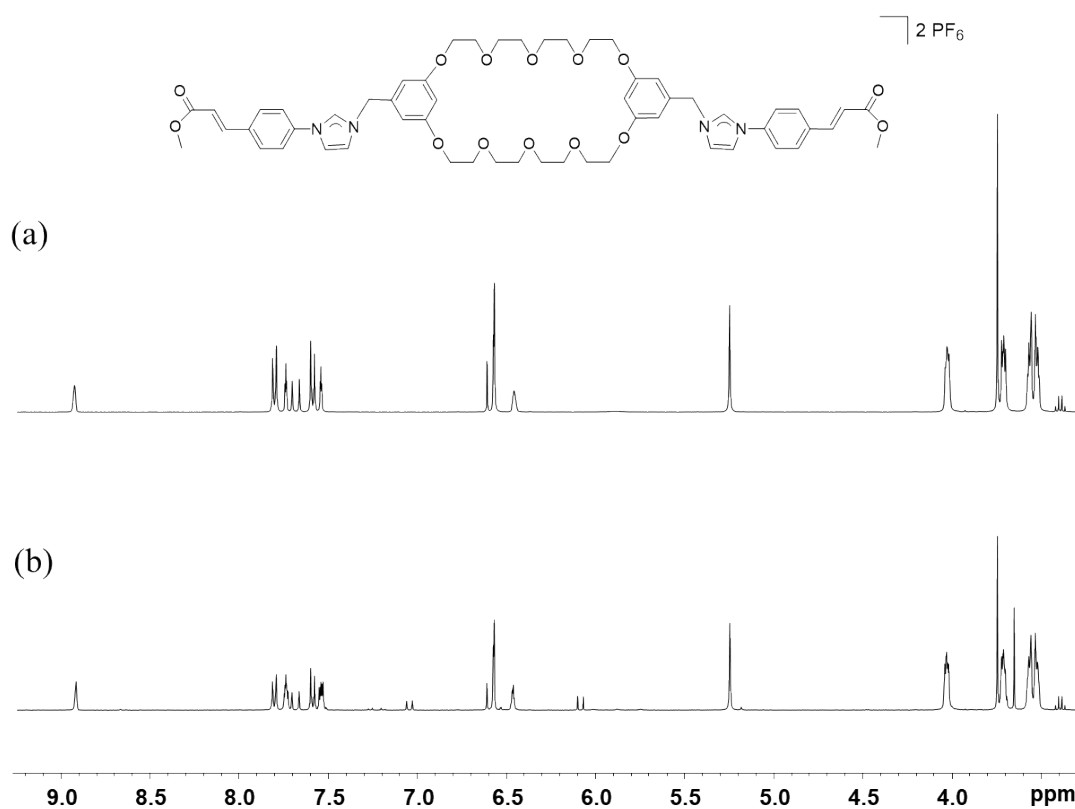


Fig. S6 ^1H NMR spectra (400 MHz, CD_3CN) of $\text{H}_2\text{-1}(\text{PF}_6)_2$ (a) before irradiation and (b) after irradiation at $\lambda = 365$ nm for 12 h. $c = 0.01$ M. Exclusive unimolecular *trans-cis* photoisomerization was observed.

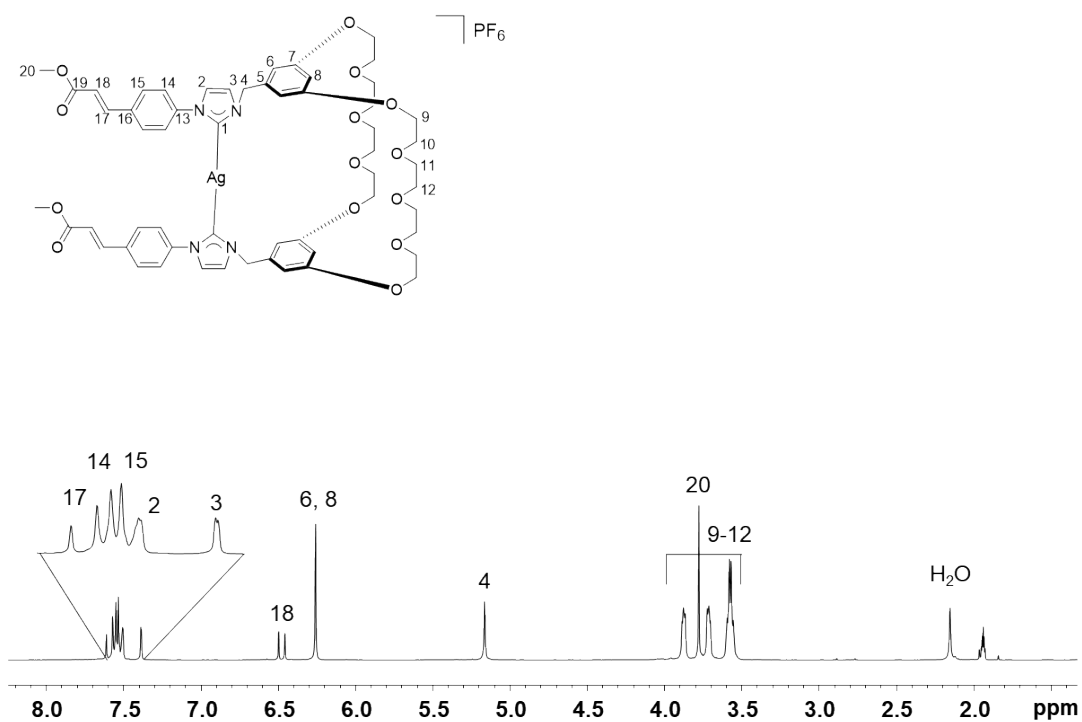


Fig. S7 ¹H NMR spectrum (400 MHz, CD₃CN, *c* = 0.01 M) of [Ag(1)](PF₆).

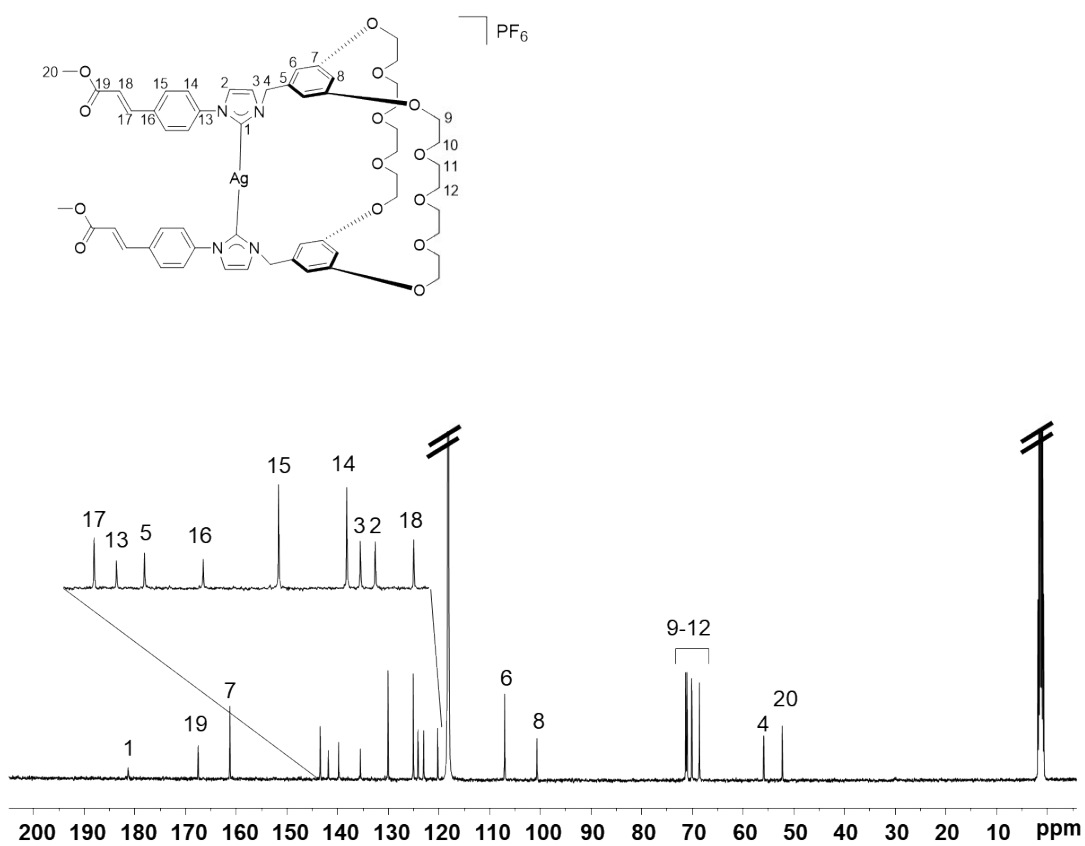


Fig. S8 ¹³C{¹H} NMR spectrum (100 MHz, CD₃CN, *c* = 0.02 M) of [Ag(1)](PF₆).

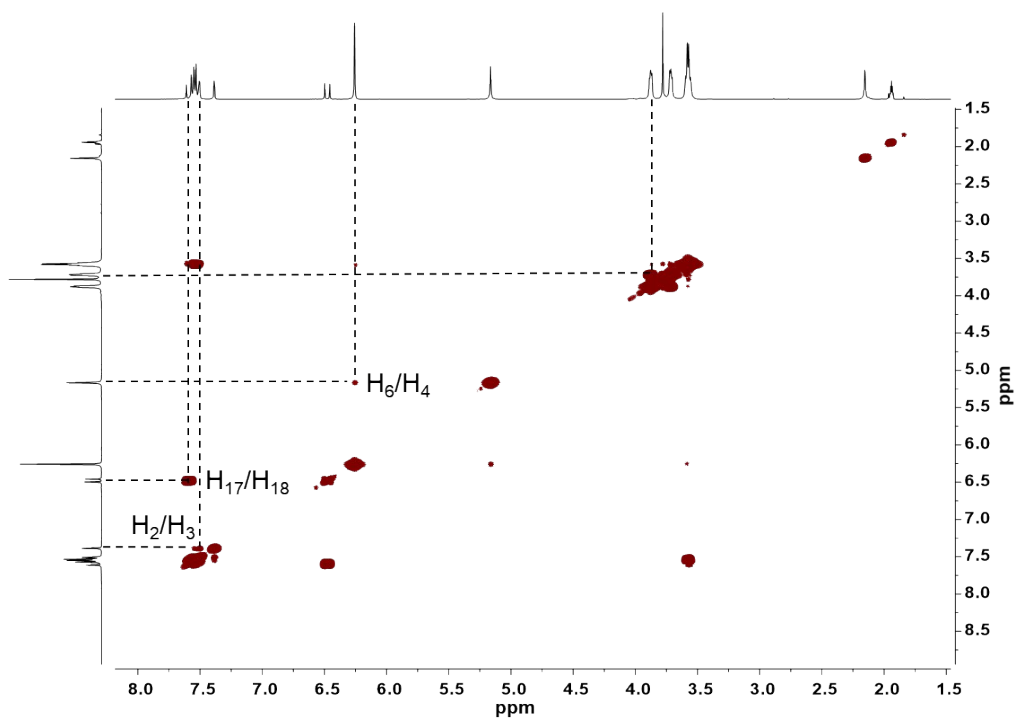


Fig. S9 ^1H - ^1H COSY spectrum (400 MHz, CD_3CN , $c = 0.02$ M) of $[\text{Ag}(\mathbf{1})](\text{PF}_6)$.

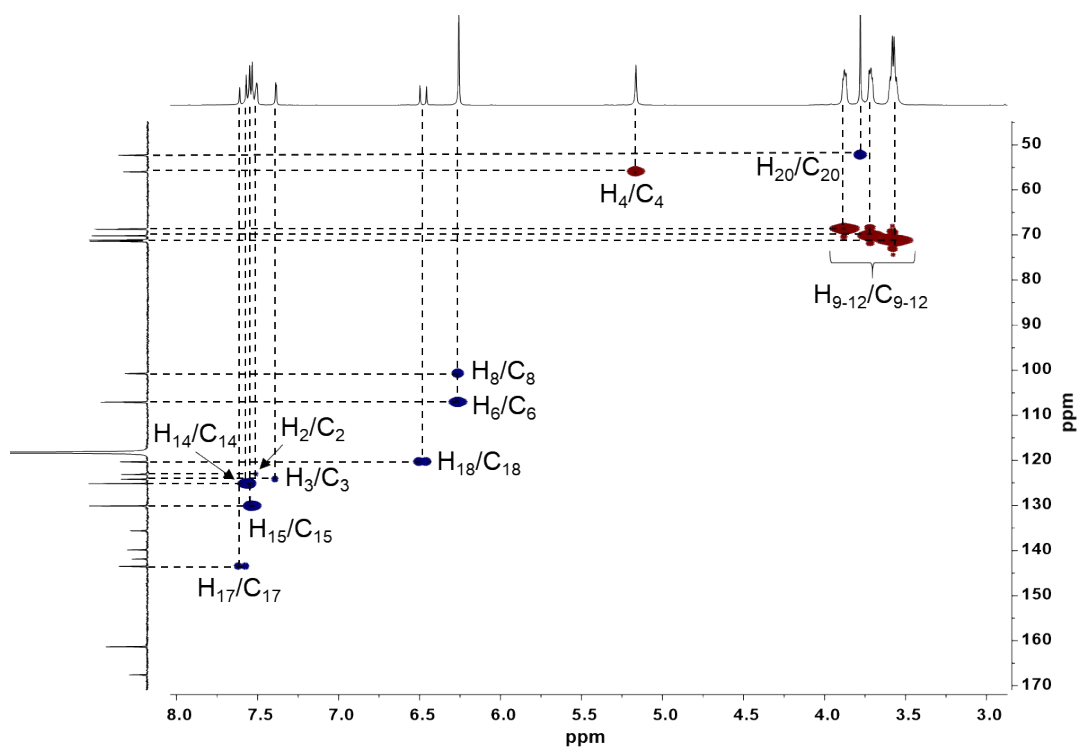


Fig. S10 ^1H - ^{13}C HSQC NMR spectrum (400 MHz, CD_3CN , $c = 0.02$ M) of $[\text{Ag}(\mathbf{1})](\text{PF}_6)$.

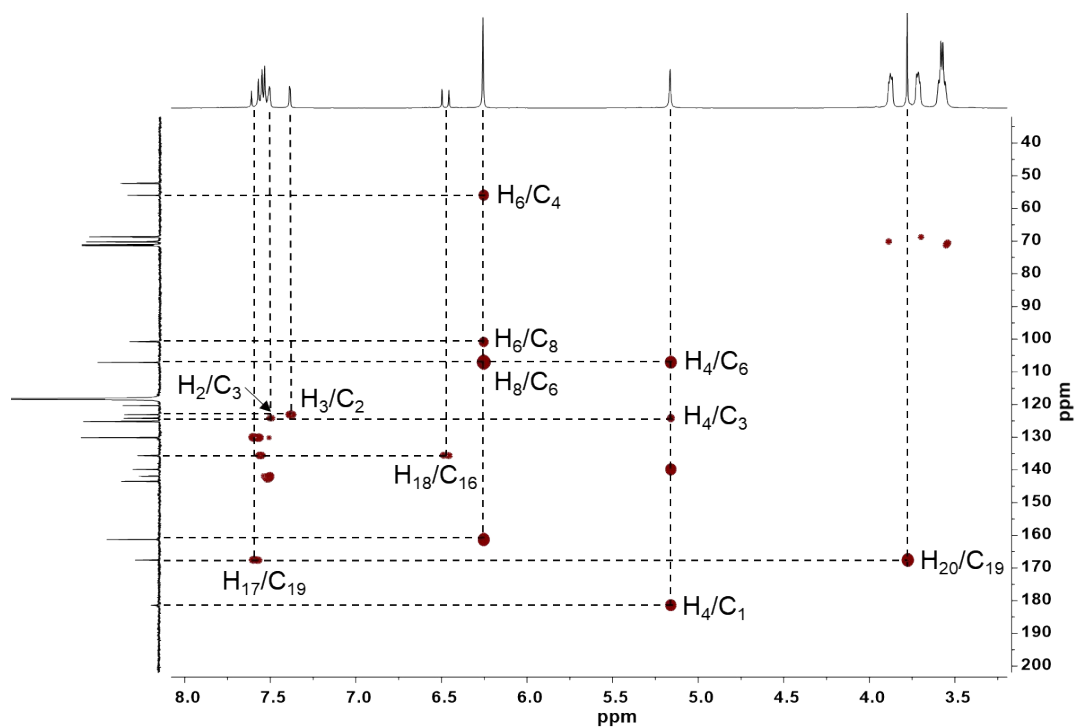


Fig. S11 ^1H - ^{13}C HMBC NMR spectrum (400 MHz, CD_3CN , $c = 0.02$ M) of $[\text{Ag}(1)](\text{PF}_6)$.

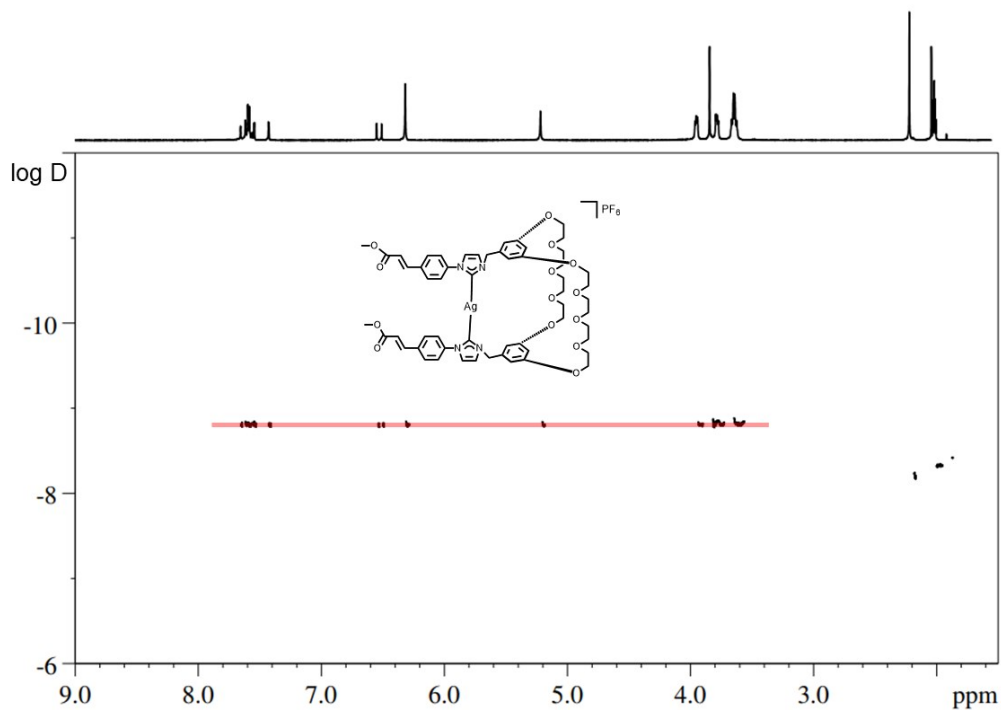


Fig. S12 ^1H DOSY NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $[\text{Ag}(1)](\text{PF}_6)$.

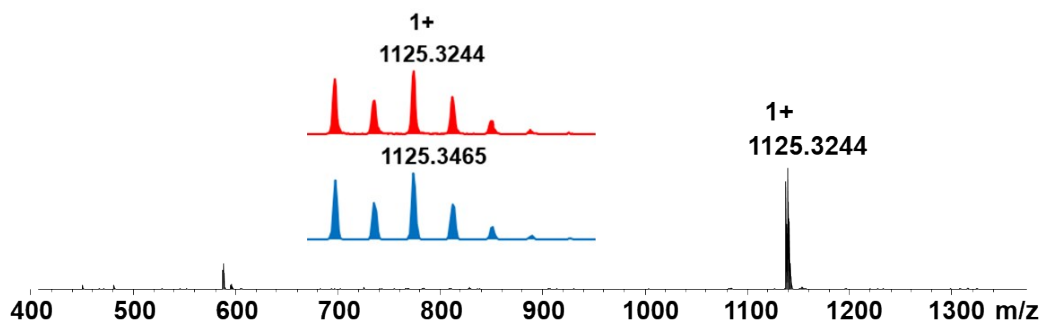


Fig. S13 HR-ESI mass spectrum (positive ions) of $[\text{Ag}(\mathbf{1})](\text{PF}_6)$ (experimental in red, calculated in blue, PF_6^- counterion).

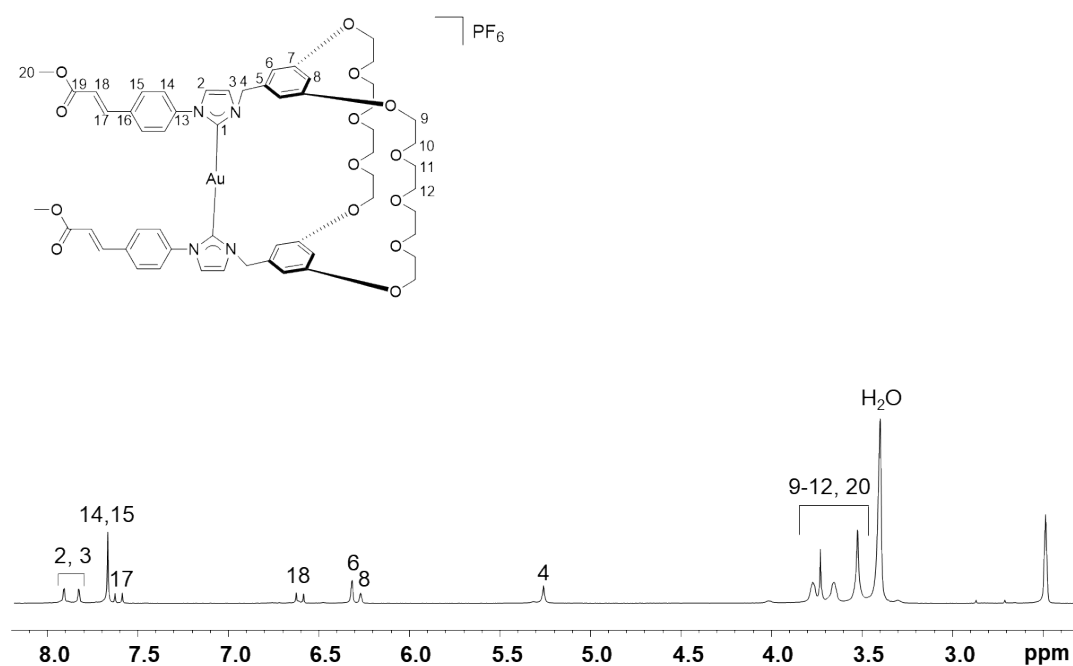


Fig. S14 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, $c = 0.01$ M) of $[\text{Au}(\mathbf{1})](\text{PF}_6)$.

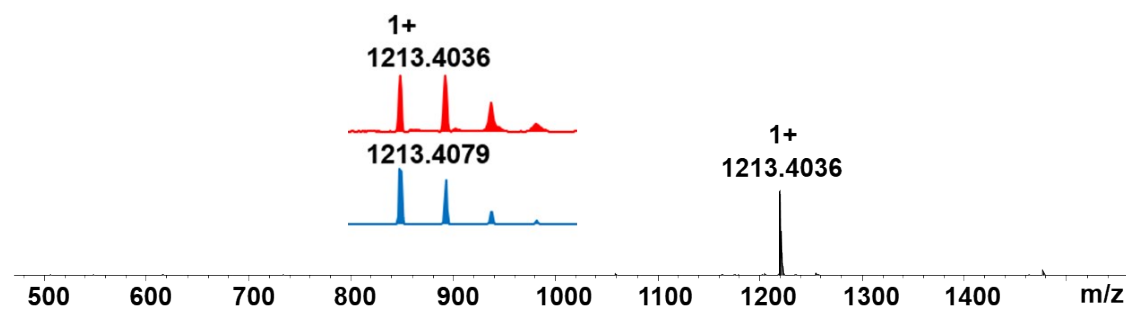


Fig. S15 HR-ESI mass spectrum (positive ions) of $[\text{Au}(\mathbf{1})](\text{PF}_6)$ (experimental in red, calculated in blue, PF_6^- counterion).

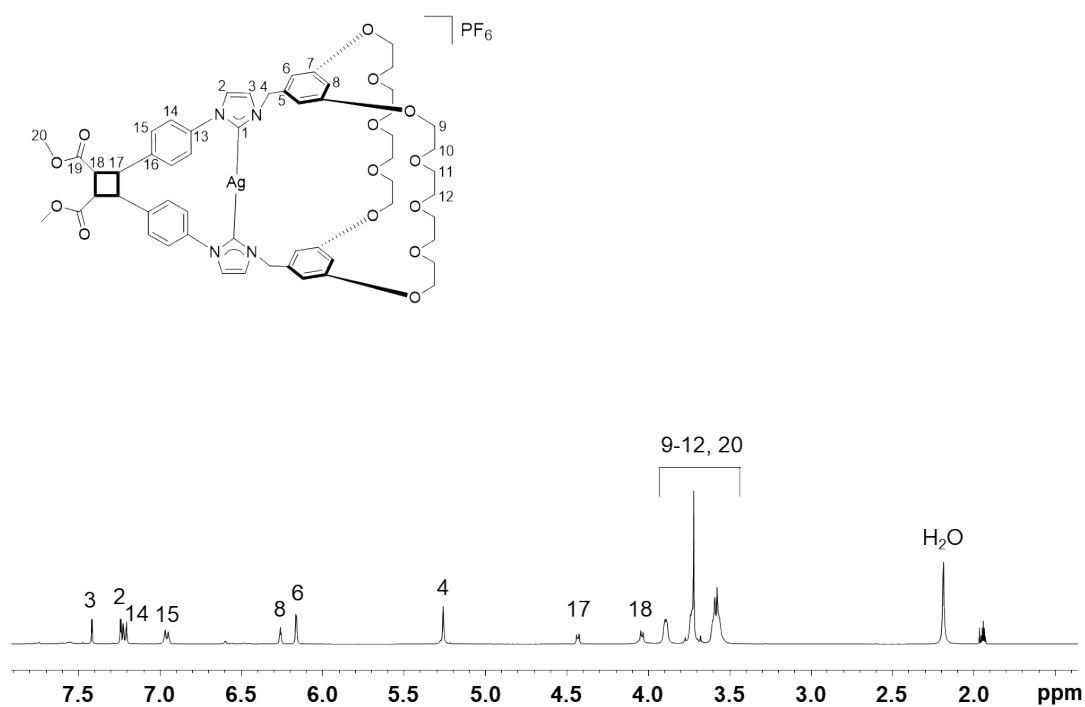


Fig. S16 ¹H NMR spectrum (400 MHz, CD₃CN, *c* = 0.01 M) of [Ag(2)](PF₆).

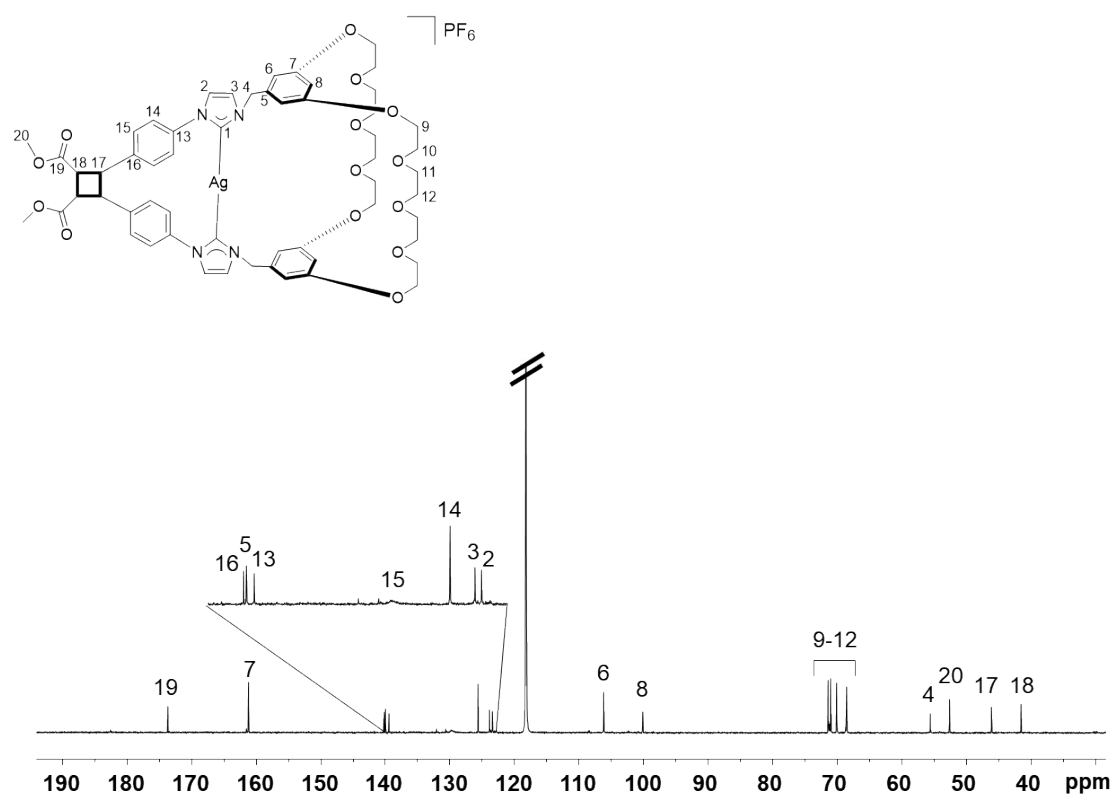


Fig. S17 ¹³C{¹H} NMR spectrum (100 MHz, CD₃CN, *c* = 0.02 M) of [Ag(2)](PF₆).

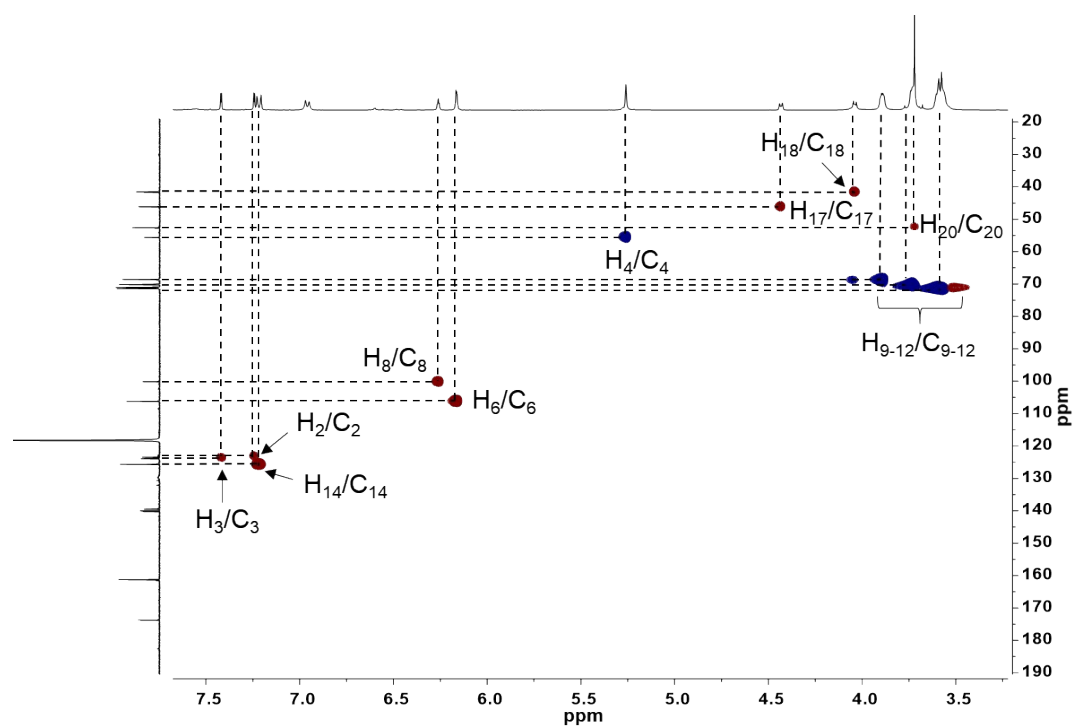


Fig. S18 ^1H - ^{13}C HSQC NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $[\text{Ag}(\mathbf{2})](\text{PF}_6)$.

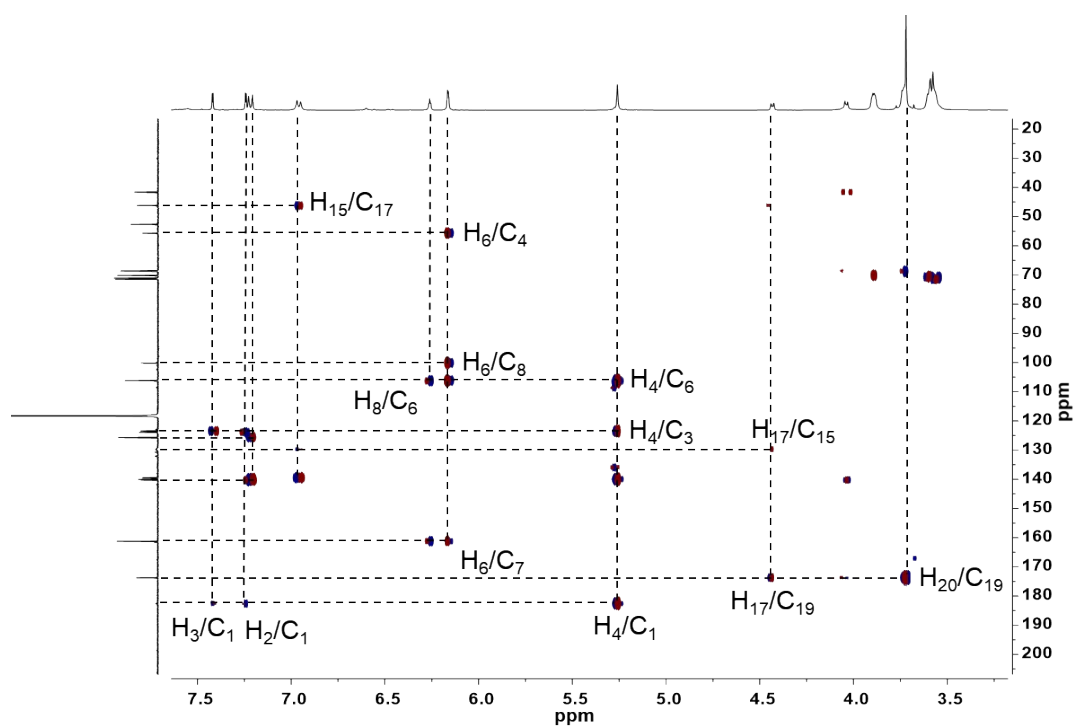


Fig. S19 ^1H - ^{13}C HMBC NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $[\text{Ag}(\mathbf{2})](\text{PF}_6)$.

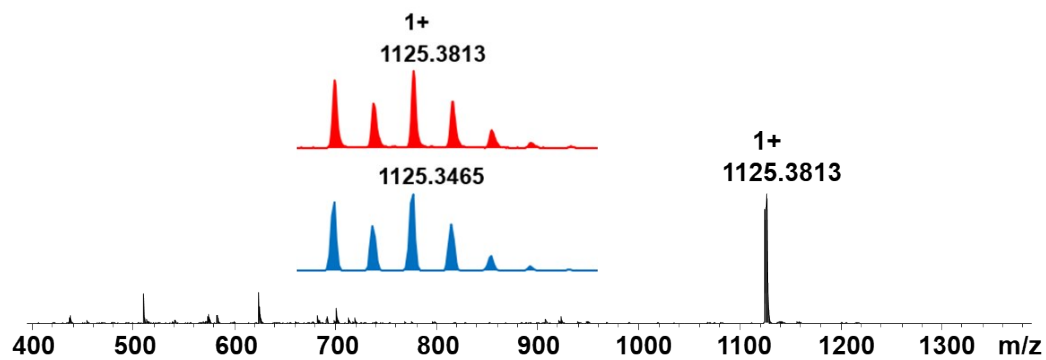


Fig. S20 HR-ESI mass spectrum (positive ions) of $[\text{Ag}(\mathbf{2})](\text{PF}_6)$ (experimental in red, calculated in blue, PF_6^- counterion).

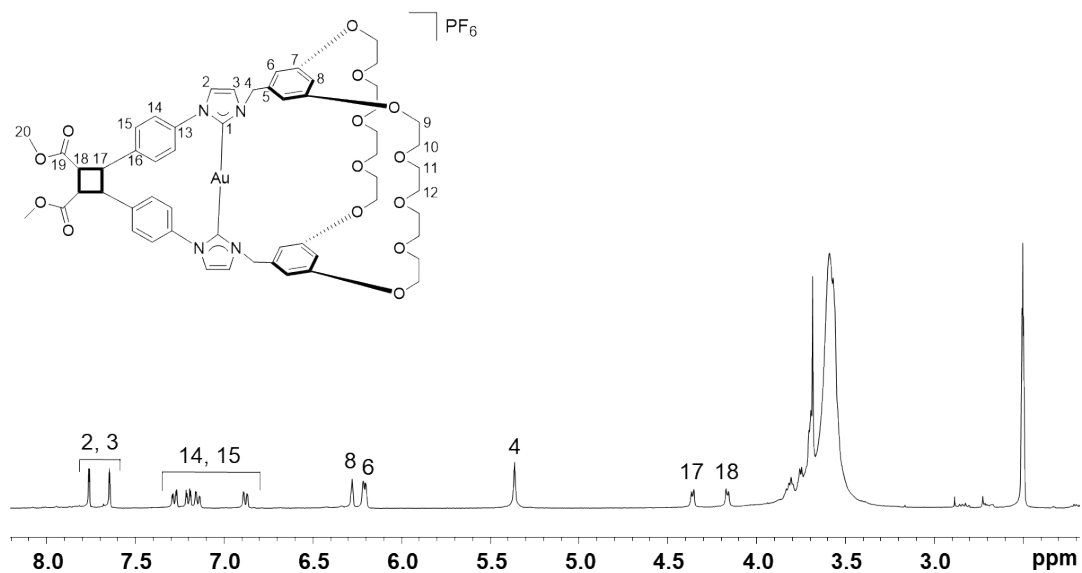


Fig. S21 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, $c = 0.01$ M) of $[\text{Au}(\mathbf{2})](\text{PF}_6)$.

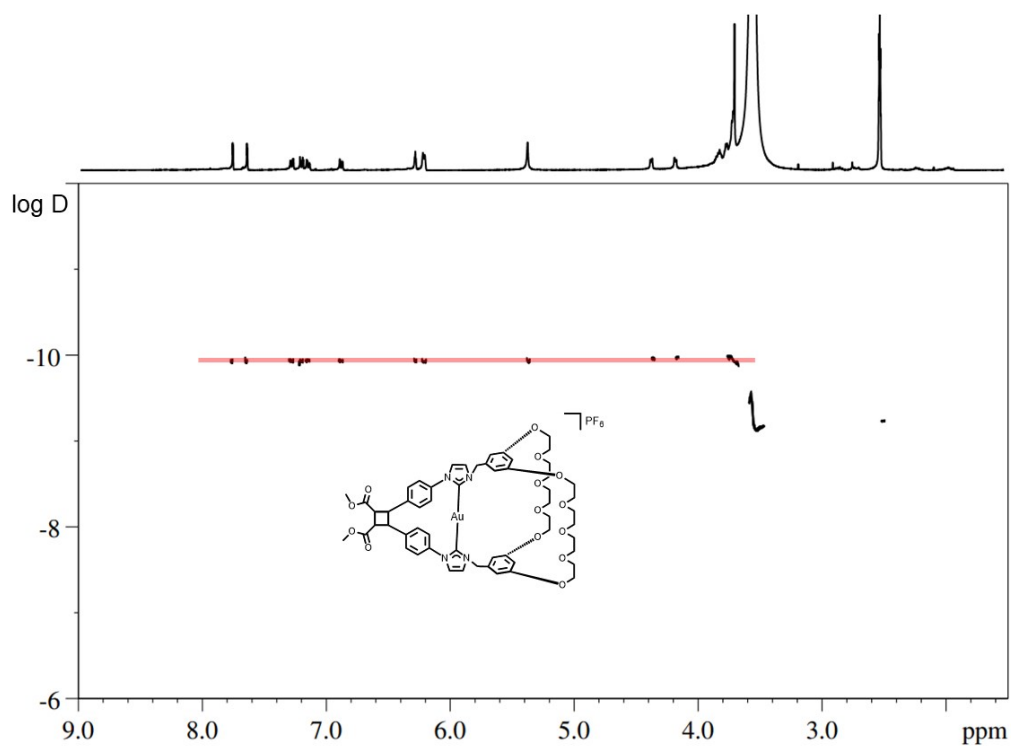


Fig. S22 ^1H DOSY NMR spectrum (400 MHz, $\text{DMSO-}d_6$, $c = 0.01$ M) of $[\text{Au}(\mathbf{2})](\text{PF}_6)$.

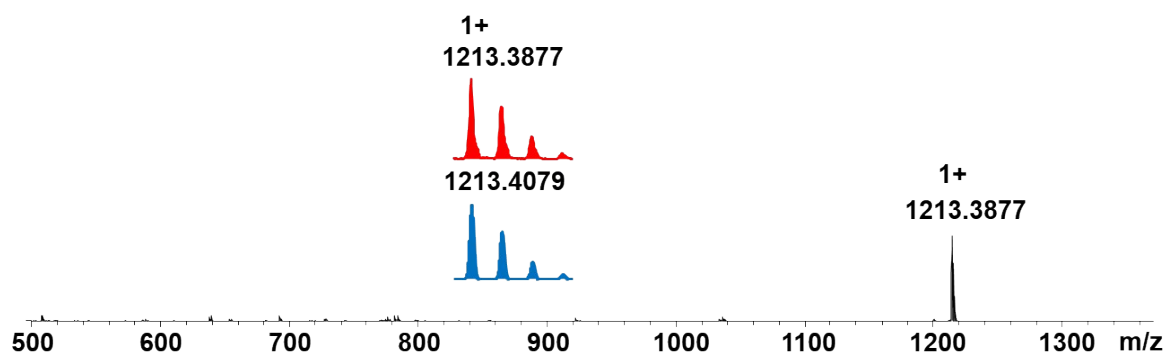


Fig. S23 HR-ESI mass spectrum (positive ions) of $[\text{Au}(\mathbf{2})](\text{PF}_6)$ ([2+2] cycloaddition reaction in $\text{DMSO-}d_6$ solution, experimental in red, calculated in blue, PF_6^- counterion).

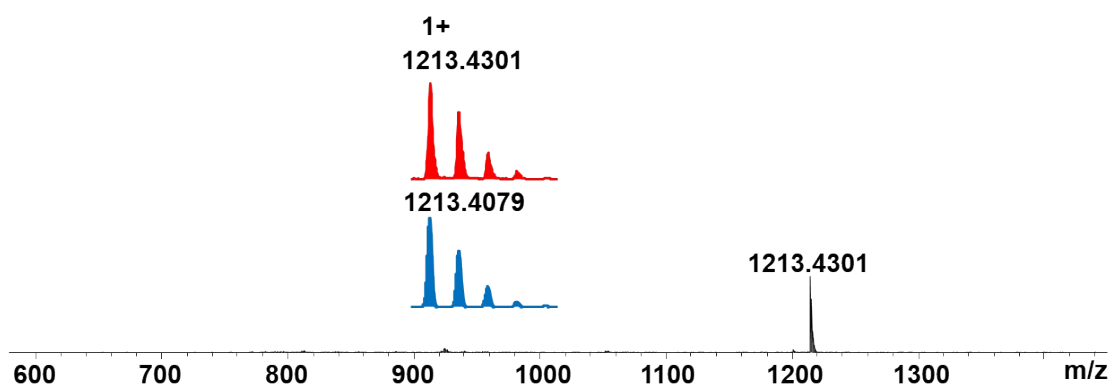


Fig. S24 HR-ESI mass spectrum (positive ions) of $[\text{Au}(\mathbf{2})](\text{PF}_6)$ ($[\mathbf{2}+\mathbf{2}]$ cycloaddition reaction in the solid-state, experimental in red, calculated in blue, PF_6^- counterion).

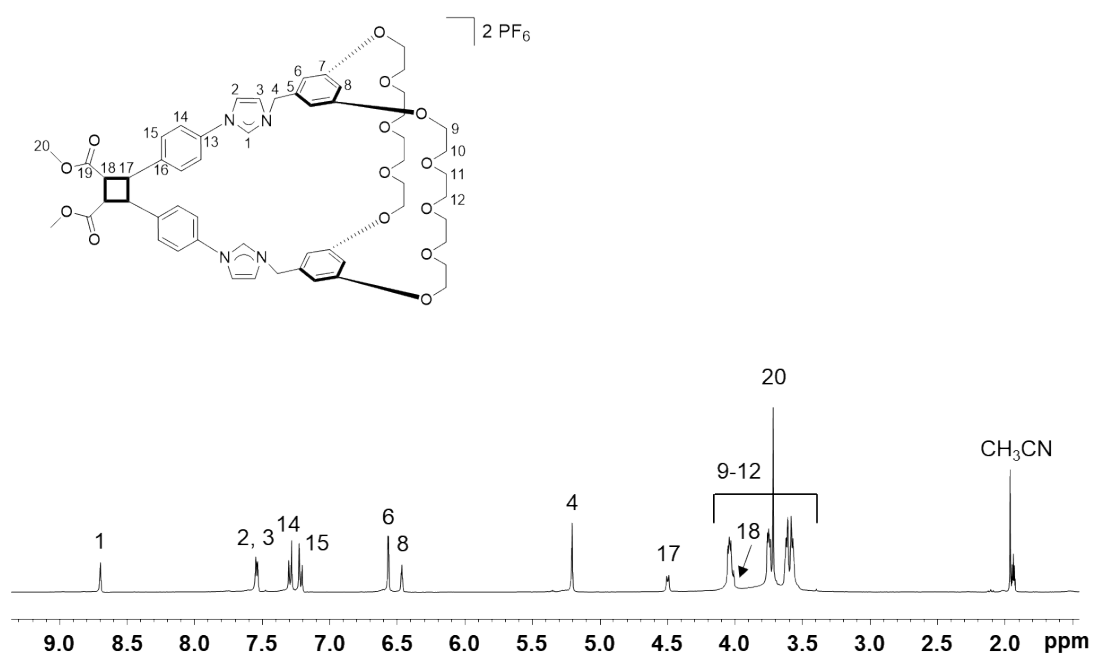


Fig. S25 ^1H NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $\text{H}_2\text{-}\mathbf{2}(\text{PF}_6)_2$.

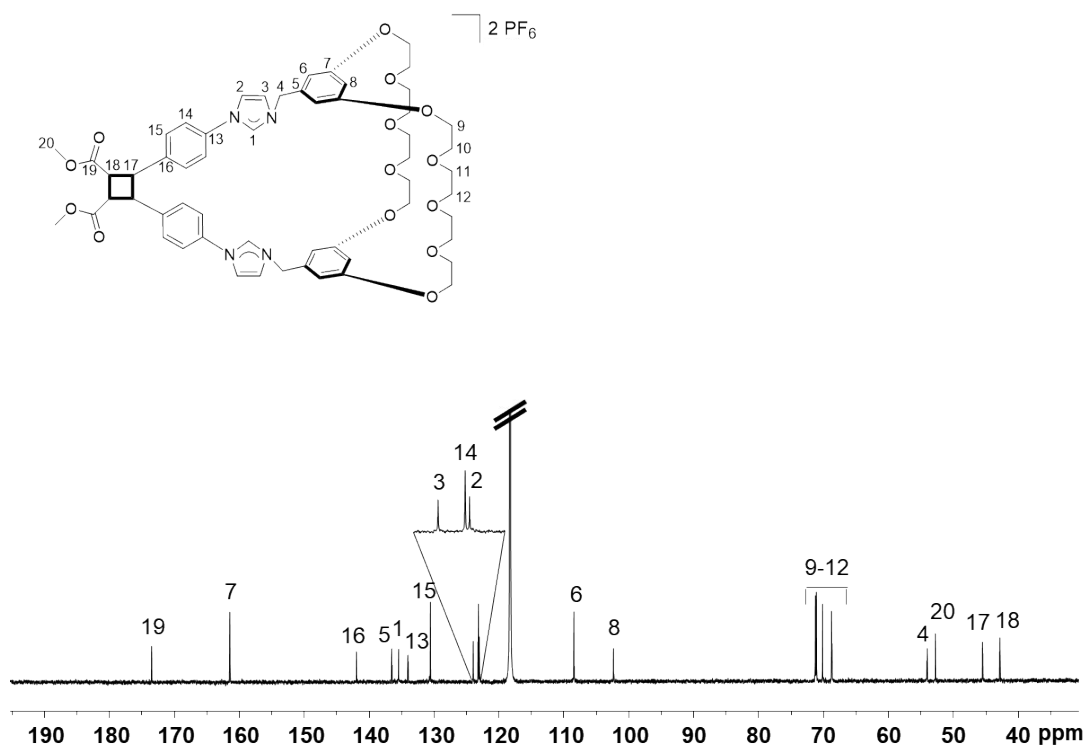


Fig. S26 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CD_3CN , $c = 0.03$ M) of $\text{H}_2\text{-2}(\text{PF}_6)_2$.

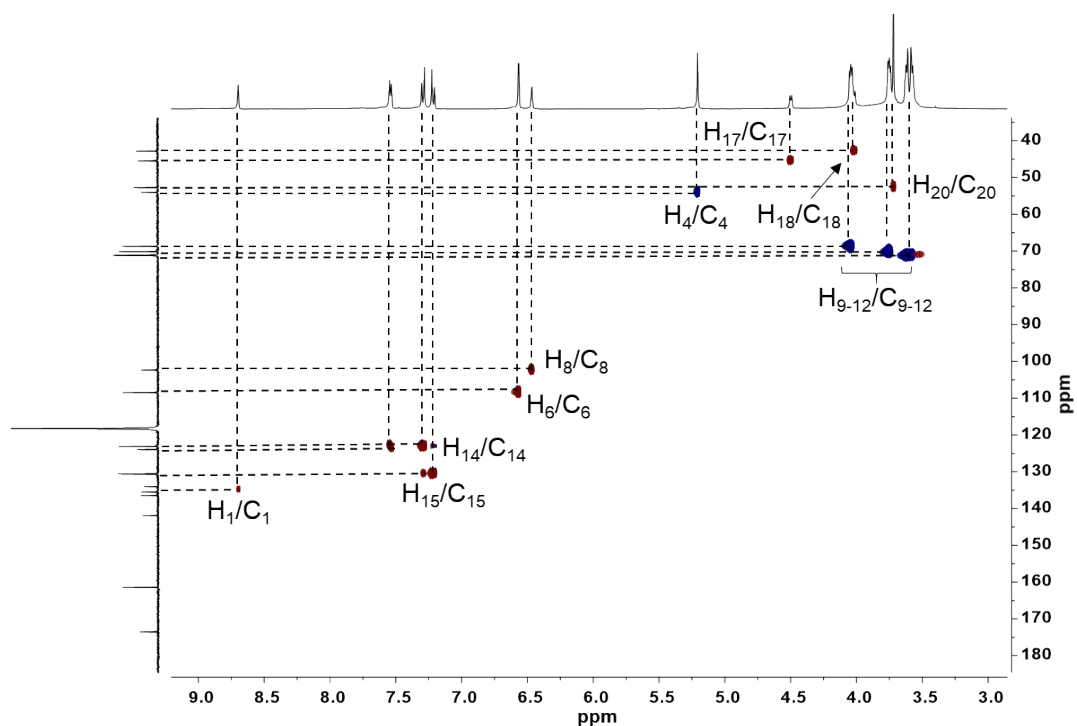


Fig. S27 $^1\text{H}\text{-}^{13}\text{C}$ HSQC NMR spectrum (400 MHz, CD_3CN , $c = 0.03$ M) of $\text{H}_2\text{-2}(\text{PF}_6)_2$.

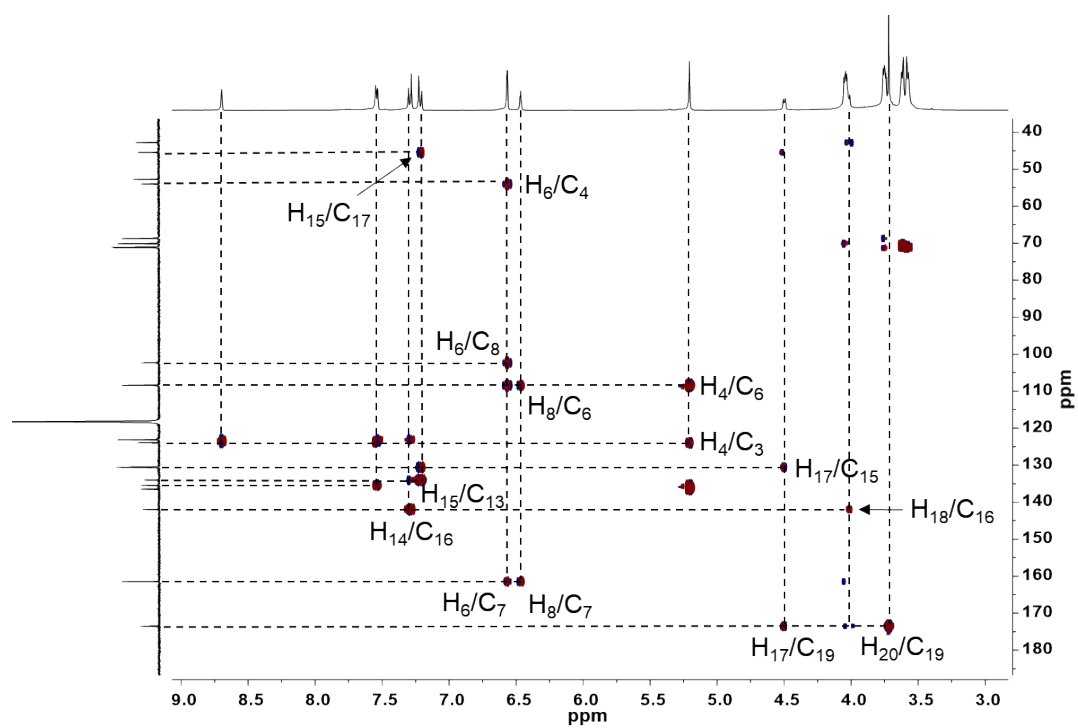


Fig. S28 ^1H - ^{13}C HMBC NMR spectrum (400 MHz, CD_3CN , $c = 0.03$ M) of $\text{H}_2\text{-2}(\text{PF}_6)_2$.

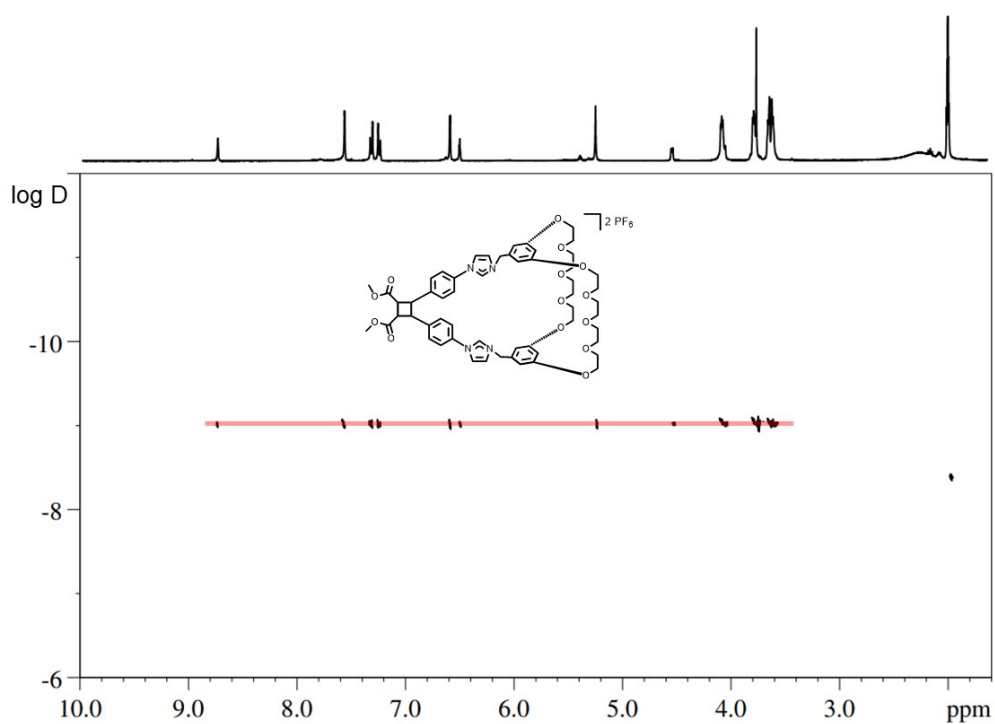


Fig. S29 ^1H DOSY NMR spectrum (400 MHz, CD_3CN , $c = 0.01$ M) of $\text{H}_2\text{-2}(\text{PF}_6)_2$.

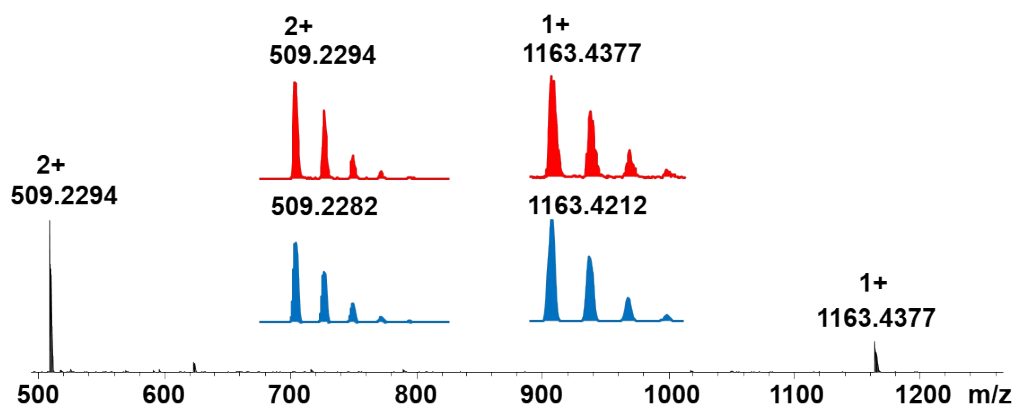


Fig. S30 HR-ESI mass spectrum (positive ions) of $\text{H}_2\text{-2}(\text{PF}_6)_2$ (experimental in red, calculated in blue, PF_6^- counterions).

7. UV-Vis measurements

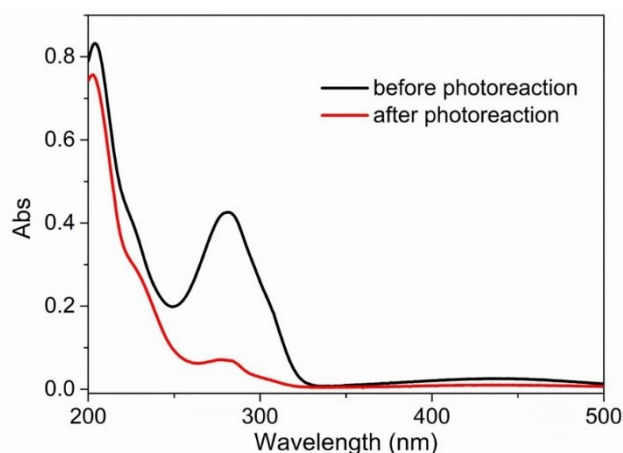


Fig. S31 UV-Vis spectra of [Ag(1)](PF₆) (5 μM) in CH₃CN before (dark line) and after (red line) photoreaction.

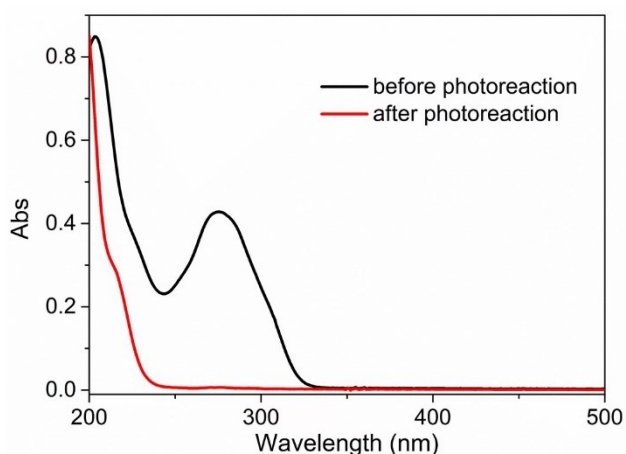


Fig. S32 UV-Vis spectra of [Au(1)](PF₆) (5 μM) in CH₃CN before (dark line) and after (red line) photoreaction.

8. X-ray diffraction analysis of H₂-1(PF₆)₂

Single crystals of H₂-1(PF₆)₂ for X-ray diffraction analysis have been obtained by slow diffusion of diethyl ether into an acetonitrile solution of the salt H₂-1(PF₆)₂ at ambient temperature. Diffraction data was collected at 150 K with a Bruker APEX-II CCD diffractometer. Using the Olex2 program, the structures was solved with the olex2.solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization.³⁻⁵ The structure graphics shown were generated made using the program Diamond. The crystal data of H₂-1(PF₆)₂ and selected structural parameters are summarized in Table S1.

Table S1 Crystal data of H₂-1(PF₆)₂.

Empirical formula	C ₆₀ H ₇₂ F ₁₂ N ₆ O ₁₅ P ₂
Formula weight	1407.17
Temperature/K	151.0
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	25.2644(10)
<i>b</i> /Å	17.7940(8)
<i>c</i> /Å	15.8935(7)
α /°	90
β /°	112.9860(10)
γ /°	90
Volume/Å ³	6577.7(5)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	1.421
μ (mm ⁻¹)	0.169
<i>F</i> (000)	2928.0
Crystal size/mm ³	0.24 × 0.22 × 0.21
Radiation	Mo <i>K</i> α (λ = 0.71073)
2 θ range for data collection/°	4.456 to 50.688
Index ranges	-30 ≤ <i>h</i> ≤ 28, -21 ≤ <i>k</i> ≤ 20, -19 ≤ <i>l</i> ≤ 19
Reflections collected	51054
Independent reflections	6019 [<i>R</i> _{int} = 0.0723, <i>R</i> _{sigma} = 0.0327]
Data/restraints/parameters	6019/39/469
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> _{<i>I</i>} = 0.0512, <i>wR</i> ₂ = 0.1300
Final <i>R</i> indexes [all data]	<i>R</i> _{<i>I</i>} = 0.0779, <i>wR</i> ₂ = 0.1476
Largest diff. peak/hole / e Å ⁻³	0.47/-0.38
CCDC	2090008

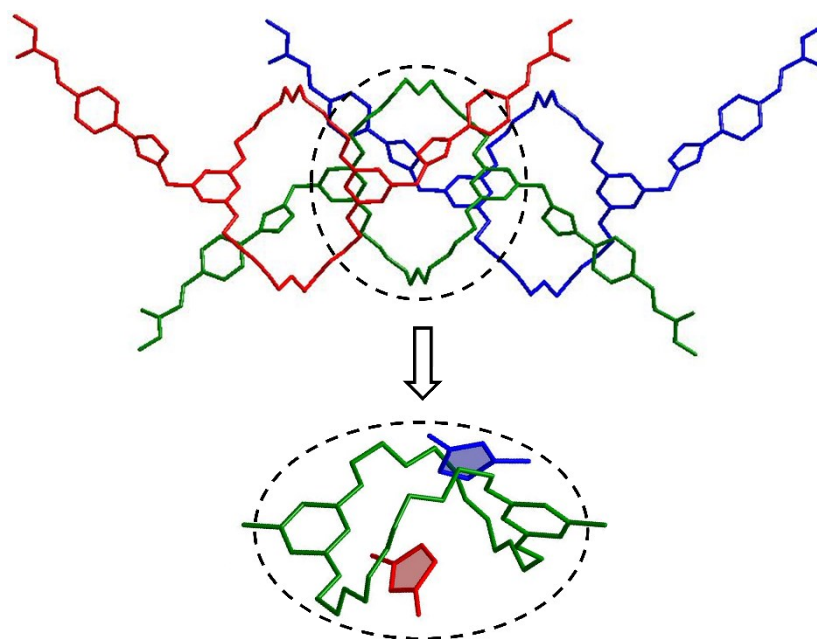


Fig. S33 Packing diagram of [H₂-1]²⁺.

9. References

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