Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Template-driven construction of [8]-imidazolium macrocycles

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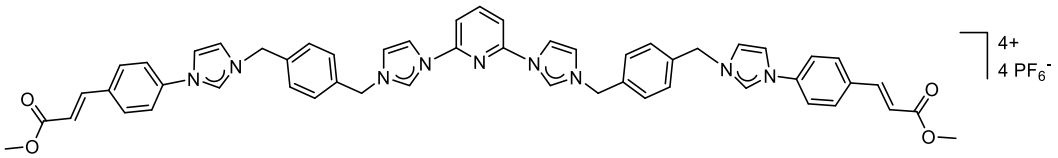
1. General information

N-*p*-bromoemethylbenzene-N'-cinnamicacidmethylester imidazolium bromide was synthesized according to the literature procedure.[1] All manipulations were performed under an 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. ^{1}H, $^{13}C\{^{1}H\}$ and 2D NMR spectra were recorded on Bruker AVANCE III 400, JEOL ECZ400R and JEOL ECZ600R spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz. Mass spectra were obtained with a Bruker microTOF−Q II mass spectrometer (Bruker Daltonics USA) in electrospray ionisation (ESI) mode. UV−vis spectra were obtained using an Agilent Cary-100 spectrophotometer.

2. General procedure

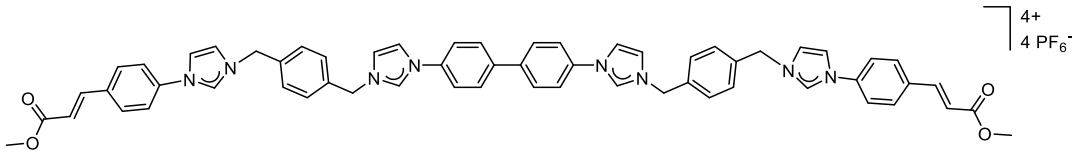
2.1 Synthesis of H_4-1a$(PF_6)_4$



Compounds 2,6-di(1H-imidazol-1-yl)pyridine (21.0 mg, 0.1 mmol) and N-*p*-bromoemethylbenzene-N'-cinnamicacidmethylester imidazolium bromide(147.0 mg, 0.3 mmol) were added to a 25 mL Schlenk flask. To this mixture was added DMF (2.5 mL), and the reaction mixture was heated to 120 °C for 24 h. A white solid was isolated by filtration, washed with ethyl acetate and dried *in vacuo*. The obtained solid was transferred to a bottle containing 30 mL methanol. Upon addition of a solution of NH_4PF_6 (164.0 mg, 1.0 mmol) in methanol (10 mL) to this solution, the colorless hexafluorophosphate salt H_4-**1a**$(PF_6)_4$ precipitated immediately. The precipitated solid was collected by filtration, washed with small portions of water and methanol, and dried *in vacuo*. Yield: 120.0 mg (0.080 mmol, 83%, over two steps). ^{1}H NMR (400 MHz, CD_3CN): δ 9.61 (s, 2H), 9.00 (s, 2H), 8.43 (t, 1H, J = 8.0 Hz), 8.23 (s, 2H), 7.92 (d, 2H, J = 8.2 Hz), 7.86 (d, 4H, J = 8.4 Hz), 7.81 (s, 2H), 7.74 (d, 2H, J = 16.0 Hz), 7.64 (d, 4H, J = 8.4 Hz), 7.60 (d, 2H, J = 8.2 Hz), 7.55 (br, 10H), 6.64 (d, 2H, J = 16.0 Hz), 5.52 (s, 4H), 5.45 (s, 4H), 3.77 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz,

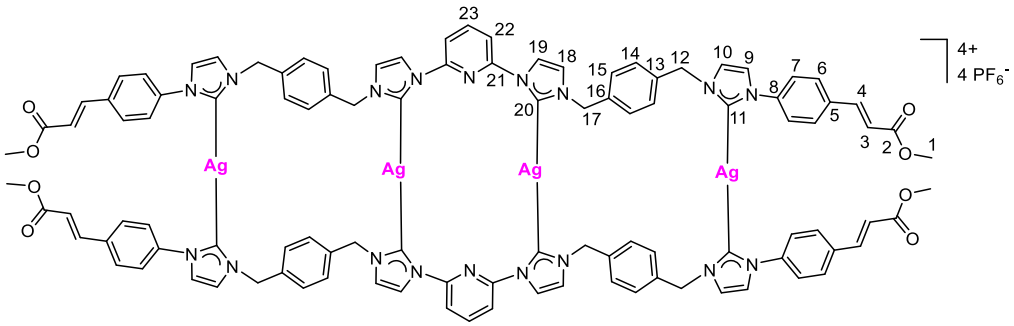
CD_3CN): δ 167.3, 146.1, 145.6, 142.8, 137.0, 136.3, 135.7, 135.5, 135.2, 134.9, 130.5, 130.3, 130.2, 124.3, 123.9, 123.5, 122.8, 121.1, 120.8, 115.7, 53.8, 53.4, 52.1 ppm. HRMS (ESI, positive ions): *m/z* = 582.6545 (calcd for [H_4-**1a** + 2PF_6]$^{2+}$ 582.6590), *m/z* = 218.8559 (calcd for [H_4-**1a**]$^{4+}$ 218.8471).

2.2 Synthesis of H_4-1b$(PF_6)_4$



Tetrakisimidazolium salt H_4-**1b**$(PF_6)_4$ was synthesized as described for H_4-**1a**$(PF_6)_4$ from 4,4'-bis(1-imidazolyl)biphenyl (20.0 mg, 0.06 mmol), N-*p*-bromoemethylbenzene-N'-cinnamicacidmethylester imidazolium bromide (75.0 mg, 0.15 mmol) and NH_4PF_6 (113.1 mg, 0.69 mmol). Yield: 75.0 mg (0.050 mmol, 71%, over two steps). ^{1}H NMR (400 MHz, CD_3CN): δ 9.06 (s, 2H), 9.01 (s, 2H), 7.96 (d, 4H, *J* = 8.6 Hz), 7.88 (s, 2H), 7.86 (s, 4H), 7.83-7.82 (m, 2H), 7.76 (d, 2H, *J* = 16.0 Hz), 7.73 (s, 2H), 7.72 (s, 1H), 7.65 (d, 4H, *J* = 8.6 Hz), 7.58-7.55 (m, 5H), 7.54 (s, 8H), 6.64 (d, 2H, *J* = 16.0 Hz), 5.48 (s, 4H), 5.46 (s, 4H), 3.77 (s, 6H) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ 167.3, 142.7, 141.2, 136.7, 136.1, 135.4, 135.1, 135.0, 134.9, 130.3, 130.1, 129.4, 123.7, 123.6, 123.4, 123.3, 122.7, 122.6, 120.7, 53.2, 52.0 ppm. HRMS (ESI, positive ions): *m/z* = 365.1406 (calcd for [H_4-**1b** + PF_6]$^{3+}$ 365.1298), *m/z* = 237.6204 (calcd for [H_4-**1b**]$^{4+}$ 237.6062).

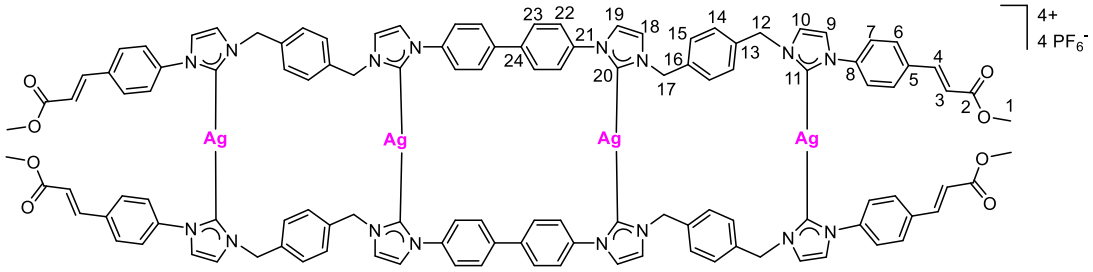
2.3 Synthesis of $[Ag_4(1a)_2](PF_6)_4$



A sample of H_4-**1a**$(PF_6)_4$ (50.0 mg, 0.03 mmol) was dissolved in 15 mL of CH_3CN, and Ag_2O was added to this solution (40.0 mg, 0.17 mmol). The resulting suspension

was heated to 65 °C for 24 h under exclusion of light. After cooling to ambient temperature, the obtained suspension was filtered slowly through a short pad of Celite to obtain a clear solution. The filtrate was concentrated to 2 mL and diethyl ether (15 mL) was added. This led to the precipitation of a white solid. The solid was collected by filtration, washed with diethyl ether and dried *in vacuo* to give $[Ag_4(\mathbf{1a})_2](PF_6)_4$, as a colorless solid. Yield: 40.0 mg (0.014 mmol, 88%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.33 (t, 2H, J = 8.0 Hz, H23), 7.91-7.88 (m, 4H), 7.79 (d, 4H, J = 8.0 Hz), 7.56 (d, 4H, J = 16.0 Hz, H4), 7.48-7.47 (m, 8H), 7.45 (s, 16H), 7.37-7.35 (m, 4H), 7.23 (d, 8H, J = 8.0 Hz), 7.01 (d, 8H, J = 8.0 Hz), 6.45 (d, 4H, J = 16.0 Hz, H3), 5.24 (s, 8H, H17/H12), 4.73 (br, 8H, H17/H12), 3.77 (s, 12H, H1) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ 183.7 (C11/C20), 180.5 (C11/C20), 167.5 (C2), 149.8, 144.6, 143.4, 141.6, 137.4, 137.1, 135.6, 130.0, 129.4, 129.1, 125.0, 124.5, 123.5, 120.7, 120.3, 115.0, 55.7 (C17/C12), 52.2 (C1) ppm. HRMS (ESI, positive ions): m/z = 773.1167 (calcd for $[Ag_4(\mathbf{1a})_2 + PF_6]^{3+}$ 773.1005), m/z = 543.5964 (calcd for $[Ag_4(\mathbf{1a})_2]^{4+}$ 543.5842).

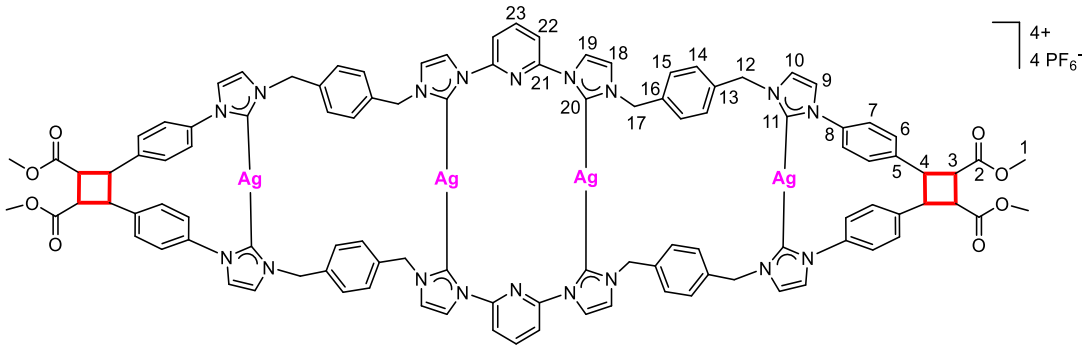
2.4 Synthesis of $[Ag_4(1b)_2](PF_6)_4$



Complex $[Ag_4(\mathbf{1b})_2](PF_6)_4$ was synthesized as described for $[Ag_4(\mathbf{1a})_2](PF_6)_4$ from H_4-$\mathbf{1b}(PF_6)_4$ (40.0 mg, 0.03 mmol) and Ag_2O (50.0 mg, 0.22 mmol) in 20 mL of acetonitrile at 65 °C for 24 h under exclusion of light. Yield: 33.0 mg (0.011 mmol, 87%). ^{1}H NMR (600 MHz, CD_3CN): δ 7.62 (m, 16H, H22/H23), 7.57 (d, 4H, J = 16.0 Hz, H4), 7.54 (s, 4H, H9), 7.52 (br, 16H, H7/H6), 7.50 (s, 4H, H10), 7.42 (s, 4H, H18), 7.40 (s, 4H, H19), 7.19 (d, 8H, J = 7.4 Hz, H14), 7.16 (d, 8H, J = 7.4 Hz, H15), 6.46 (d, 4H, J = 16.0 Hz, H3), 5.27 (s, 8H, H12), 5.22 (s, 8H, H17), 3.77 (s, 12H, H1) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ 181.3 (C11/C20), 167.5 (C2), 143.4 (C4), 141.8 (C24), 140.4 (C22), 139.1 (21), 137.8 (16), 135.7 (C5), 130.2 (C6), 128.9 (C13), 128.8 (C14), 126.3 (C15), 125.4 (C7), 125.1 (C23), 124.2 (C18), 124.1 (C9), 123.5 (C10), 123.3 (C19), 120.4 (C3), 55.6 (C17/C12), 52.3 (C1) ppm. HRMS (ESI,

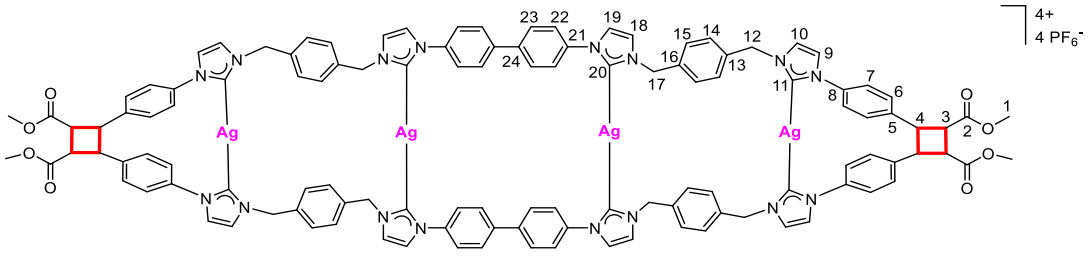
positive ions): *m/z* = 823.1503 (calcd for $[Ag_4(\mathbf{1b})_2 + PF_6]^{3+}$ 823.1246), *m/z* = 581.1319 (calcd for $[Ag_4(\mathbf{1b})_2]^{4+}$ 581.1022).

2.5 Synthesis of $[Ag_4(2a)](PF_6)_4$



A solution of $[Ag_4(\mathbf{1a})_2](PF_6)_4$ (40.0 mg, 0.014 mmol) in CD_3CN (0.5 mL) in an NMR tube was irradiated with a Philips mercury high-pressure lamp (λ= 365 nm) at ambient temperature for 24 h. Over this time the initially colorless solution turned brown. The conversion to $[Ag_4(\mathbf{2a})](PF_6)_4$ was quantitative, as judged by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, CD_3CN): δ 8.28 (t, 2H, J = 8.0 Hz, H23), 7.93-7.89 (m, 4H), 7.77 (s, 2H), 7.75 (s, 2H), 7.50-7.46 (m, 4H), 7.39-7.37 (m, 4H), 7.36 (s, 4H), 7.34 (s, 4H), 7.33 (s, 4H), 7.15-7.11 (m, 16H), 6.93 (s, 8H), 5.37 (s, 8H, H17/H12), 4.85 (br, 8H, H17/H12), 4.41 (s, 4H, H4), 4.02 (s, 4H, H3), 3.70 (s, 12H, H1) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ 180.7 (C11/C20), 173.4 (C2), 149.6, 144.2, 139.9, 138.9, 137.3, 129.1, 128.7, 125.2, 124.0, 123.9, 122.4, 120.9, 114.9, 55.6 (C17/C12), 52.3 (C1), 45.8 (C4), 41.2 (C3) ppm. HRMS (ESI, positive ions): *m/z* = 543.5932 (calcd for $[Ag_4(\mathbf{2a})_2]^{4+}$ 543.5842).

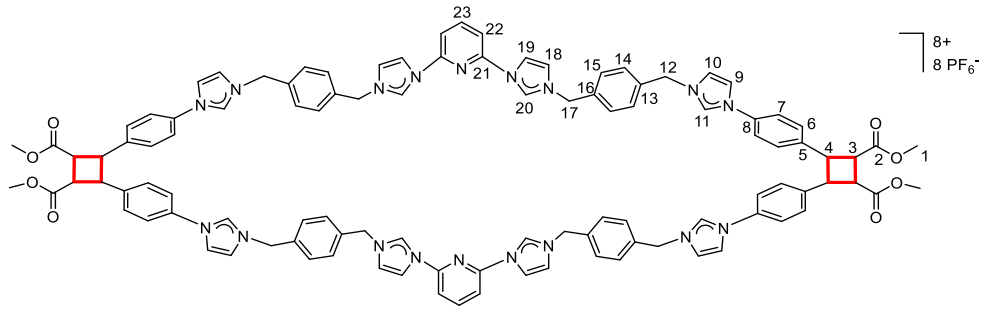
2.6 Synthesis of $[Ag_4(2b)](PF_6)_4$



Complex $[Ag_4(\mathbf{2b})](PF_6)_4$ was synthesized as described for $[Ag_4(\mathbf{2a})](PF_6)_4$ from $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (33.0 mg, 0.011 mmol) in CD_3CN (0.5 mL). ^{1}H NMR (600 MHz, CD_3CN): δ 7.64 (s, 16H, H22/H23), 7.55 (d, 4H, J = 1.8 Hz, H10), 7.45 (d, 4H, J =

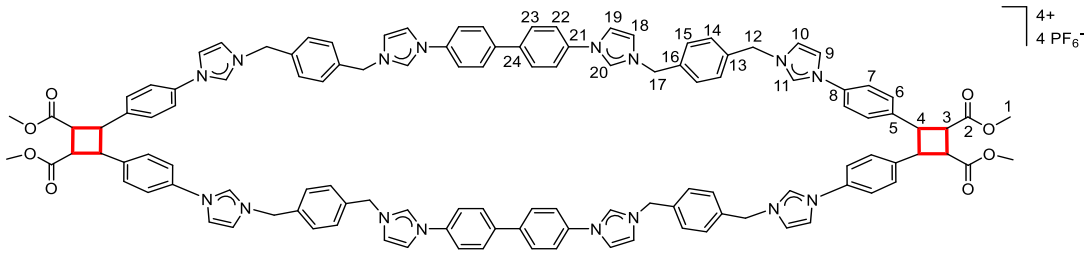
1.8 Hz, H9), 7.43 (d, 4H, J = 1.8 Hz, H19), 7.37 (d, 4H, J = 1.8 Hz, H18), 7.19 (d, 8H, J = 8.2 Hz, H14), 7.16 (s, 8H, H7/H6), 7.13 (d, 8H, J = 8.2 Hz, H15), 6.95 (s, 8H, H7/H6), 5.45 (s, 8H, H12), 5.38 (s, 8H, H17), 4.42 (s, 4H, H4), 4.02 (s, 4H, H3), 3.71 (s, 12H, H1) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_3CN): δ 182.0 (C20), 180.7 (C11), 173.7 (C2), 140.3 (C6), 140.2 (C5), 139.3 (C24/C21), 139.1 (C8), 137.9 (C16), 137.5 (C13), 128.6 (14), 128.4 (15), 128.3 (C22), 125.5 (C7), 125.3 (C23), 123.9 (C10), 123.8 (C9), 123.7 (C19), 123.5 (C18), 55.7 (C12), 55.3 (C17), 52.6 (C1), 46.1 (C4), 41.5 (C3) ppm. HRMS (ESI, positive ions): m/z = 581.1019 (calcd for $[Ag_4(\mathbf{2b})_2]^{4+}$ 581.1022).

2.7 Synthesis of H_8-2a$(PF_6)_8$



A sample of $[Ag_4(\mathbf{2a})](PF_6)_4$ (40.0 mg, 0.014 mmol) was dissolved in a mixture of MeOH (30 mL) and CD_3CN (0.5 ml), and NH_4Cl (14.0 mg, 0.262 mmol) was added to this solution. A white solid (AgCl) precipitated immediately. The reaction mixture was stirred for 4 h. The resulting suspension was filtered through Celite to obtain a clear solution. The solvent was removed from this solution to give a white solid. The white solid was dissolved in MeOH (15 mL) and a solution of NH_4PF_6 (80.0 mg, 0.15 mmol) in methanol (5 mL) was added. The mixture was stirred at ambient temperature for 8 h. After this period a white solid precipitated, which was isolated by filtration, washed with water and methanol, and dried *in vacuo*. Yield: 35.0 mg (0.012 mmol, 86%). ^{1}H NMR (400 MHz, CD_3CN): δ 10.39 (s, 4H, H20/H11), 8.96 (s, 4H, H20/H11), 8.43 (t, 2H, J = 8.2 Hz, H23), 8.23 (s, 4H), 7.93 (s, 2H), 7.91 (s, 2H), 7.64 (s, 4H), 7.59 (s, 4H), 7.55 (d, 8H, J = 8.0 Hz), 7.49 (s, 4H), 7.47 (d, 8H, J = 8.0 Hz), 7.35 (d, 8H, J = 8.4 Hz), 7.27 (d, 8H, J = 8.4 Hz), 5.53 (s, 8H, H17/H12), 5.39 (s, 8H, H17/H12), 4.50 (s, 4H, H4), 4.00 (s, 4H, H3), 3.71 (s, 12H, H1) ppm. HRMS (ESI, positive ions): m/z = 825.5483 (calcd for $[H_8\text{-}\mathbf{2a} + 5PF_6]^{3+}$ 825.5346), m/z = 582.9164 (calcd for $[H_8\text{-}\mathbf{2a} + 4PF_6]^{4+}$ 582.9098).

2.8 Synthesis of H_8-2b$(PF_6)_8$



Octakisimidazolium salt H_8-**2b**$(PF_6)_8$ was synthesized as described for H_8-**2a**$(PF_6)_8$ from [Ag_4(**2b**)]$(PF_6)_4$ (36.0 mg, 0.012 mmol), NH_4Cl (14.0 mg, 0.262 mmol) and NH_4PF_6 (102.0 mg, 0.520 mmol). Yield: 36.0 mg (0.011 mmol, 94%). ^{1}H NMR (600 MHz, CD_3CN): δ 9.08 (s, 4H, H20), 8.94 (s, 4H, H11), 7.92 (d, 8H, J = 8.4 Hz, H15), 7.83 (s, 4H, H9), 7.72 (d, 8H, J = 8.4 Hz, H14), 7.65 (s, 4H, H19), 7.56 (s, 4H, H10), 7.55-7.49 (m, 16H, H22/H23), 7.46 (s, 4H, H18), 7.38 (d, 8H, J = 8.4 Hz, H7), 7.30 (d, 8H, J = 8.4 Hz, H6), 5.45 (s, 8H, H12), 5.41 (s, 8H, H17), 4.50 (s, 4H, H4), 4.00 (s, 4H, H3), 3.71 (s, 12H, H1) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): δ 173.4 (C2), 142.1 (C5), 141.7 (C23), 141.5 (C16), 135.7 (C21), 135.6 (C13), 135.5 (C11), 135.3 (C20), 134.1 (C8), 130.7 (C6), 130.5 (C22), 129.8 (C15), 124.1 (C10), 123.9 (C19), 123.8 (C14), 123.7 (C18), 123.1 (C9), 122.9 (C7), 53.6 (C12), 53.5 (C17), 52.7 (C1), 45.2 (C4), 43.4 (C3) ppm. HRMS (ESI, positive ions): m/z = 1385.8143 (calcd for [H_8-**2b** + 6PF_6]$^{2+}$ 1385.8203), m/z = 875.5479 (calcd for [H_8-**2b** + 5PF_6]$^{3+}$ 875.5587), m/z = 620.4241 (calcd for [H_8-**2b** + 4PF_6]$^{4+}$ 620.4278), m/z = 467.3423 (calcd for [H_8-**2b** + 3PF_6]$^{5+}$ 467.3493).

3. Selected NMR, UV-vis and MS spectra for new compounds

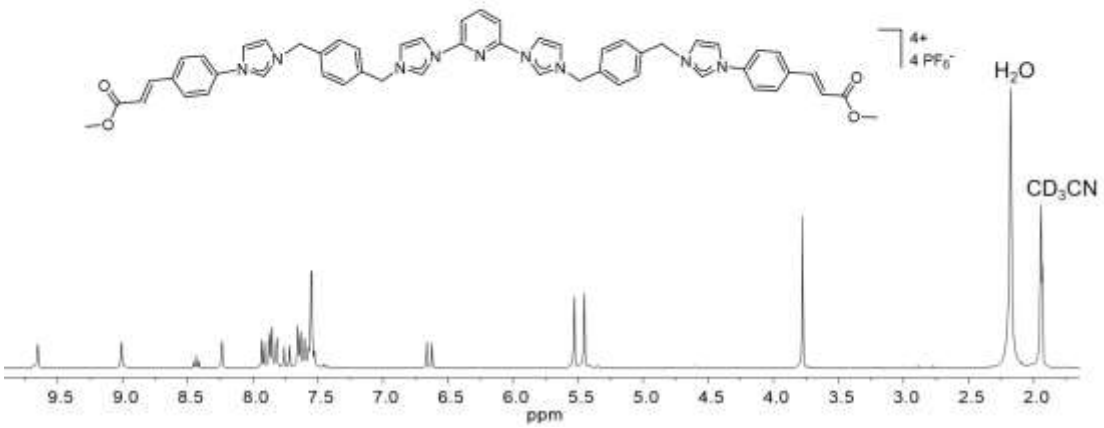


Fig. S1 ^{1}H NMR spectrum of H_4-**1a**$(PF_6)_4$ (400 MHz, CD_3CN).

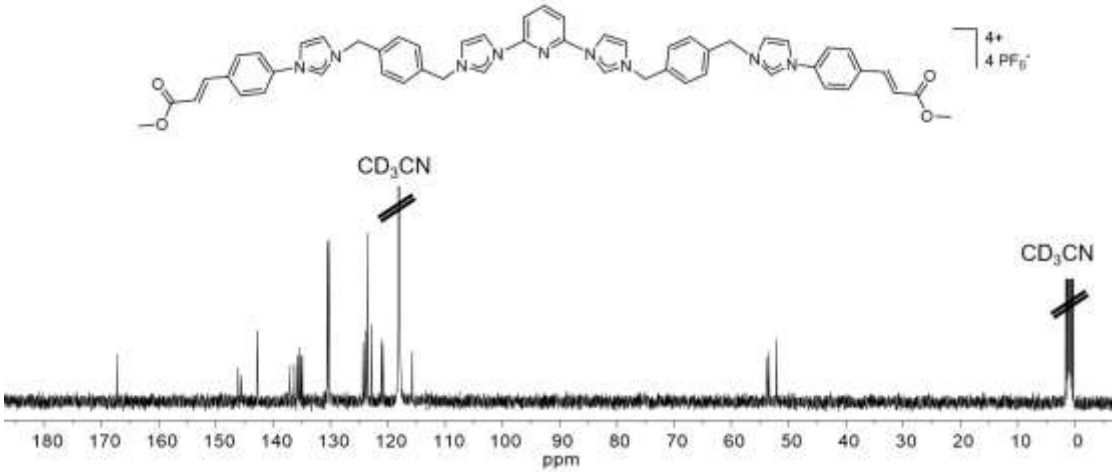


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of H_4-**1a**$(PF_6)_4$ (100 MHz, CD_3CN).

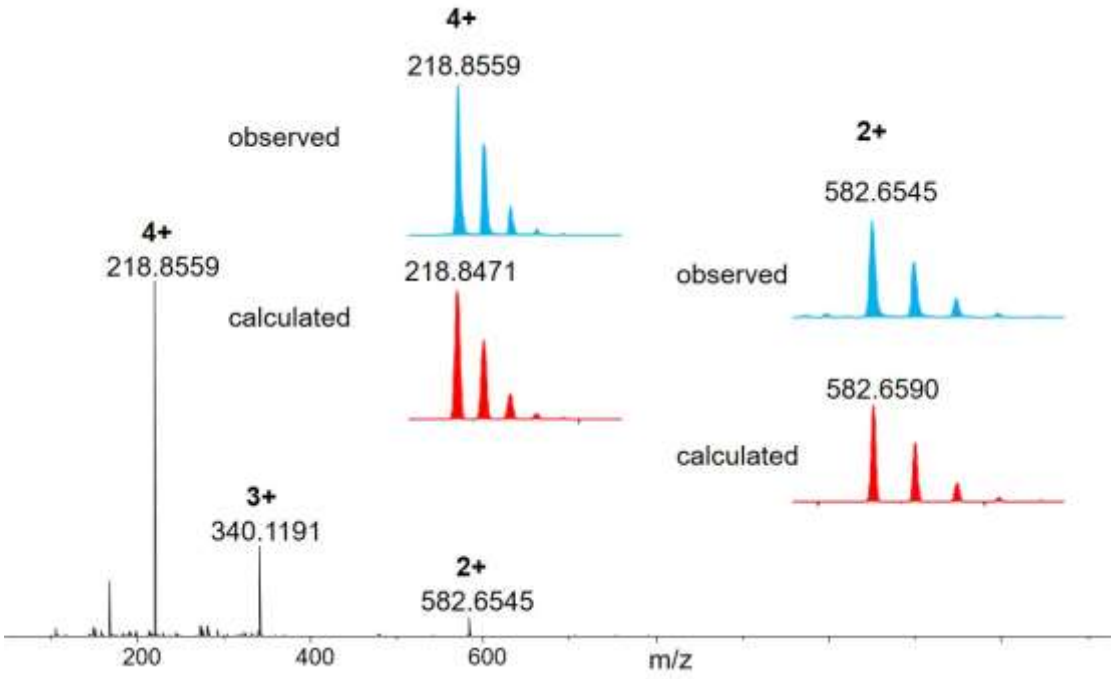


Fig. S3 HR-ESI mass spectrum (positive ions) of H_4-**1a**$(PF_6)_4$.

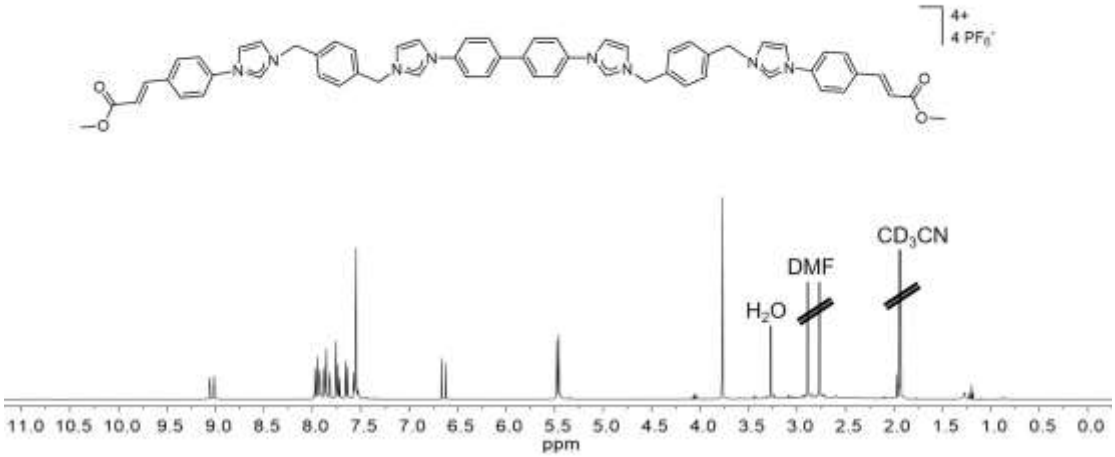


Fig. S4 ^{1}H NMR spectrum of H_4-**1b**$(PF_6)_4$ (400 MHz, CD_3CN).

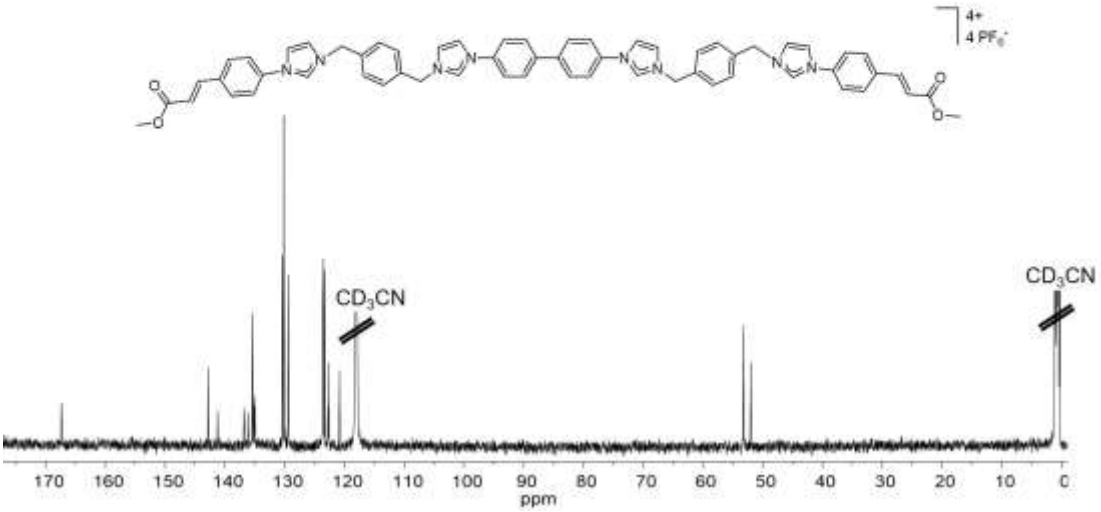


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum of H_4-**1b**$(PF_6)_4$ (150 MHz, CD_3CN).

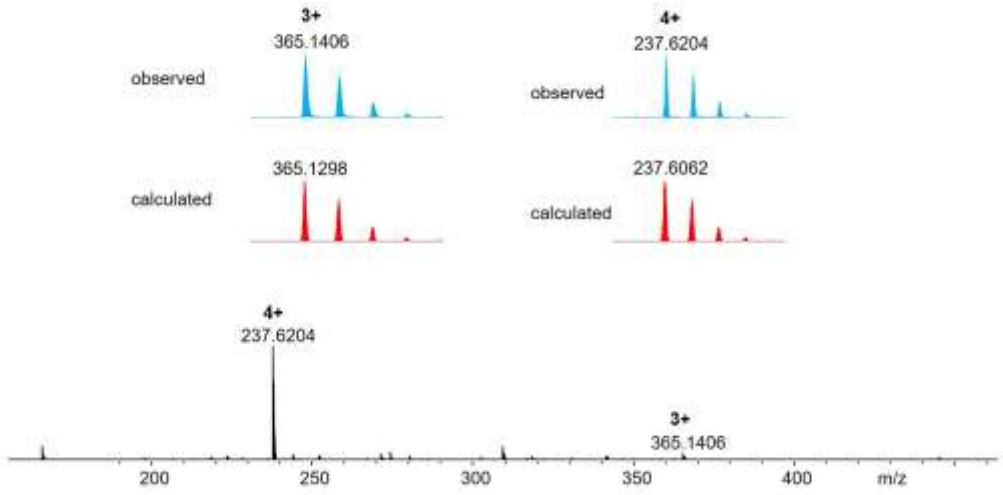


Fig. S6 HR-ESI mass spectrum (positive ions) of H_4-**1b**$(PF_6)_4$.

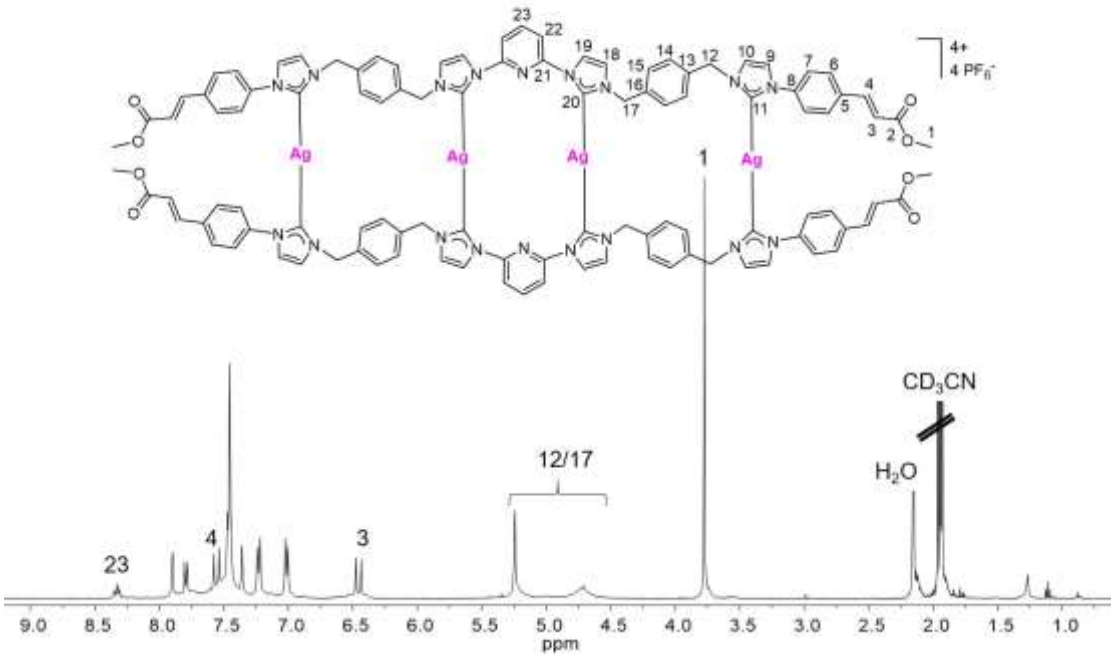


Fig. S7 ^{1}H NMR spectrum of $[Ag_4(\mathbf{1a})_2](PF_6)_4$ (400 MHz, CD_3CN).

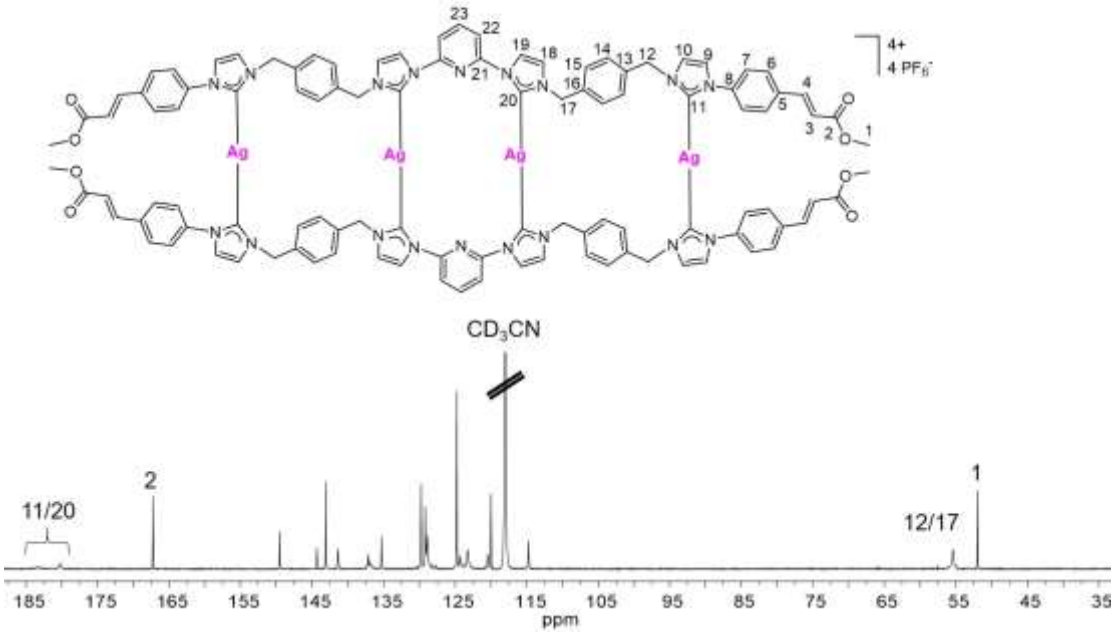


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of $[Ag_4(\mathbf{1a})_2](PF_6)_4$ (150 MHz, CD_3CN).

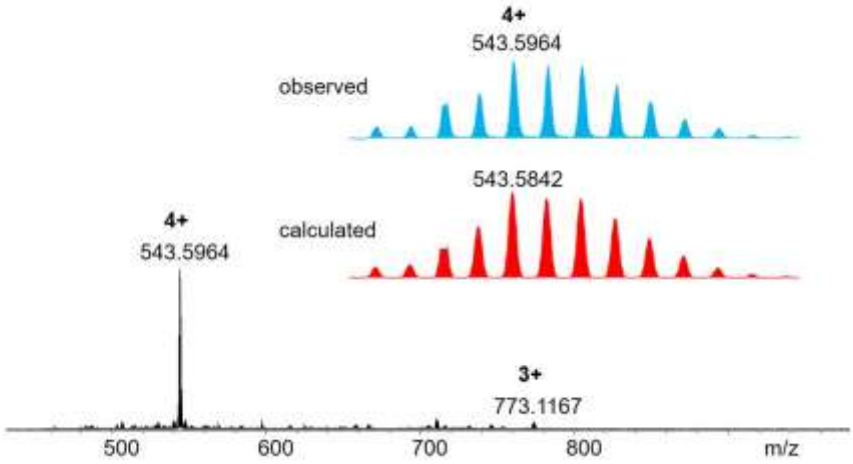


Fig. S9 HR-ESI mass spectrum (positive ions) of $[Ag_4(\mathbf{1a})_2](PF_6)_4$.

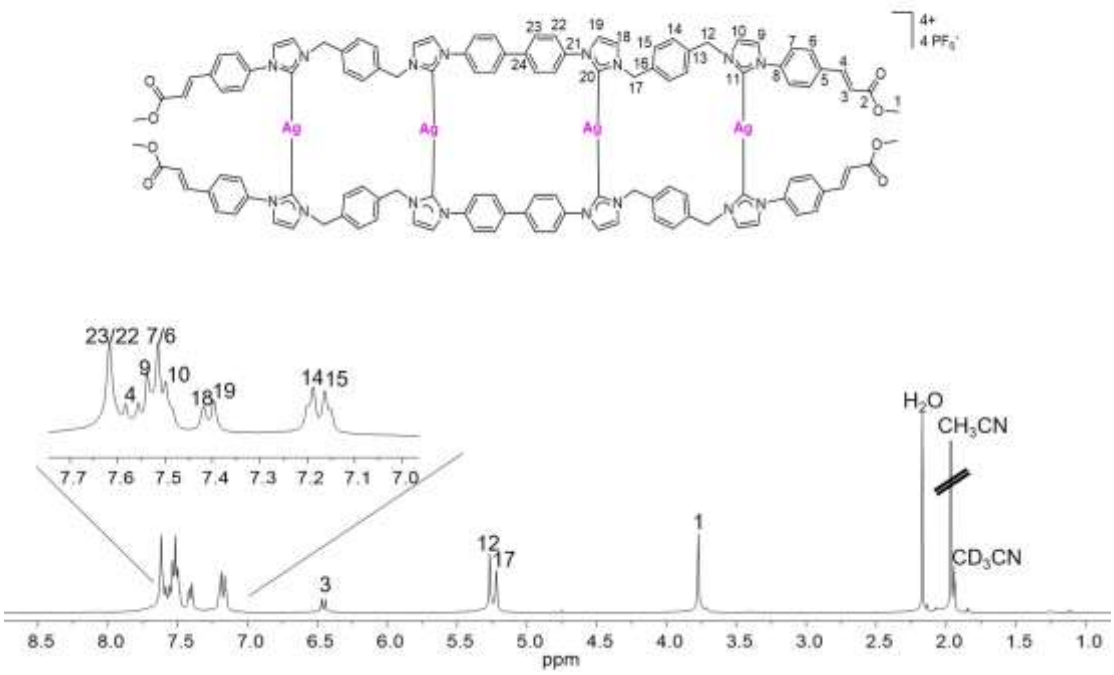


Fig. S10 ^{1}H NMR spectrum of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (600 MHz, CD_3CN).

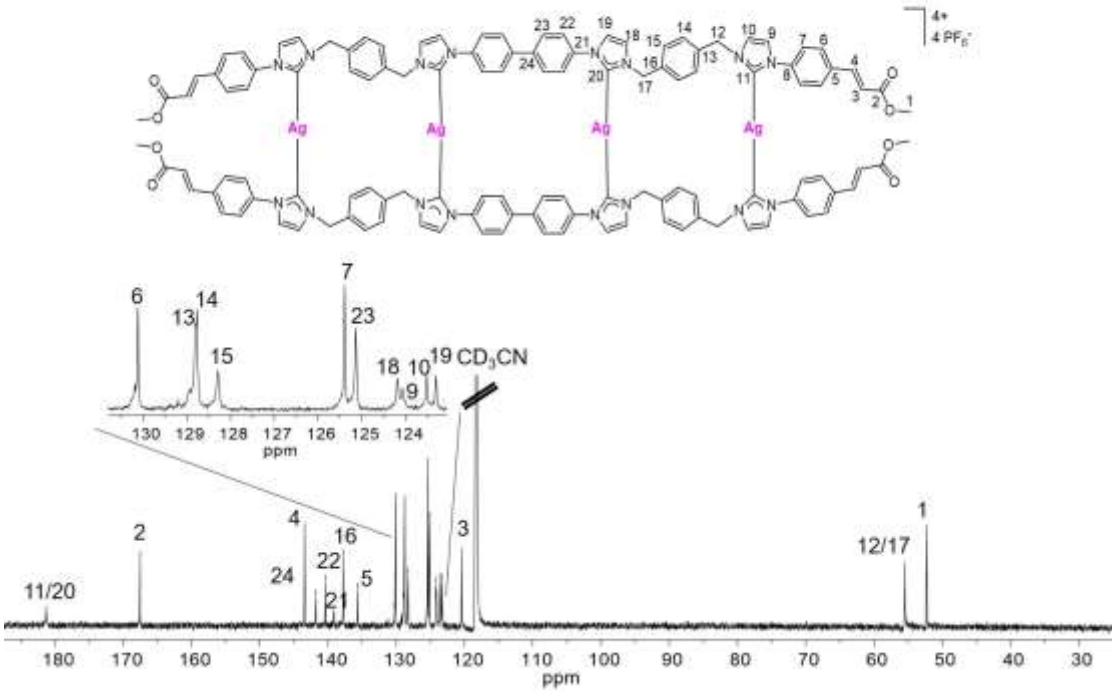


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (150 MHz, CD_3CN).

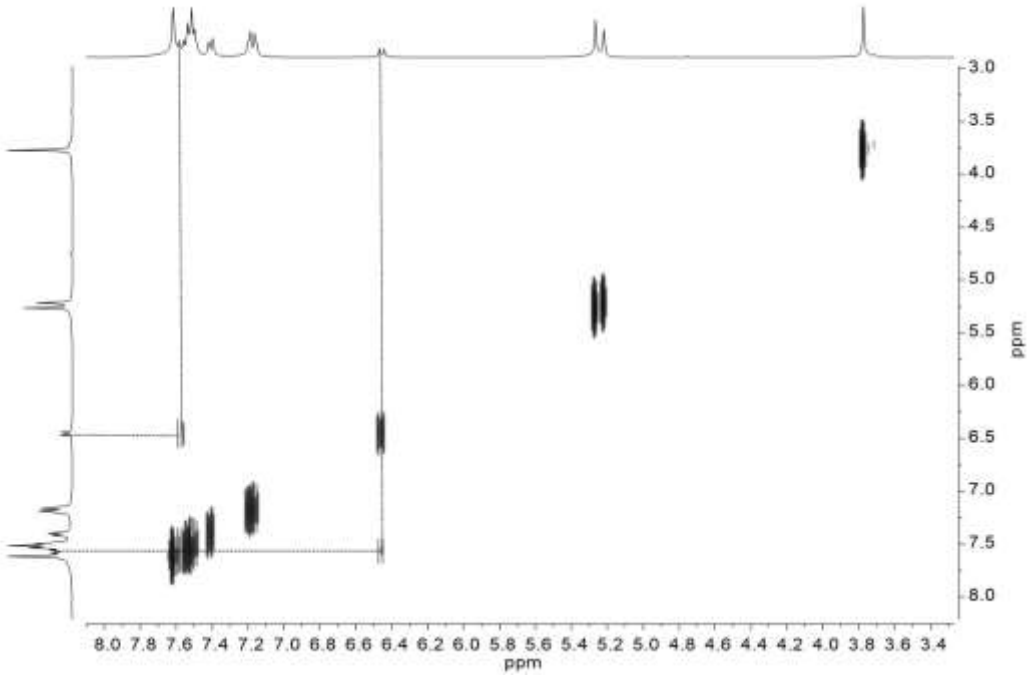


Fig. S12 ^{1}H-^{1}H COSY NMR spectrum of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (600 MHz, CD_3CN).

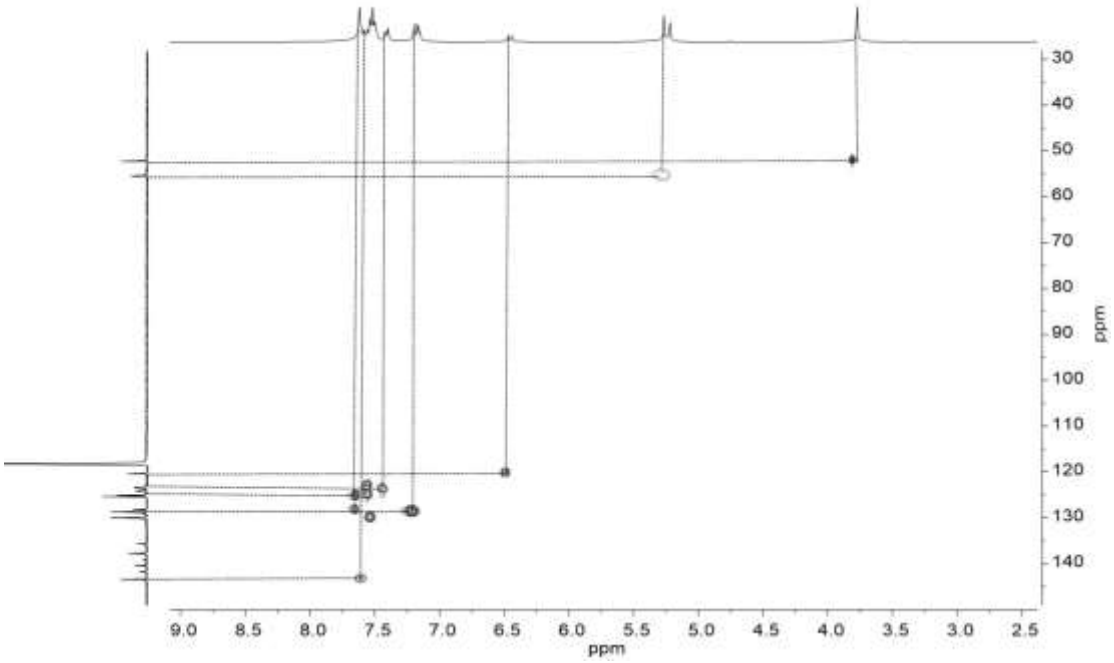


Fig. S13 ^{1}H-^{13}C HSQC NMR spectrum of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (600 MHz, CD_3CN).

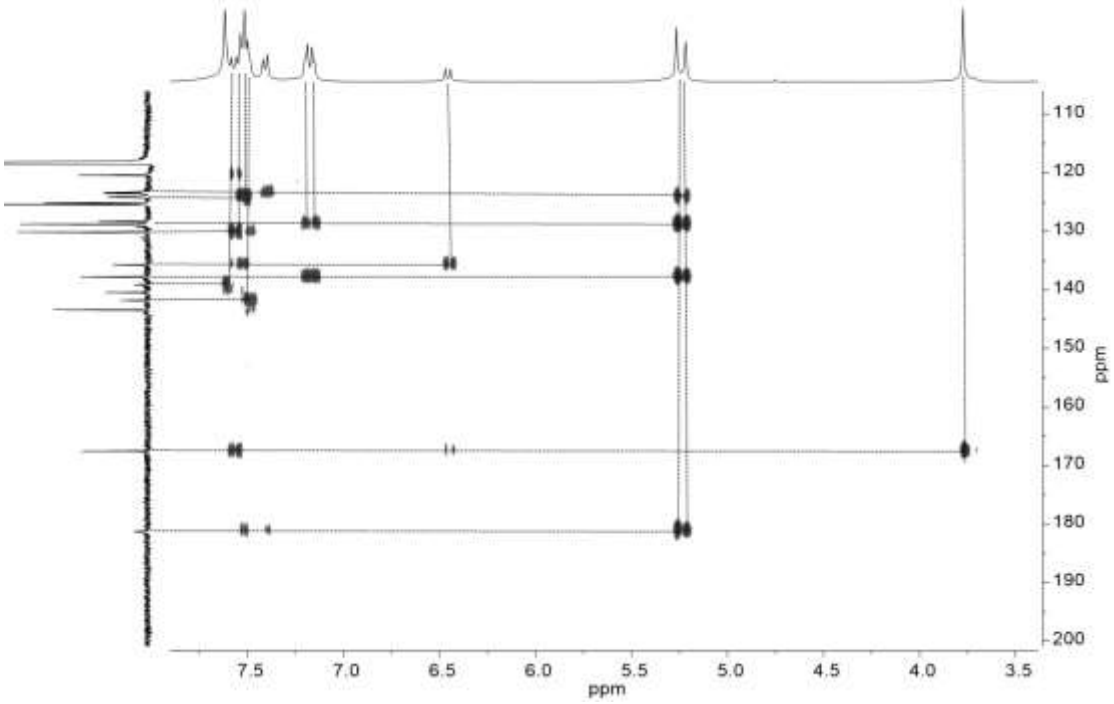


Fig. S14 ^{1}H-^{13}C HMBC NMR spectrum of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (600 MHz, CD_3CN).

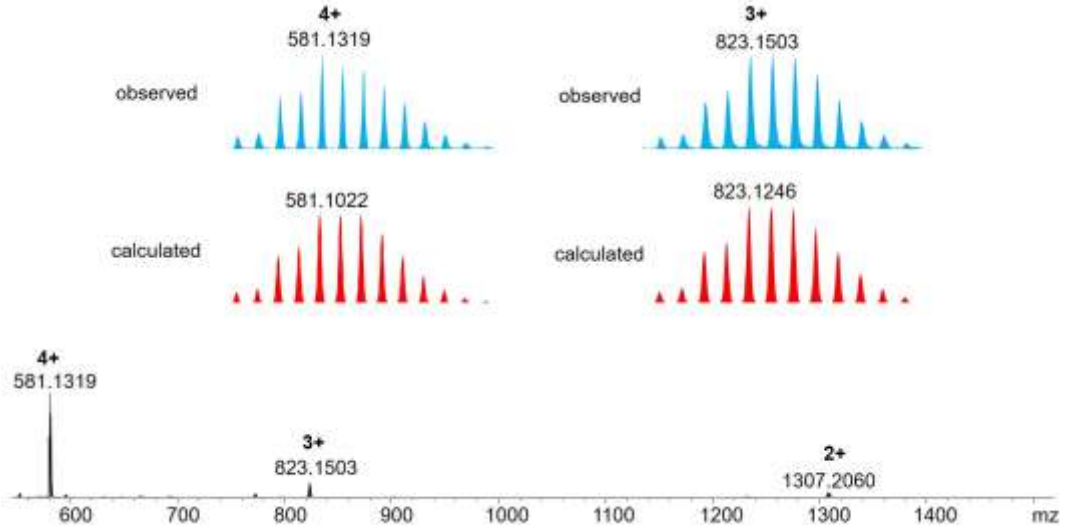


Fig. S15 HR-ESI mass spectrum (positive ions) of $[Ag_4(\mathbf{1b})_2](PF_6)_4$.

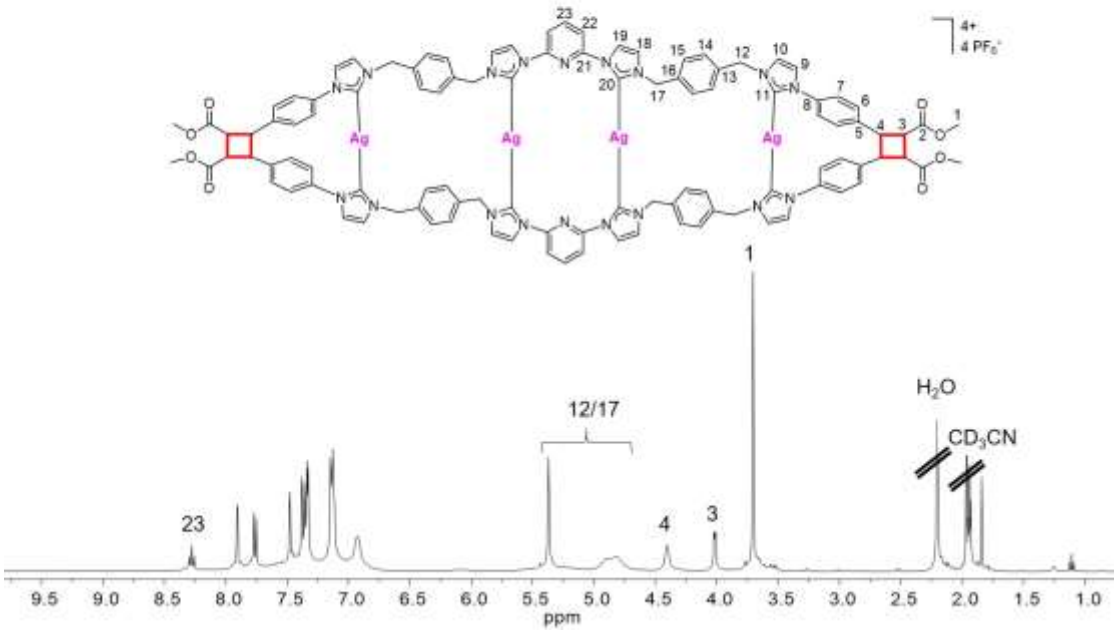


Fig. S16 ^{1}H NMR spectrum of $[Ag_4(\mathbf{2a})](PF_6)_4$ (600 MHz, CD_3CN).

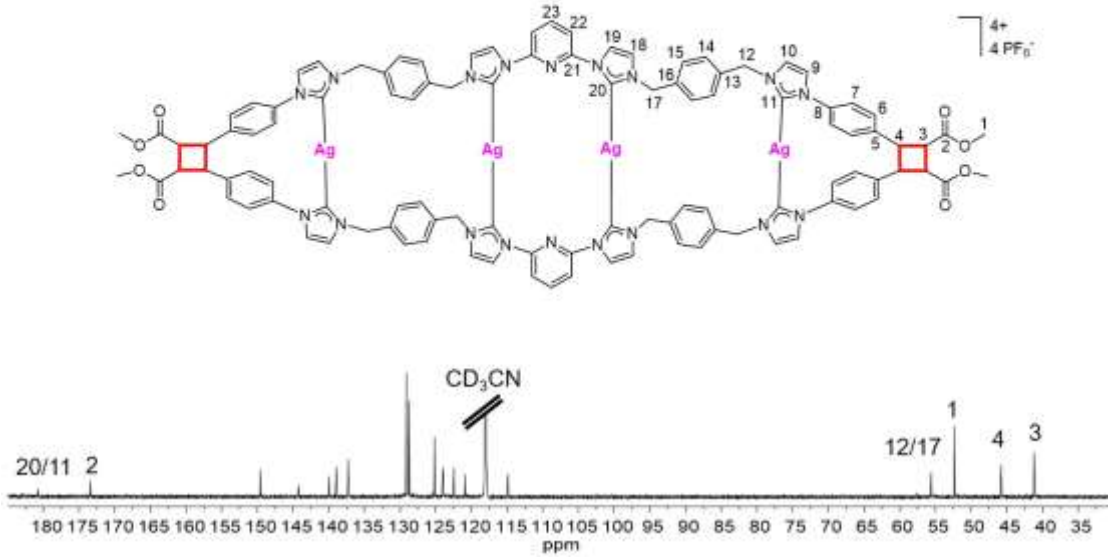


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of $[Ag_4(\mathbf{2a})](PF_6)_4$ (150 MHz, CD_3CN).

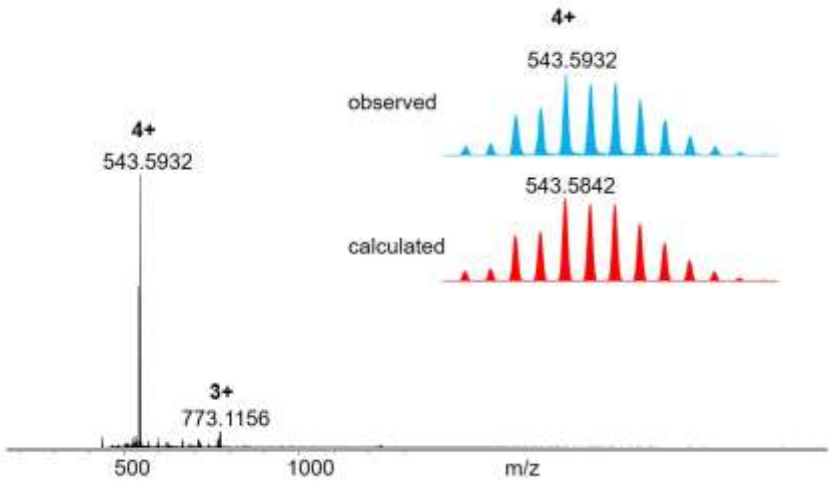


Fig. S18 HR-ESI mass spectrum (positive ions) of $[Ag_4(\mathbf{2a})](PF_6)_4$.

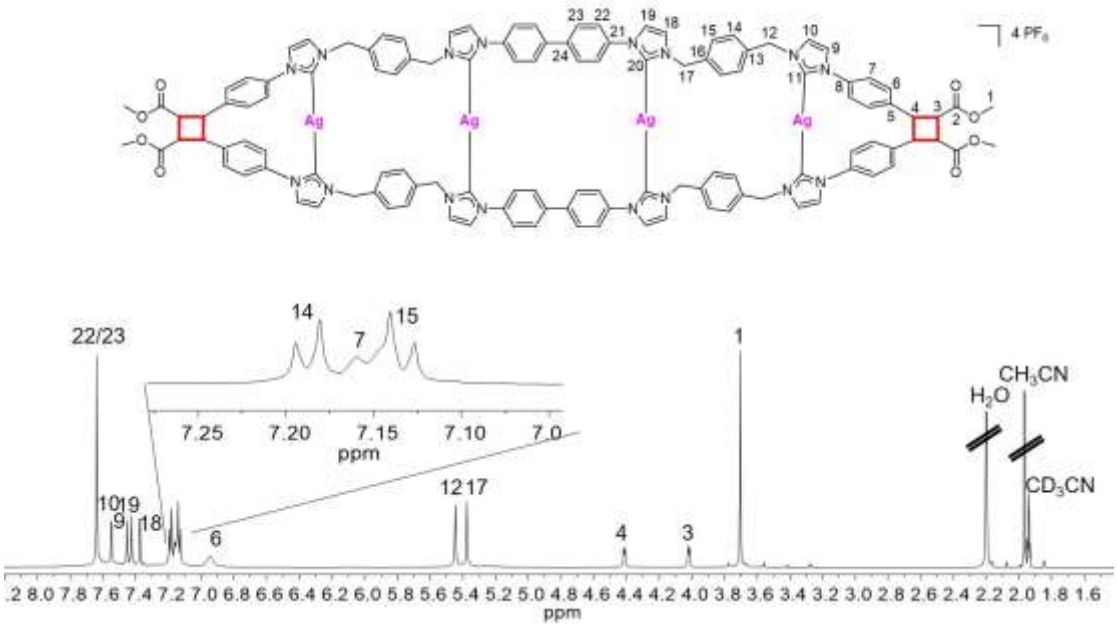


Fig. S19 ^{1}H NMR spectrum of [Ag$_4$(**2b**)](PF$_6$)$_4$ (600 MHz, CD$_3$CN).

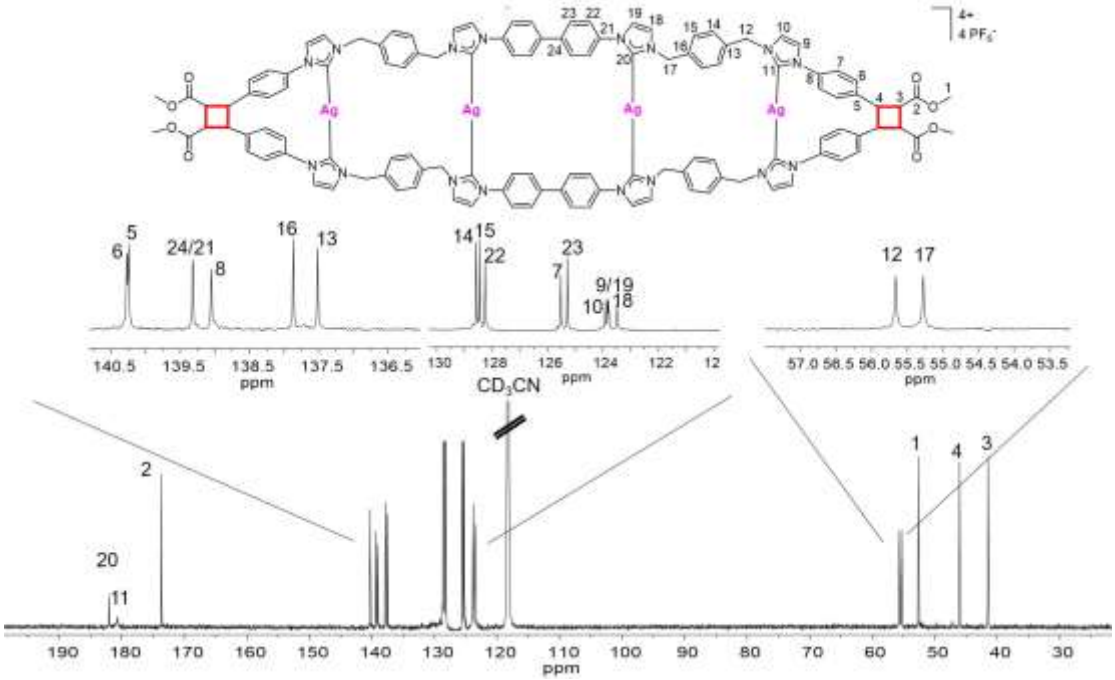


Fig. S20 ^{13}C{^{1}H} NMR spectrum of [Ag$_4$(**2b**)](PF$_6$)$_4$ (150 MHz, CD$_3$CN).

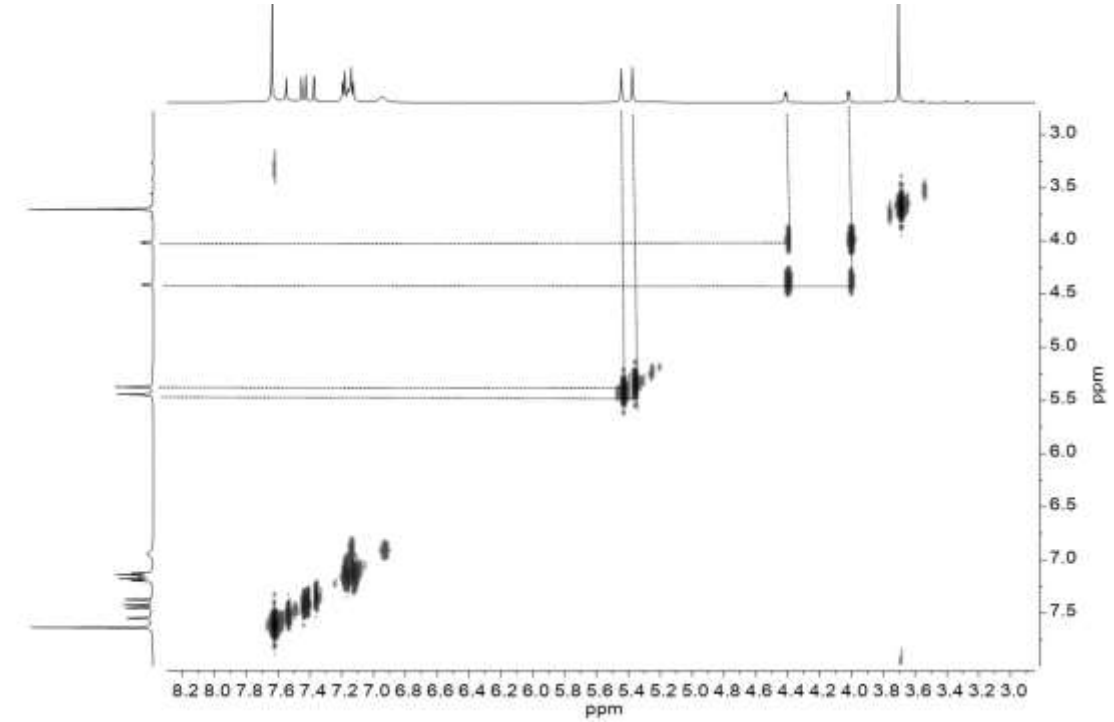


Fig. S21 ^{1}H-^{1}H COSY NMR spectrum of $[Ag_4(\mathbf{2b})](PF_6)_4$ (600 MHz, CD_3CN).

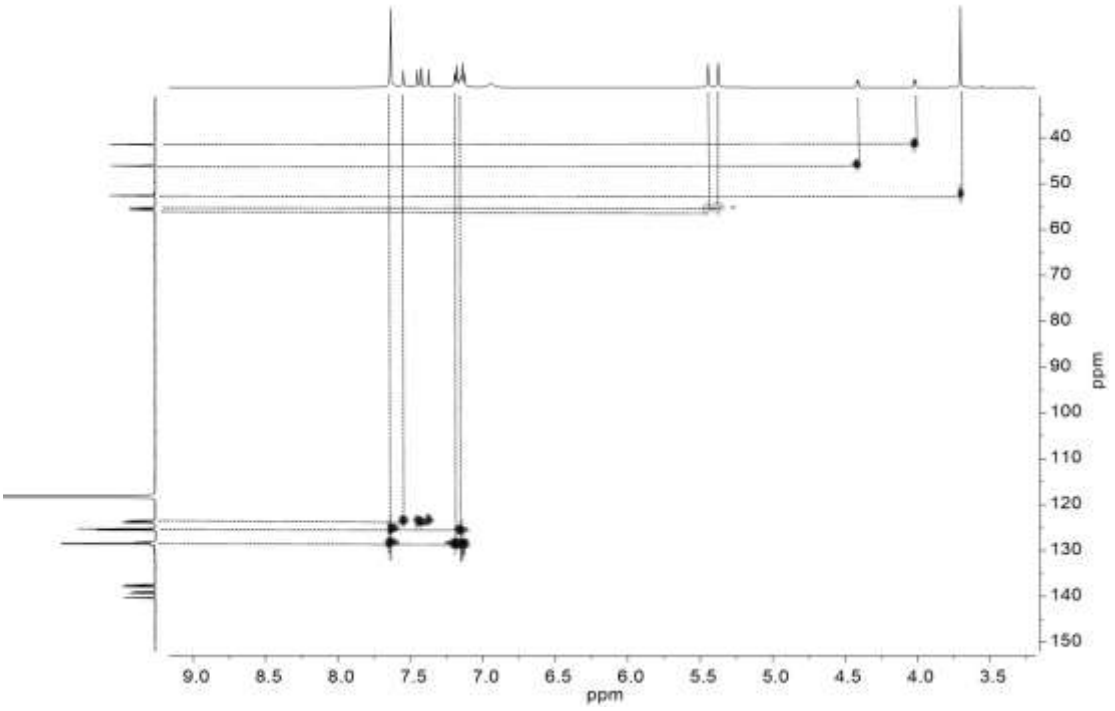


Fig. S22 ^{1}H-^{13}C HSQC NMR spectrum of $[Ag_4(\mathbf{2b})](PF_6)_4$ (600 MHz, CD_3CN).

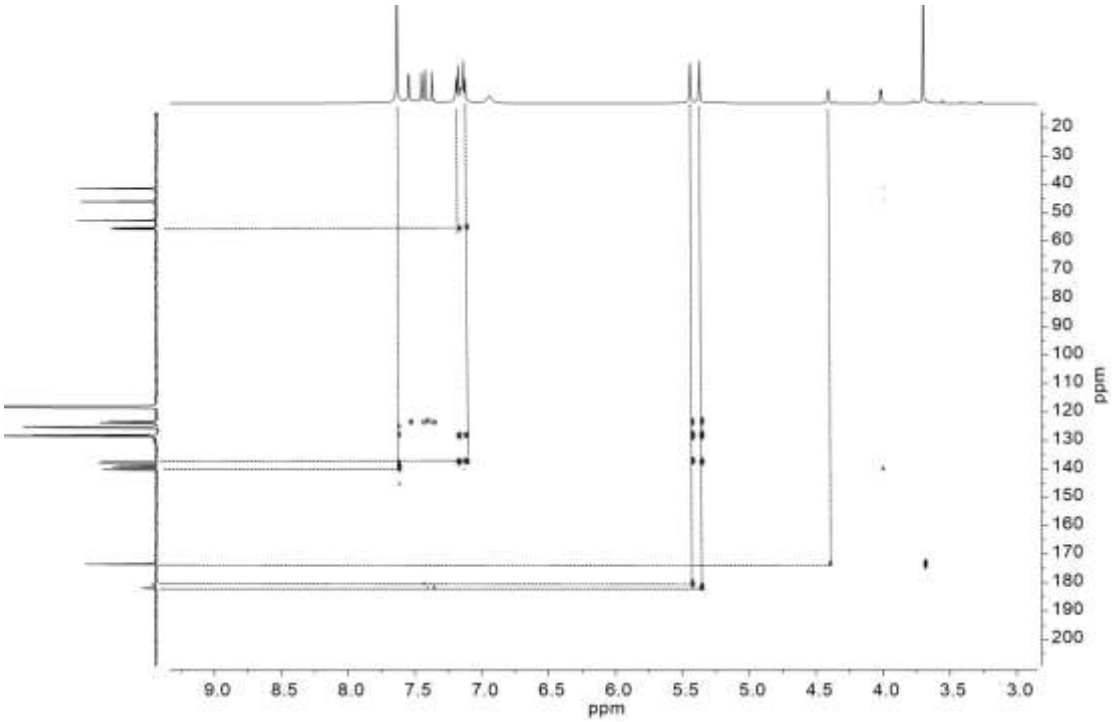


Fig. S23 ^{1}H-^{13}C HMBC NMR spectrum of $[Ag_4(\mathbf{2b})](PF_6)_4$ (600 MHz, CD_3CN).

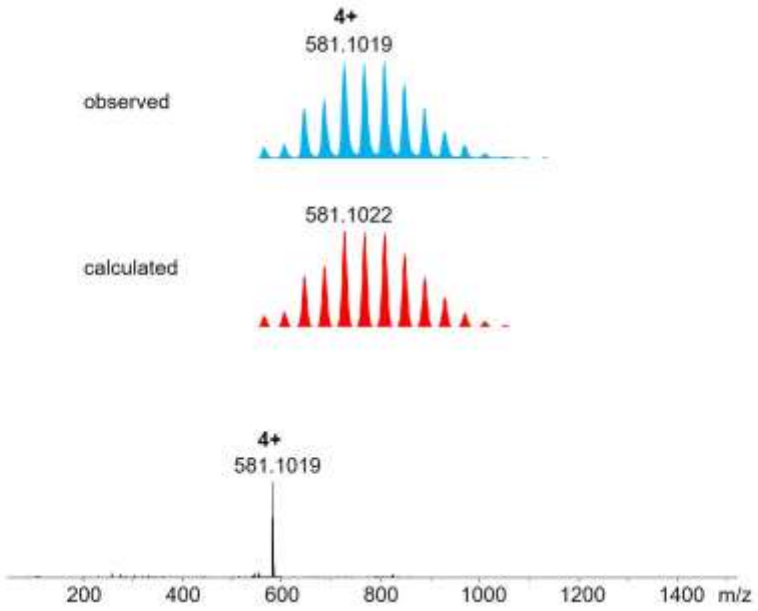


Fig. S24 HR-ESI mass spectrum (positive ions) of $[Ag_4(\mathbf{2b})](PF_6)_4$.

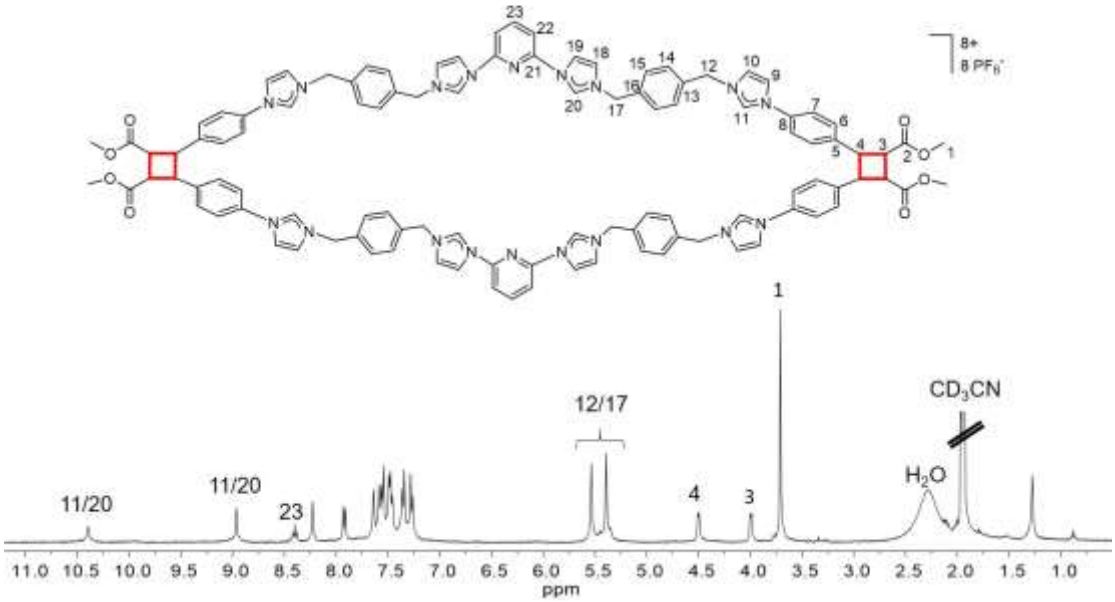


Fig. S25 ^{1}H NMR spectrum of H_8-**2a**$(PF_6)_8$ (400 MHz, CD_3CN).

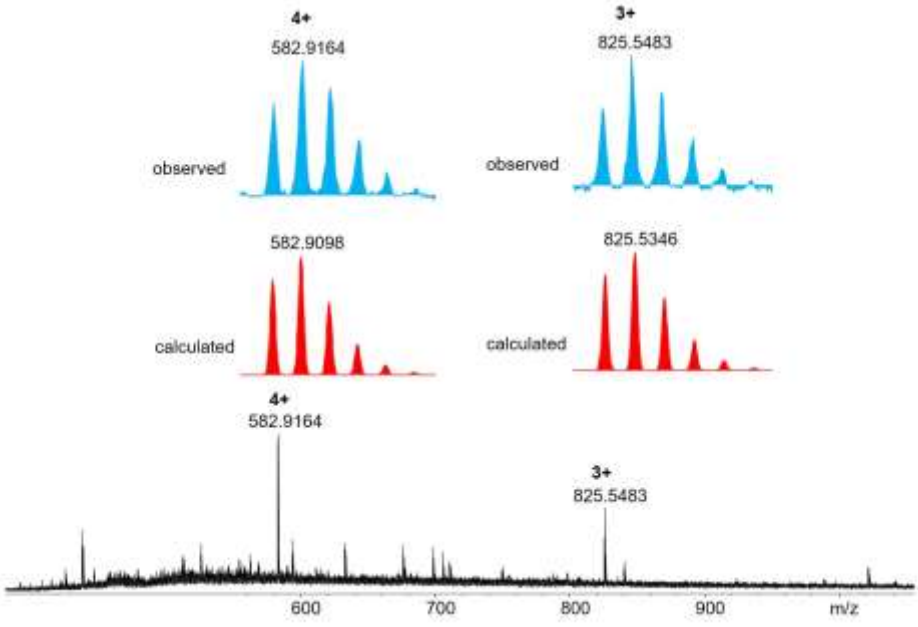


Fig. S26 HR-ESI mass spectrum (positive ions) of H_8-**2a**$(PF_6)_8$.

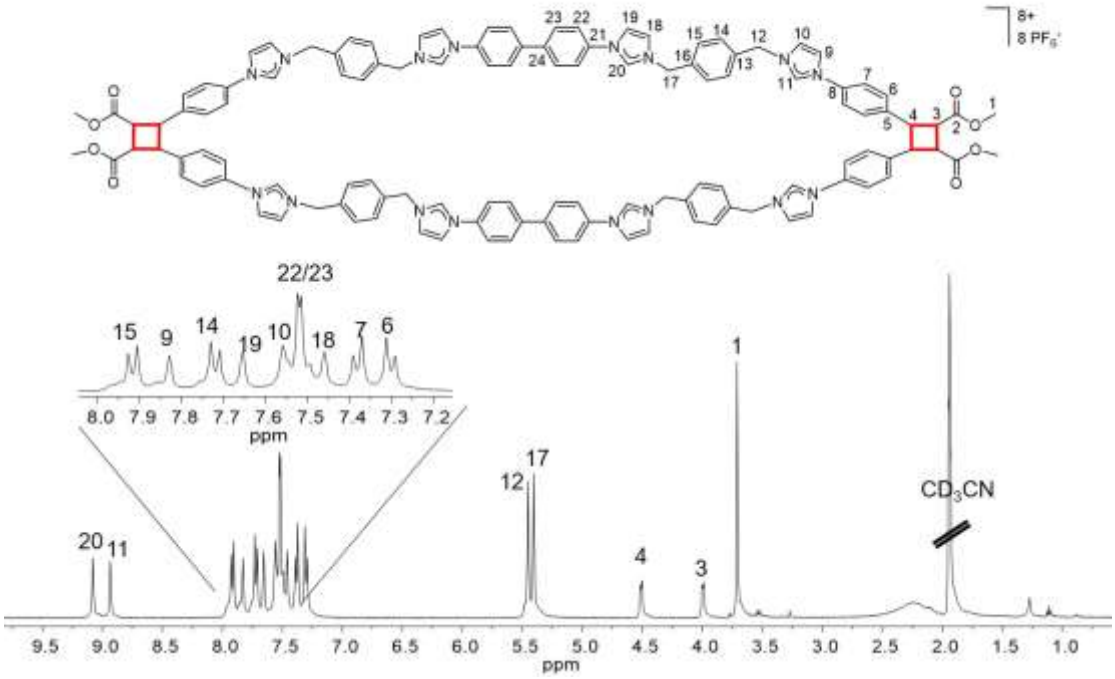


Fig. S27 ^{1}H NMR spectrum of H_8-**2b**$(PF_6)_8$ (400 MHz, CD_3CN).

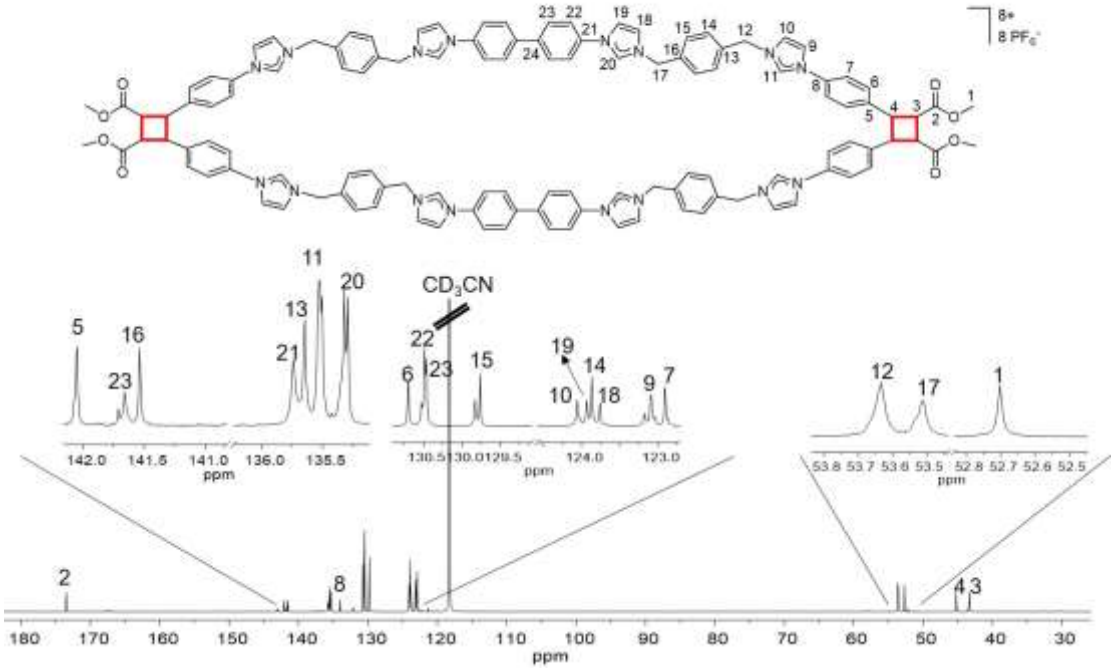


Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of H_8-**2b**$(PF_6)_8$ (150 MHz, CD_3CN).

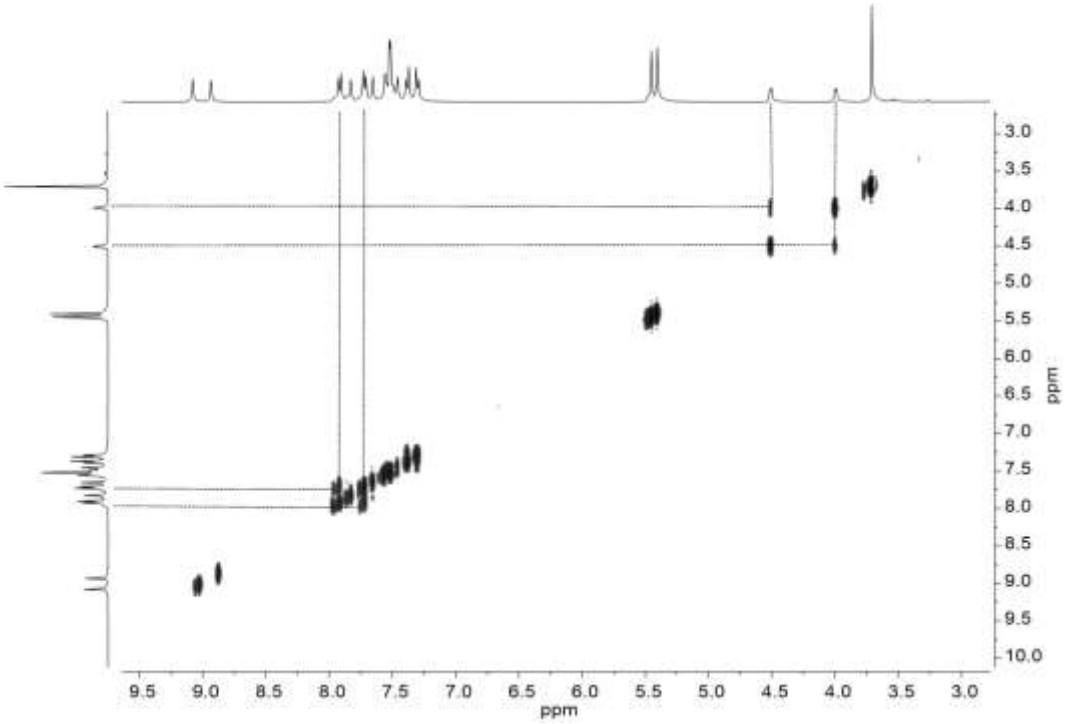


Fig. S29 ^{1}H-^{1}H COSY NMR spectrum of H_8-**2b**$(PF_6)_8$ (600 MHz, CD_3CN).

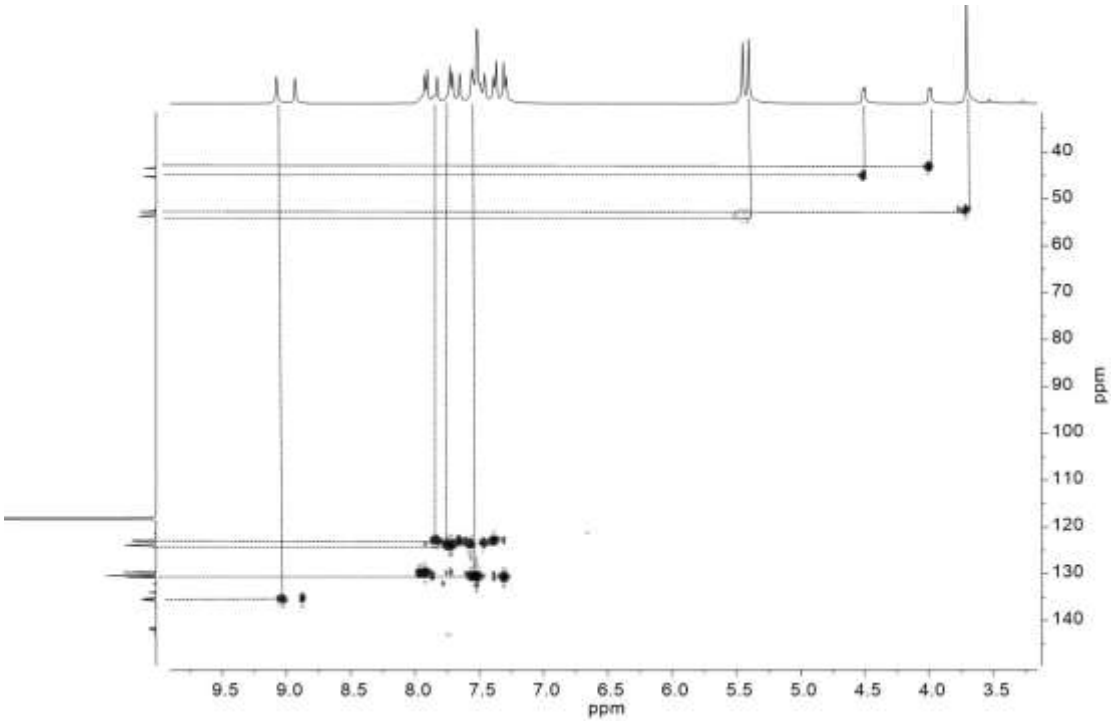


Fig. S30 ^{1}H-^{13}C HSQC NMR spectrum of H_8-**2b**$(PF_6)_8$ (600 MHz, CD_3CN).

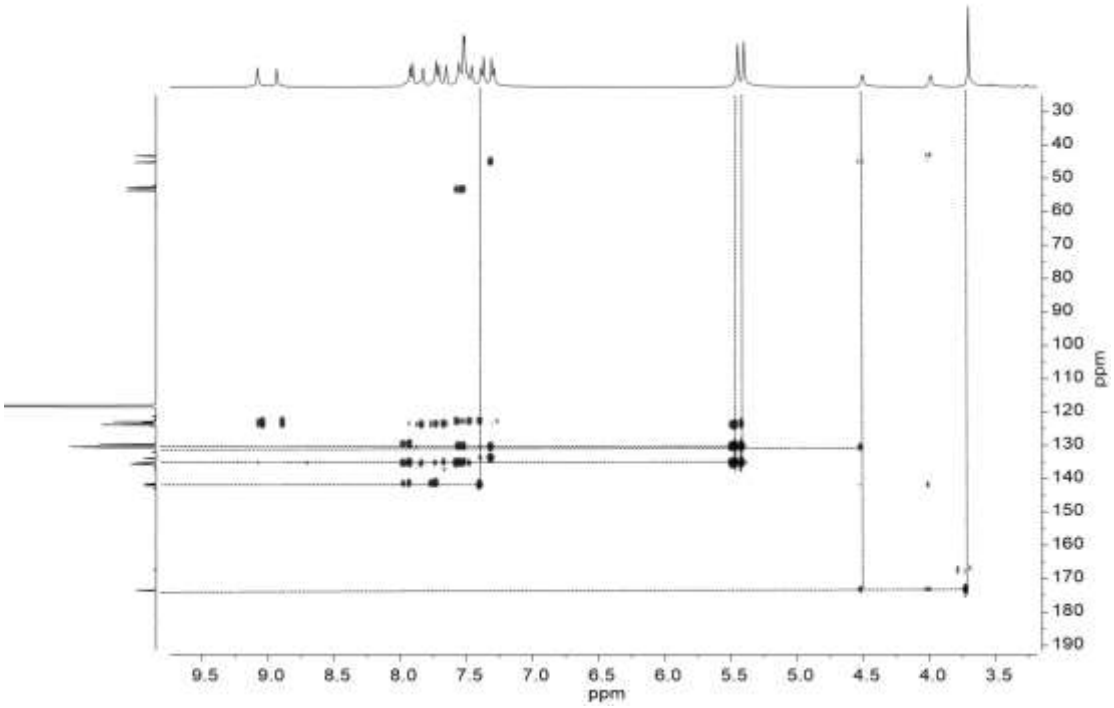


Fig. S31 ^{1}H-^{13}C HMBC NMR spectrum of H_8-**2b**$(PF_6)_8$ (600 MHz, CD_3CN).

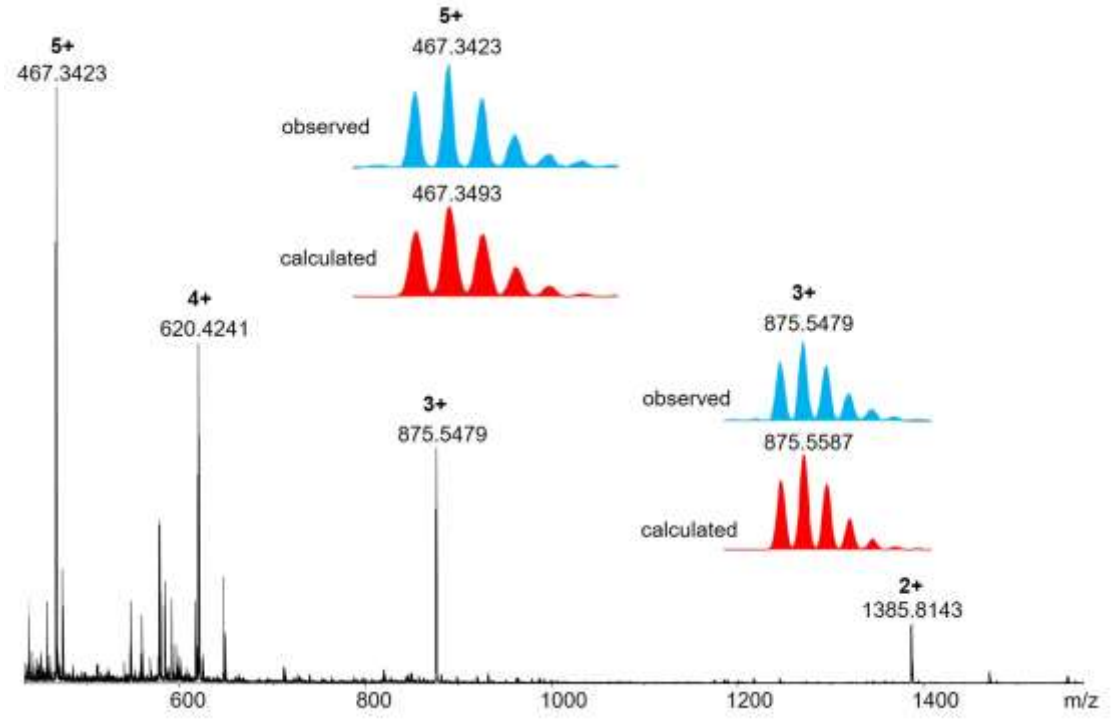


Fig. S32 HR-ESI mass spectrum (positive ions) of H_8-**2b**$(PF_6)_8$.

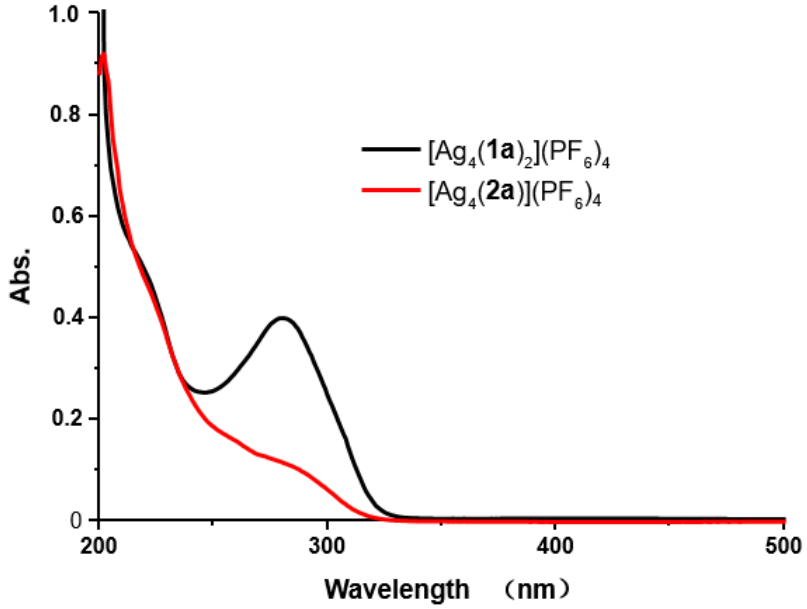


Fig. S33 UV-Vis spectra of $[Ag_4(\mathbf{1a})_2](PF_6)_4$ (5 μM) in CH_3CN before (dark line) and after (red line) photoreaction.

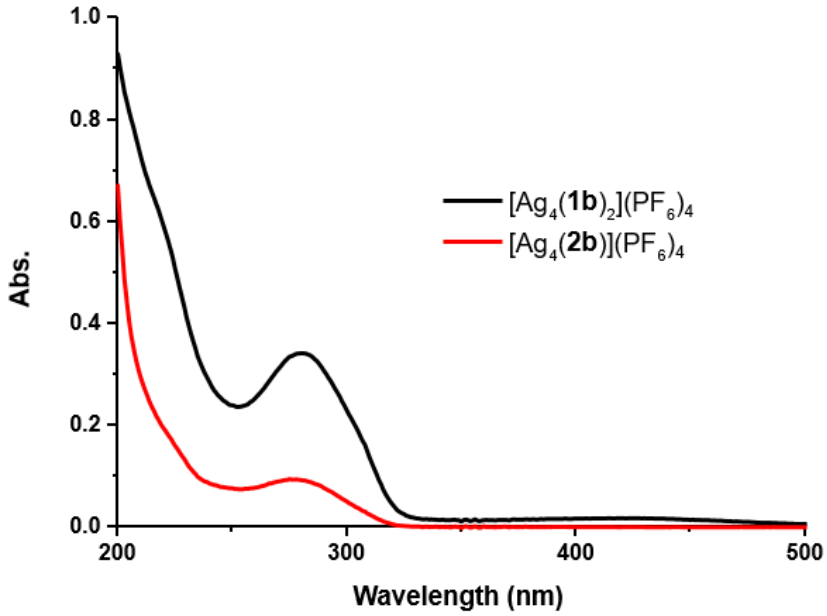


Fig. S34 UV-Vis spectra of $[Ag_4(\mathbf{1b})_2](PF_6)_4$ (5 μM) in CH_3CN before (dark line) and after (red line) photoreaction.

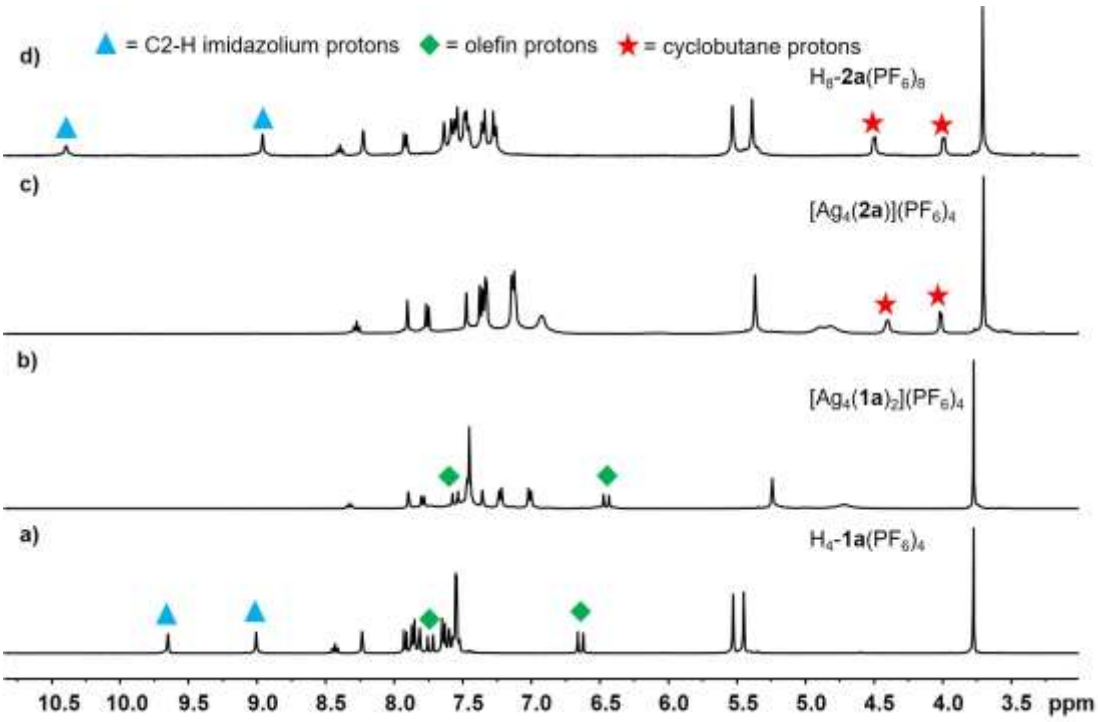


Fig. S35 Partial ^{1}H NMR spectra (400 MHz, 298 K) in CD_3CN of (a) tetrakisimidazolium salt H_4-**1a**$(PF_6)_4$, (b) complex $[Ag_4(\mathbf{1a})_2](PF_6)_4$ before irradiation, (c) complex $[Ag_4(\mathbf{2a})](PF_6)_4$ obtained after irradiation, (d) octakisimidazolium salt H_8-**2a**$(PF_6)_8$.

Fig. S36 Partial ^{1}H NMR spectra (400 MHz, 298 K) in CD_3CN of tetrakisimidazolium salt H_4-**1a**$(PF_6)_4$ (a) before and (b) after irradiation.

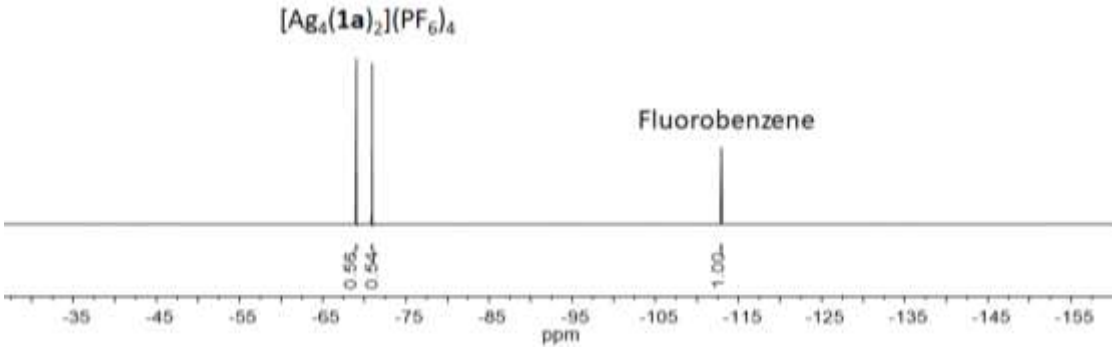


Fig. S37 Partial ^{19}F NMR spectra (400 MHz, 298 K) in DMSO-*d*$_6$ of $[Ag_4(\mathbf{1a})_2](PF_6)_4$, with 24 equiv. fluorobenzene as internal standard.

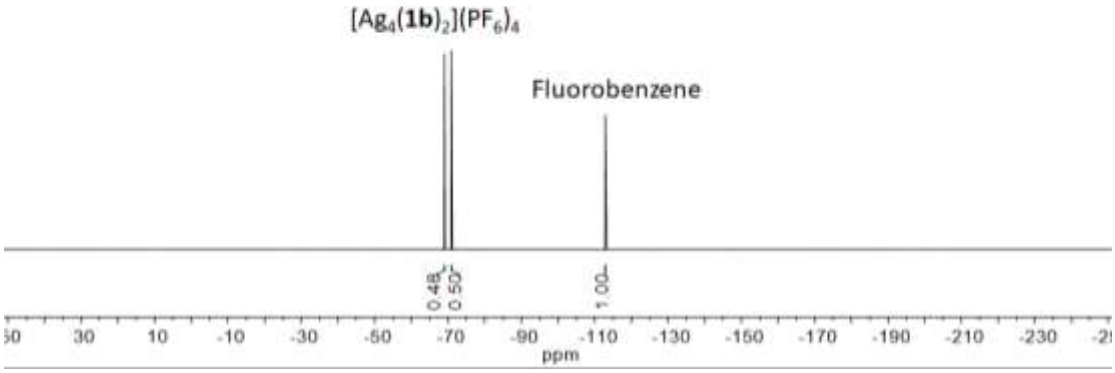


Fig. S38 Partial ^{19}F NMR spectra (400 MHz, 298 K) in DMSO-*d*$_6$ of $[Ag_4(\mathbf{1b})_2](PF_6)_4$, with 24 equiv. fluorobenzene as internal standard.

4. UV-Vis, fluorescence and ^{1}H NMR titration studies on the recognition of aromatic sulfonates

Stock solutions of **G8**, **G9** (10 μM) and H$_8$-**2a**(PF$_6$)$_8$ (60 mM) were prepared in DMSO to each measurement, respectively. A solution of **G8** or **G9** (2.4 mL) was added to the quartz cell and then the spectrum was recorded at room temperature when excited at 260 nm. An aliquot of a H$_8$-**2a**(PF$_6$)$_8$ solution (4 μL, 0.1 equiv.) was added to the solution of **G8** or **G9**, and the spectra were recorded.

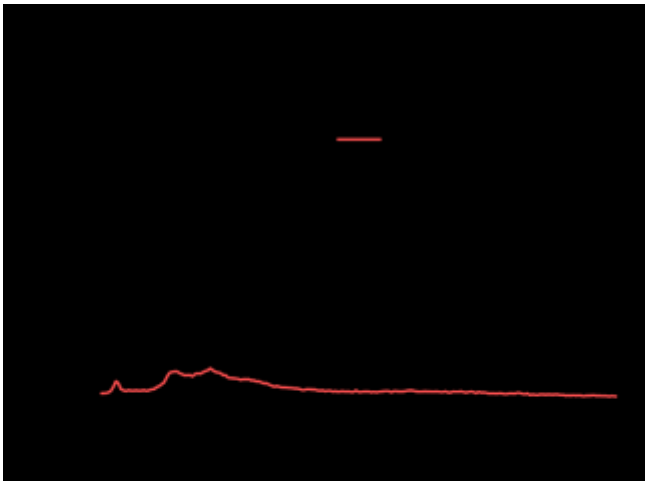


Fig. S39 Fluorescence spectra of sodium naphthalene-2,6-disulfonate **G8** (λ_{ex} = 260 nm, c = 15 μM) with and without addition of 1.0 equiv. H$_8$-**2a**(PF$_6$)$_8$ in DMSO.

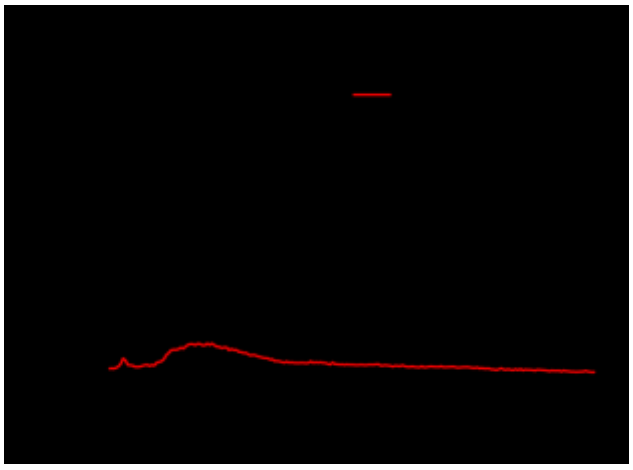


Fig. S40 Fluorescence spectra of sodium naphthalene-1,6-disulfonate **G9** (λ_{ex} = 260 nm, c = 15 μM) with and without addition of 1.0 equiv. H$_8$-**2a**(PF$_6$)$_8$ in DMSO.

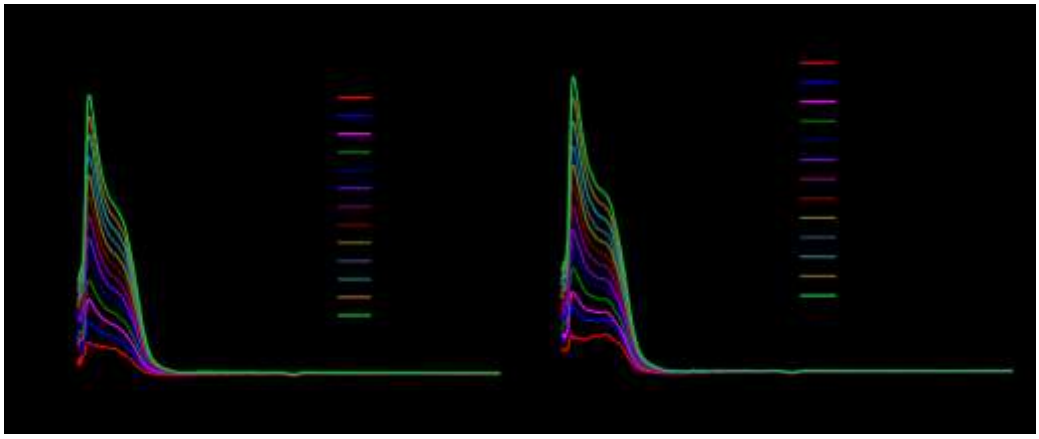


Fig. S41 UV-Vis titration of (a) **G8** and (b) **G9** with gradual addition of H_8-**2a**$(PF_6)_8$ in DMSO.

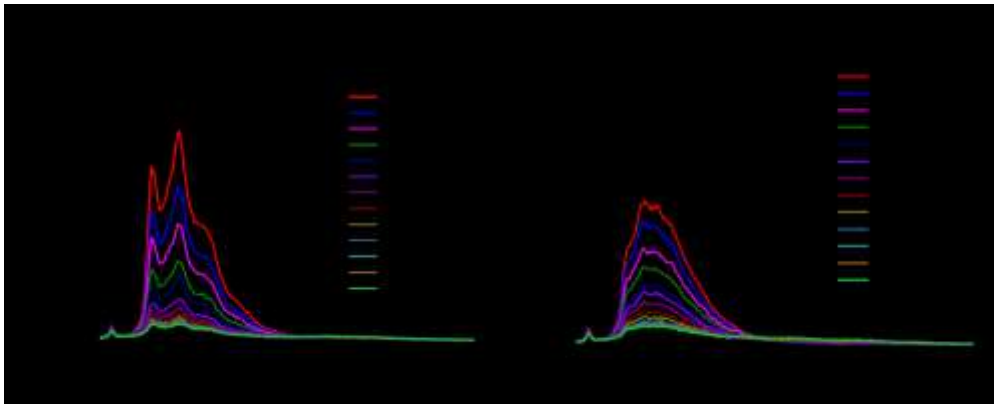


Fig. S42 Fluorescence titration of (a) **G8** (λ_{ex} = 260 nm, c = 10 μM) and (b) **G9** (λ_{ex} = 260 nm, c = 10 μM) with gradual addition of H_8-**2a**$(PF_6)_8$ in DMSO.

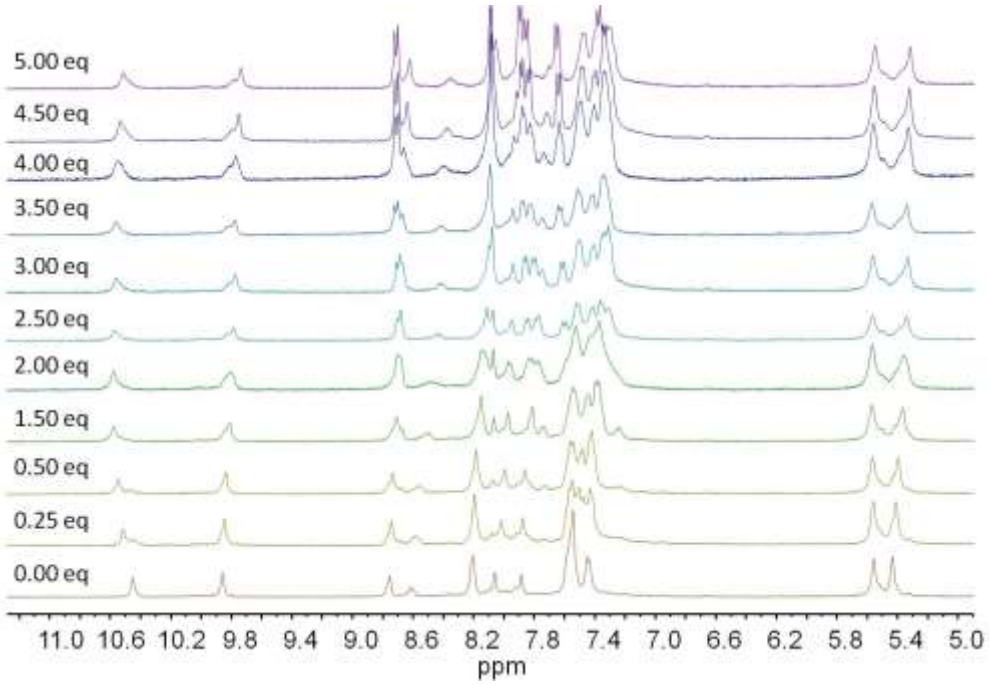


Fig. S43 Partial ^{1}H NMR spectra of H_8-**2a**$(PF_6)_8$ (3.4 mM) upon titration **G9** in DMSO-d_6 at room temperatre.

5. References

(1) L. Zhang, R. Das, C.-T. Li, Y.-Y. Wang, F. E. Hahn, K. Hua, L.-Y. Sun and Y.-F. Han, C3-Symmetric Assemblies from Trigonal Polycarbene Ligands and M^{I} Ions for the Synthesis of Three-Dimensional Polyimidazolium Cations, *Angew. Chem. Int. Ed.,* 2019, **58**, 13360–13364.