Experimental details

1,3,5-trimethylimidazole-2,4,6-triethylbenzene: To a mixture of 1,3,5-tribromomethyl-2,4,6-triethylbenzene (4.0 g, 9.1 mmol) and imidazole (10.0 g, 146.9 mmol) was added MeOH (100 mL). The mixture was heated at reflux for 48 hours. The solvent was removed *in vacuo* resulting in yellow oil. Water (20 mL) was added to give a white precipitate, which was filtered and washed with water.

Yield = 56 %. ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.49 (s, 3H, N(CH)N), 6.94 (s, 3H, $N(CH)_2N$), 6.89 (s, 3H, $N(CH)_2N$), 5.25 (s, 6H, CH_2), 2.64 (q, $^{3}J_{H-H}$ = 7.4 Hz, 6H, CH_2), 0.80 (t, $^{3}J_{H-H}$ = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, d_6-DMSO): δ 144.9 (N(CH)N), 136.6 (Ar), 128.4 ($N(CH)_2N$), 118.8 ($N(CH)_2N$), 44.0 (CH_2), 22.7 (CH_2), 15.1 (CH_3). Elemental Analysis: Calculated for $C_{24}H_{30}N_6 \cdot 2H_2O$ C 65.73, H 7.81, N 19.16. Found C 66.08, H 7.79, N 18.73 %.

Cyclophane-3Br: To a mixture of 1,3,5-tribromomethyl-2,4,6-triethylbenzene (0.150 g, 0.34 mmol) and 1,3,5-trimethylimidazole-2,4,6-triethylbenzene (0.137 g, 0.34 mmol) was added acetone (30 mL). The mixture was stirred at room temperature for 18 hours and the solvent was removed *in vacuo* resulting in white oil. THF (30 mL) was added to give a white precipitate, which was filtered and washed with THF.

Yield = 79 %. ^{1}H NMR (400 MHz, CD_3OD): δ 8.13 (s, 6H, $N(CH)_2N$), 5.80 (s, 3H, N(CH)N), 5.57 (s, 12H, CH_2), 2.47 (q, $^{3}J_{H-H}$ = 7.2 Hz, 12H, CH_2), 1.16 (t, $^{3}J_{H-H}$ = 7.2 Hz, 18H, CH_3). MS (ES+) m/z 684.0 ($[M - 2Br]^+$, 5%).

Cyclophane-3PF_6: The white solid was dissolved in MeOH (10 mL) and NH_4PF_6 (10 equivalents) was added. This was stirred at room temperature for 1 hour and the resulting white precipitate was filtered and washed with MeOH.

Yield = 93 %. ^{1}H NMR (400 MHz, CD_3CN): δ 7.83 (s, 6H, $N(CH)_2N$), 5.61 (s, 3H, N(CH)N), 5.37 (s, 12H, CH_2), 2.29 (q, $^{3}J_{H-H}$ = 7.4 Hz, 12H, CH_2), 1.10 (t, $^{3}J_{H-H}$ = 7.4 Hz, 18H, CH_3). $^{13}C\{^{1}H\}$NMR (100.6 MHz, CD_3CN): δ 149.5 (Ar), 130.3 (CH), 126.5 (CH), 48.4 (CH_2), 23.8 (CH_2), 15.9 (CH_3). MS (ES+) m/z 893.1 ($[M - PF6]^+$, 100%), 747.4 ($[M - 2PF_6 - H]^+$, 13%). Elemental Analysis: Calculated for $C_{39}H_{51}F_{18}N_6P_3$ C 45.09, H 4.95, N 8.09. Found C 44.59, H 5.00, N 7.77.

Cyclophane-[$FeCl_4$]$_2$Br: To a hot water solution (2mL) containing pyridine (0.5 mL) of 1,3,5-trimethylimidazole-2,4,6-triethylbenzene (0.01g, 0.025 mmol) was added a hot water solution (2 mL) of $FeCl_3 \cdot 6H_2O$ (0.006g, 0.022mmol). The solution was allowed to cool and the solvent slowly evaporated, resulting in colourless crystals.

Ag-Cyclophane: To a mixture of cyclophane-3PF_6 (0.165 g, 0.159 mmol) and Ag_2O (0.074 g, 0.319 mmol) was added DMSO (20 mL). The mixture was heated at 75 ºC for 72 hours under nitrogen. The mixture was filtered through celite and water (20 mL) was added to the filtrate. The resulting precipitate was filtered and washed with water.

Yield = 31 %. ^{1}H NMR (400 MHz, CD_3CN): δ 7.68 (s, 2H, $N(CH)_2N$), 7.46 (s, 4H, $N(CH)_2N$), 6.55 (s, 1H, N(CH)N), 5.35 (d, $^{2}J_{H-H}$ = 14.9 Hz, 4H, CH_2), 5.25 (d, $^{2}J_{H-H}$ = 14.9 Hz, 4H, CH_2), 5.19 (s, 4H, CH_2), 2.90 (q, $^{3}J_{H-H}$ = 7.6 Hz, 4H, CH_2), 2.00 (m, 8H,

CH_2), 1.15 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, CH_3), 0.95 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_3CN): δ 178.0 ($^1J_{C-}{}^{107}_{Ag}$ = 186.5 Hz, $^1J_{C-}{}^{109}_{Ag}$ = 215.5 Hz), 148.4 (q), 146.7 (q), 132.7 (q), 131.3 (CH), 128.6 (q), 125.5 (CH), 124.0 (CH), 49.0 (CH_2), 48.3 (CH_2), 25.8 (CH_2), 23.1 (CH_2), 16.6 (CH_3), 15.3 (CH_3). MS (ES+) m/z 853.0 ($[M - PF_6]^+$ 100%). Elemental Analysis: Calculated for $C_{39}H_{49}AgF_{12}N_6P_2$ C 46.86, H 4.94, N 8.41. Found C 46.20, H 4.93, N 8.10.