Supporting Information

A metal complex that imitates a micelle

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Experimental Section

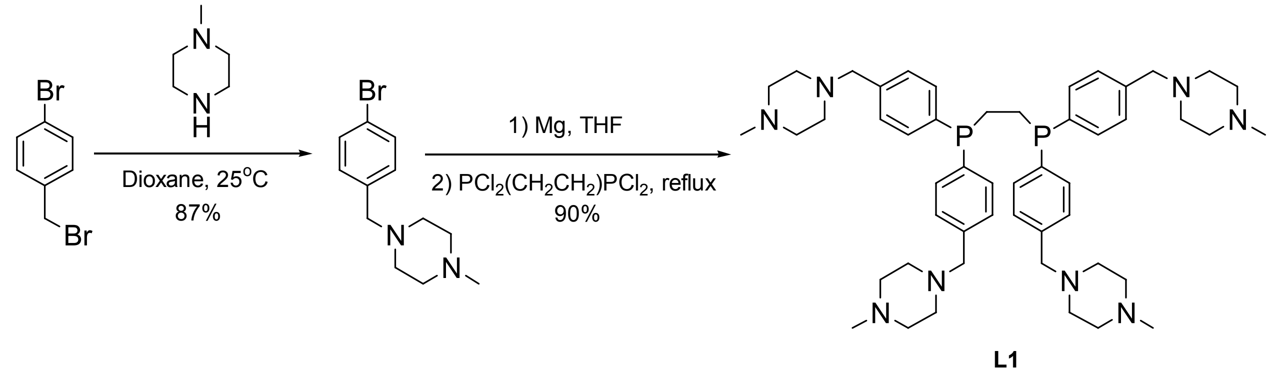
General. All reactions requiring anhydrous or inert conditions were carried out under an inert atmosphere of dry nitrogen using standard Schlenk line techniques.

Solvents and materials. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. All other solvents and reagents were used as received from commercial suppliers. Chemicals were purchased from Sigma-Aldrich Chemical Company. Solvents for extractions or cromatography were of technical grade. Flash-chromatography was carried out using Merck Silica (40-60 µ). Analytical TLC was performed with Merck Silica gel 60 F_{254} plates..

Product analysis. Electrospray mass spectra were carried out on the Waters LCT Premier™ XE benchtop orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer. ^{1}H, ^{13}C, ^{31}P and 2D (P-COSY) NMR spectra were all recorded on Bruker AM 300 MHz or AM 500 MHz referenced to the residual ^{1}H or ^{13}C containing solvent or to external 85% H_3PO_4 in the case of ^{31}P-NMR. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz. Elemental analysis were determined by the Analytical Service Department of the School of Chemistry (ASEP) using a Perkin-Elmer 2400 CHN microanalyser. A commercial Malvern Zeta-Nano Sizer was used for DLS measurements. The size distribution calculated by the Nano software is derived from a non-negative least squares (NNLS) analysis. The instrument was periodically verified by measuring polystirene latex standards from Duke Scientific Corporation. To avoid any possible dust contamination during preparation of the solutions, the dispersants were filtered using syringe filters with pore size of 200 nm. Three repeat measurements were performed on the same sample to check count rate repeatability.

CMC measurement by dye inclusion. The critical micelle concentration (CMC) was measured using the colorimetric technique based on the oil-soluble dye, 1-(2-pyridylazo)-2-naphthol (PAN). 100 ml of a saturated solution of PAN in pentane (~ 1.6 x 10^{-3} M) was prepared. A set of 10 solutions of 6 or 7 at various concentrations were made from 0 to 10^{-2} M. 2 drops of the saturated PAN solution in pentane were added to 2 ml of each solution. The solutions were gently swirled, allowing the pentane to evaporate and the color to develop, and then were filtered. The intensity of the color in each solution was noted and their absorbance measured at 470 nm (ligands absorb at 290 nm). This critical micelle concentration was supported by DLS, by analyzing size and count rate for samples at the same concentrations as in the colorimetric analysis.

Modelling: HyperChem 8.0.3 software was used: Models were constructed starting from crystallographic atomic coordinates for $[Ag(dppe)_2]^+$, $[Ag_2(d4pype)_4]^{2+}$ and $[Ag_6\{CH_3C(CH_2PPh_2)_3\}_4(OTf)_4]^{2+}$ obtained from the Cambridge Crystallographic Database (refcodes KOJRIK and JOXQOC) or from the supplementary material from reference 12. Para-H atoms were replaced with piperazinyl $CH_2N(CH_2CH_2)_2NCH_3$ substituents which were placed into approximate chair conformations with equatorial substituents prior to energy minimization by molecular mechanics using the AMBER force field.



4-[*N*-(*N*-methylpiperazinyl)methyl]bromobenzene. Bromobenzylbromide (80.0 mmol) was dissolved in 50.0 ml of dioxane and 4-methylpiperazine (17.7 ml, 160.0 mmol) was slowly added at 0°C. After stirring for one hour, the 4-methylpiperazinium bromide was filtered off, the solution diluted with 200 ml of diethylether, washed with brine and water and dried over sodium sulfate. Evaporation of the solvent under vacuum gave the pure product as yellow oil. Yield : 18.8g (87 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39 (d, 2H, $^3J_{HH}$ = 9 Hz), 7.17 (d, 2H, $^3J_{HH}$ = 9 Hz), 3.42 (s, 2H), 2.42 (bs, 8H), 2.25 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$)): δ = 137.8, 131.7, 131.2, 121.2, 62.7, 55.5, 53.5, 46.5. ES-MS (m/z): 269 $(M+H)^+$.

1,2-*Bis*{4-[*N*-(*N*-methylpiperazinyl)methyl]phenyl}phosphinoethane (**L1**). To a solution of 4-[*N*-(*N*-methylpiperazinyl)methyl]bromobenzene (5.0g 18.5 mmol) in dry THF, Mg (0.5 g, 22.2 mmol) and a crystal of iodine were added at 0°C. After the exothermic reaction had taken place, the mixture was stirred at r.t. for 1 hour. 1,2-Bis(dichlorophosphino)ethane (0.9 g, 3.7 mmol) was then added at r.t. and the mixture heated to reflux for 2 hours. The reaction was quenched with distilled water (50 ml) and the milky mixture was filtered through a short pad of Celite in order to remove the magnesium hydroxide gel. The pad was washed with chloroform. The water phase was extracted with chloroform (3 x 100 ml) and the collected organic phases dried over Na_2SO_4 and concentrated under reduced pressure. The crude solid obtained was purified by flash-column chromatography (DCM / MeOH = 95/5 + 1% ammonia 35% solution) and yielded a yellow solid. Yield = 2.7g (90 %). M.p. = 49°-50°C. ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.25 (m, 16H,), 3.48 (s, 8H), 2.45 (bs, 32H), 2.27 (s, 12H), 2.07 (t, 4H, $^2J_{HP}$ = 6 Hz). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$) □ -12.7 (s). ^{31}P-{^{1}H} NMR (121 MHz, D_2O) □ -15.3 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 137.0 (t, $^1J_{CP}$= 7 Hz), 133.0 (t, $^2J_{CP}$ = 10 Hz), 129.6, 63.1, 55.5, 53.5, 46.5, 24.4. ES-MS (m/z): 847 $(M+H)^+$. CHN analysis for $C_{50}H_{72}N_8P_2$: C, 70.89, H, 8.57, N, 13.23; found C, 70.57, H, 8.81, N, 13.04. DLS (20 mM, D_2O, Cumulant Analysis) D_H = 5.0 nm (100 %), PI = 0.04.

Ag(I) complexes of **L1**: To a solution of **L1** (0.050 g, 0.060 mmol) in D_2O (3.0 ml), AgX (0.030 mmol) was added and the mixture stirred for five minutes. D_2O was removed by freeze drying.

Ag_2(**L1**)$_4$(OTf)$_2$. ^{31}P-{^{1}H} NMR (202 MHz, D_2O): □ = 1.9 (pair of multiplets), $^1J(^{109}Ag, ^{31}P)$ = 295 Hz, 1.1 (pair of triplets of doublets) $^1J(^{109}Ag, ^{31}P)$ = 228 Hz, $^2J_{PP}$ = 44 Hz. 1H-NMR (202 MHz, D_2O): □ = 7.15-7.12(m, 32H), 7.01 (d, ^3J = 6 Hz, 12H), 6.55 (bs 16H), 3.53-3.32(m, 32H), 2.28 (bs, 144H), 2.20 (s, 24H), 2.14 (s, 24H). CHN analysis for $C_{202}H_{288}N_{32}P_8O_6S_2F_6Ag_2$: C 62.14, H 7.49, N 11.48; found C 61.52 H 6.97 N 10.75. DLS (D_2O, Intensity size distribution) D_H = 2.5 ± 0.5 nm.

$Ag_2($**L1**$)_4(NO_3)_2$. ^{31}P-{^1H} NMR (121 MHz, D_2O): □ = 2.2 (pair of multiplets), $^1J(^{109}Ag, ^{31}P)$ = 278 Hz, 1.5 (pair of triplets of doublets) $^1J(^{109}Ag, ^{31}P)$ = 225 Hz, $^2J_{PP}$ = 42 Hz.

$Ag_2($**L1**$)_4(OTs)_2$. ^{31}P-{^1H} NMR (121 Hz, D_2O): □ = 1.85 (pair of multiplets), $^1J(^{109}Ag, ^{31}P)$ = 296 Hz, 1.2 (pair of triplets of doublets) $^1J(^{109}Ag, ^{31}P)$ = 230 Hz, $^2J_{PP}$ = 40 Hz.

$Ag($**L1**$)_2(OTf)$ in acidified water. Trifluoromethansulfonic acid (42 µl, 0.0480 mmol) was added to the solution of the dinuclear complex prepared as described and the mixture stirred for five minutes. ^{31}P-{^1H} NMR (121Hz, D_2O): □ = 3.9 ppm, $^1J(^{109}Ag, ^{31}P)$ = 266 Hz. ^1H-NMR (202 MHz, D_2O): □ = 7.37-7.32 (m, 32H), 4.34 (s, 16H), 3.76-3.64 (m, 32H), 3.43-3.33 (m, 32H), 2.93 (s, 24H), 2.53 (s, 8H). DLS (D_2O, Intensity size distribution) D_H = 1.5 ± 0.3 nm.

$Ag($**L1**$)_2(OTf)$ in CD_3CN. To a solution of **L1** (0.050 g, 0.060 mmol) in CD_3CN (3.0 ml), AgX (0.030 mmol) was added and the mixture stirred for five minutes. ^{31}P-{^1H} NMR (121 MHz, CD_3CN): □ = 2.3 ppm, $^1J(^{109}Ag, ^{31}P)$ = 265 Hz.

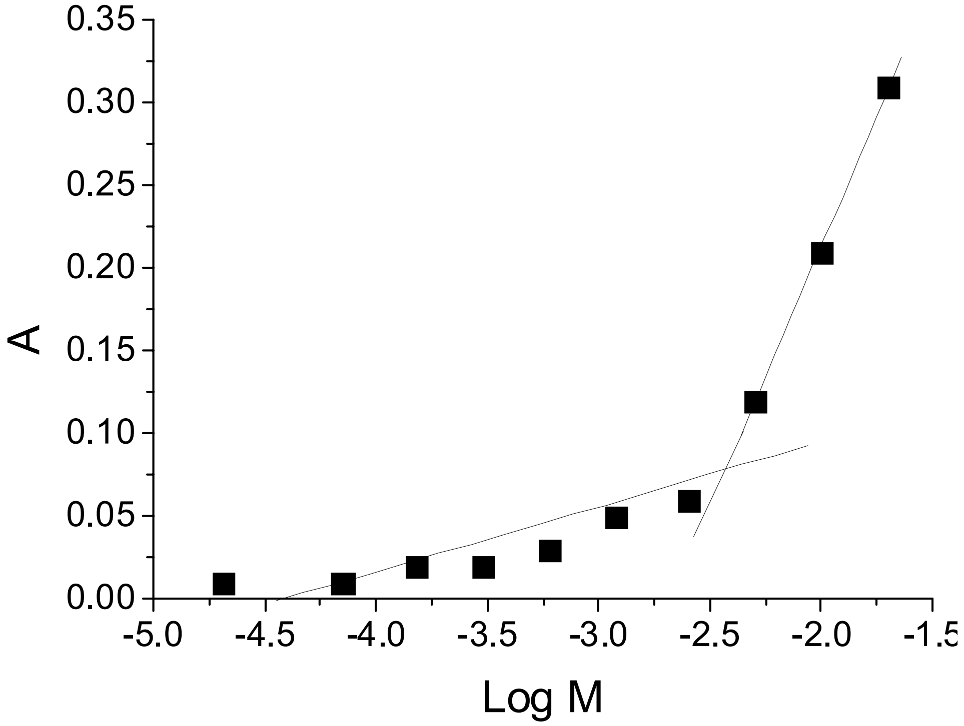


Figure S1 Colorimetric determination of critical micelle concentration (CMC) for L1 in H2O.

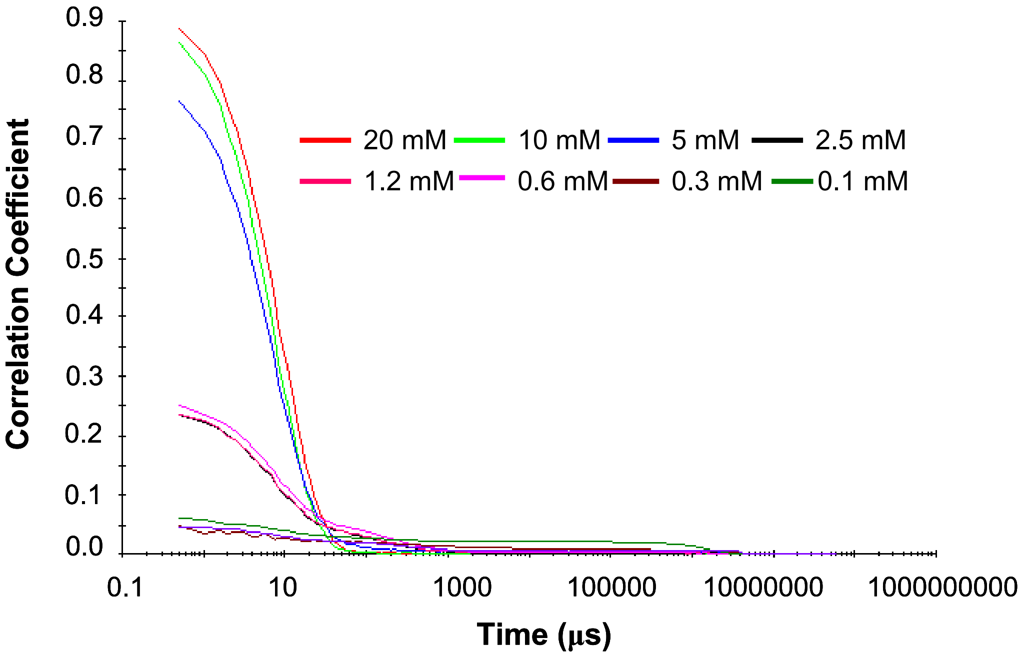


Figure S2 Raw correlation data of aqueous solution of **L1** at different concentrations.

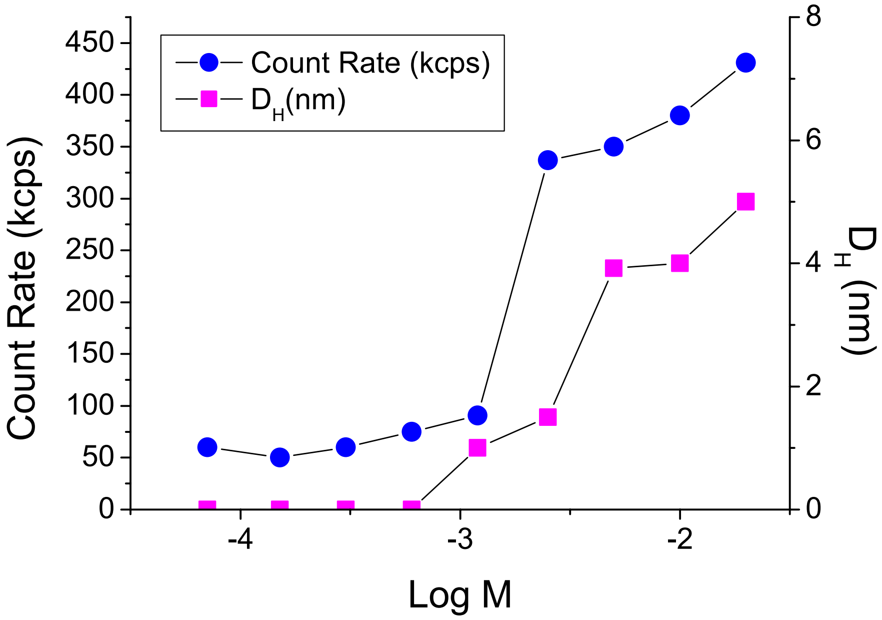


Figure S3 CMC of **L1** measured by Dynamic Light Scattering

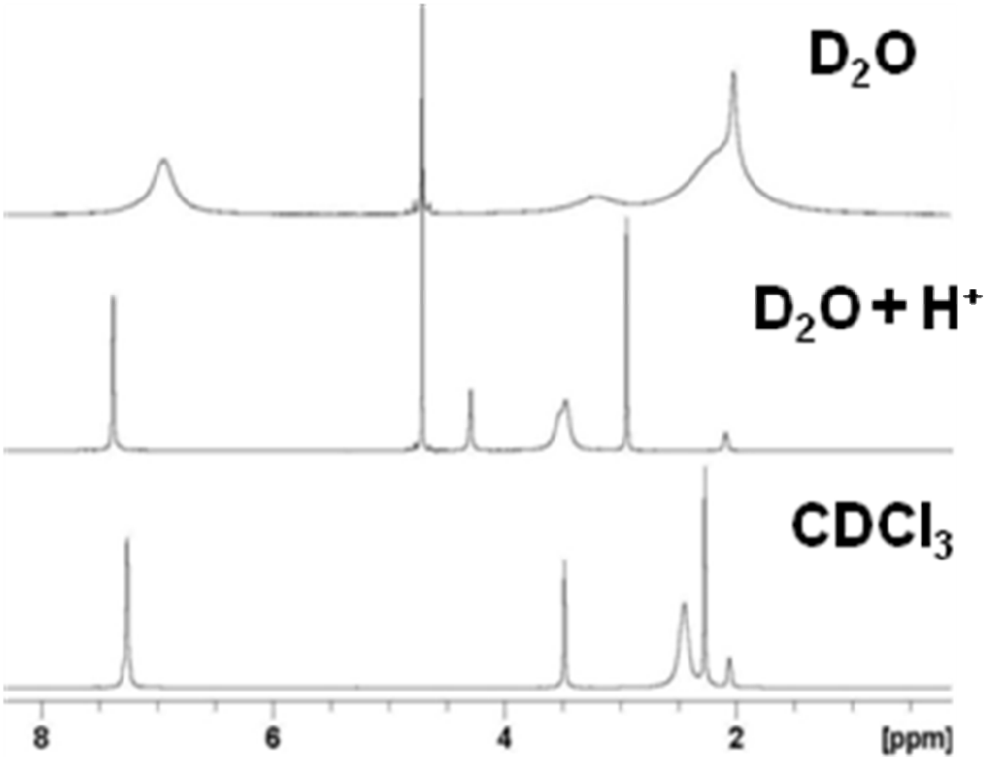


Figure S4 ^{1}H NMR spectra of L1 in D_2O, acidified D_2O and $CDCl_3$

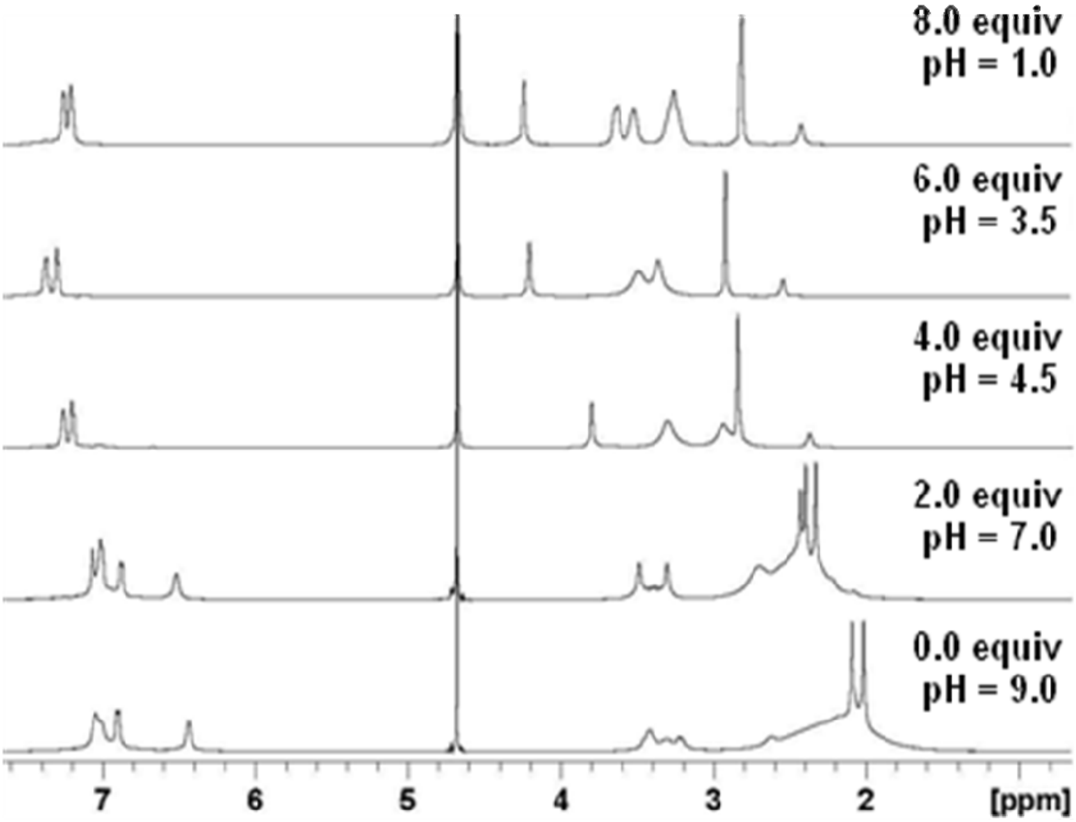


Figure S5 1H-NMR spectra showing interconversion between mono- and di-nuclear silver complexes with pH.

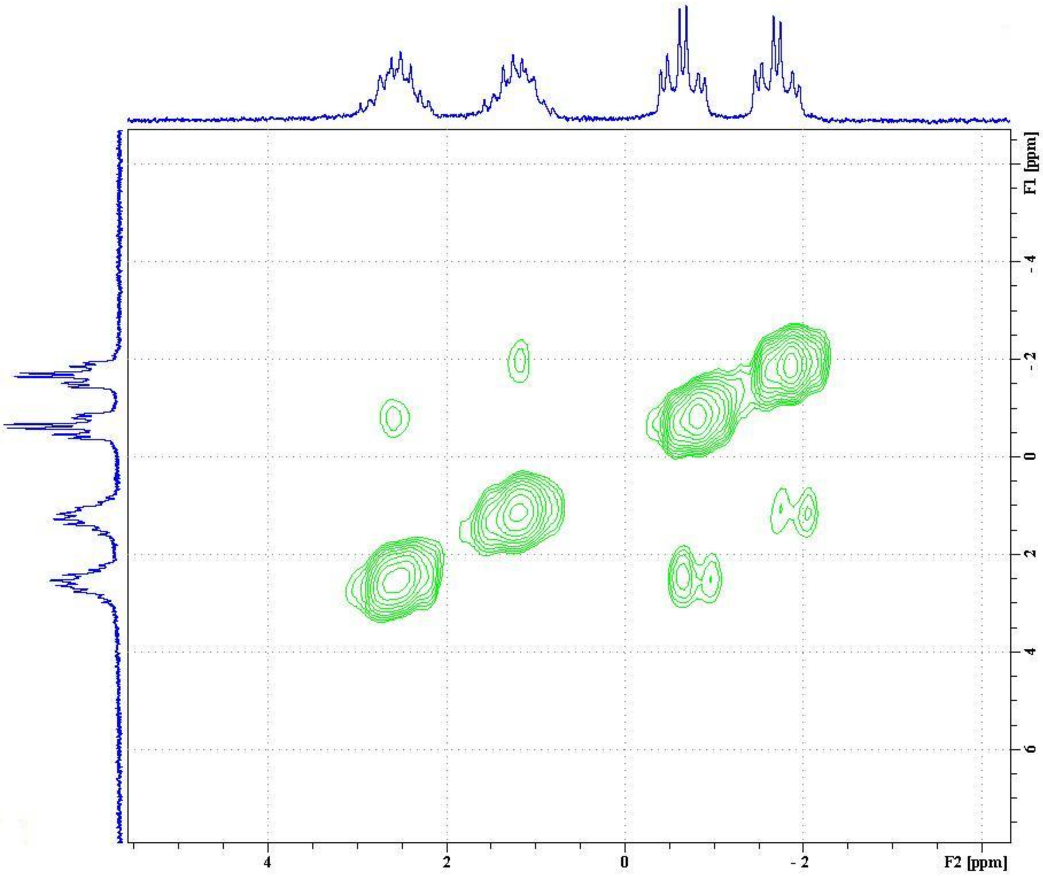


Figure S6 ^{31}P-NMR COSY of the dinuclear complex $[Ag_2(\mathbf{L1})_4]^{2+}$ in D_2O.

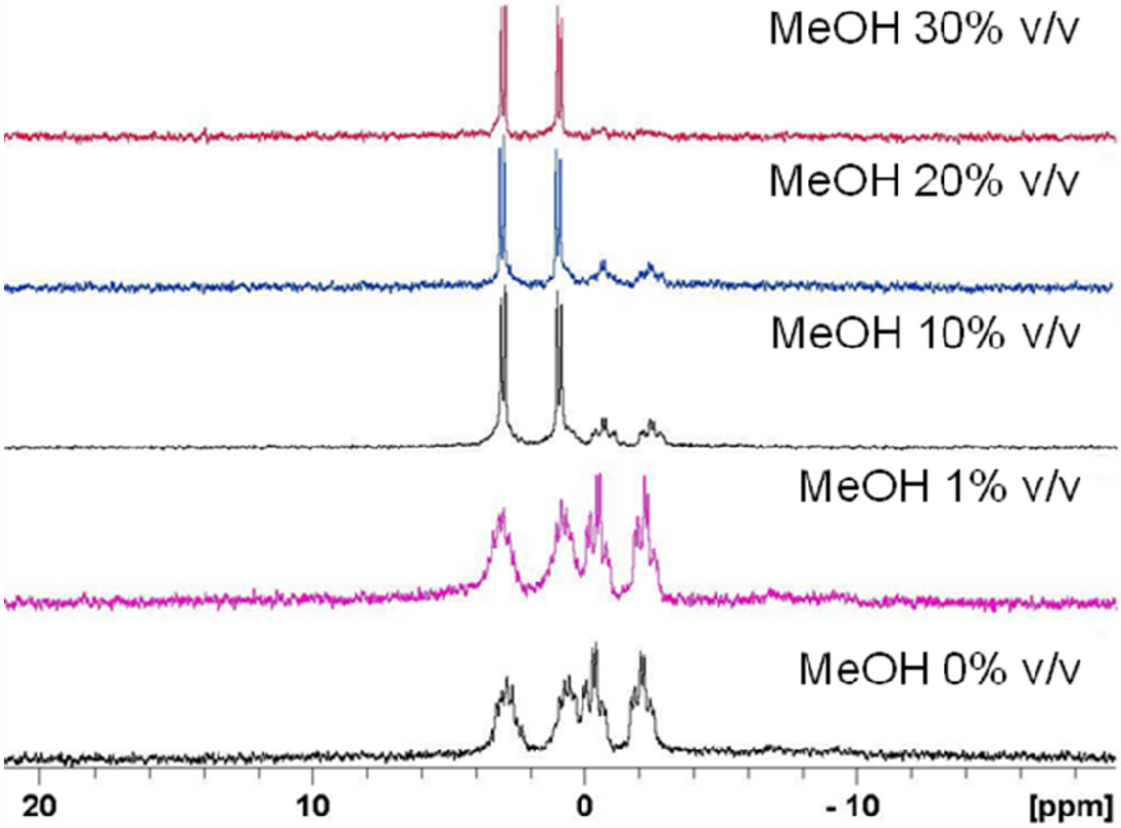


Figure S7 Effect on ^{31}P NMR (121Mhz, D_2O) spectra of addition of MeOH to $[Ag_2(\mathbf{L1})_4]^{2+}$.