Electronic Supplementary Material (ESI) for Nanoscale.

Intracluster ligand rearrangement: an NMR-based thermodynamic study

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Supporting Information

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1. Experimental procedures

Chemicals

Silver nitrate ($AgNO_3$, Merck, 99%), Tetrachloroauric(III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$, TCI >99 %) chloro(triphenylphosphine)gold(I) ($AuClPPh_3$, Merck, 99.9+%), sodium borohydride (Fluka, >96%), tetraoctylammonium bromide (TOABr, Merck, 98%), 2,4-dimethylbenzenethiol (DMBT, Merck, 95%), 1-octanethiol (Merk >98.5%), 2-phenylethanethiol (PET, >99% Merk), methanol (VWR, 99.8%), acetone (Fluka, >99.5%), methylene chloride (DCM, Merck, >99.9%), toluene (Merck, 99.9%), PTFE syringe filters (0.2 µm, Carl Roth, Karlsruhe/Germany) and BioBeads S-X1 (BioRad) were used as purchased if not mentioned otherwise. Nanopure water (> 18 MΩ) was used.

Characterization

UV–vis spectra: Varian Cary 50 spectrometer (Quartz cuvette, l = 1 cm, solvent: DCM, [C] = 0.05 mg/ml, 300 - 900 nm).

NMR spectroscopy: 1D and 2D spectra were acquired on 500 MHz Avance III and 400 MHz Avance II Bruker spectrometers equipped respectively with a CPP (D, C, H z-grad) and a BBFO (BBF-H-D z-grad) 5 mm probes and a BCU-X or SmartCooler BCU II unit. VT experiments were acquired between 248 and 368 K with 10 K interval. An appropriate equilibration time of 10 min was used when changing the temperature. At the end a control experiment at 298 K was acquired in all cases to detect any modification of the sample after thermal treatment.

NMR sample preparation

Samples were prepared in 5 mm standard glass tubes using a volume of 600 µl of deuterated solvent. A precise amount of dry MNCs was weighted and dissolved in the appropriate deuterate solvent (dimethylformamide-d_7 or toluene-d_8 were used for their high boiling point, suitable for the VT experiments in the desired temperature range). The prepared samples were used immediately or stored at 4 °C to prevent cluster modification.

2. Synthesis and characterization of the MNCs used in the study

$[Ag_{25}(DMBT)_{18}][TOA]$,[1] $[Ag_{24}Au(DMBT)_{18}][TOA]$,[1, 2] $[Au_{25}(Oct)_{18}][TOA]$[3] and $[Au_{25}(PET)_{18}][TOA]$[4] were synthesized following previously reported procedures. To reach a purity suitable for NMR analysis all the clusters were purified through size exclusion chromatography (SEC) using as substrate the BioBeads X1® and HPLC-UV grade DCM as eluent. Clusters where dried overnight in vacuum prior to analysis for compete solvent removal. Solid clusters were stored in a sealed vial under N_2 atmosphere at -20 °C in the dark. All the obtained Uv-Vis and ^{1}H NMR spectra match with the ones reported in the previously cited references. Detailed signal assignation is reported for $[Au_{25}(Oct)_{18}][TOA]$ (Fig. S9-11) since not available in the literature.

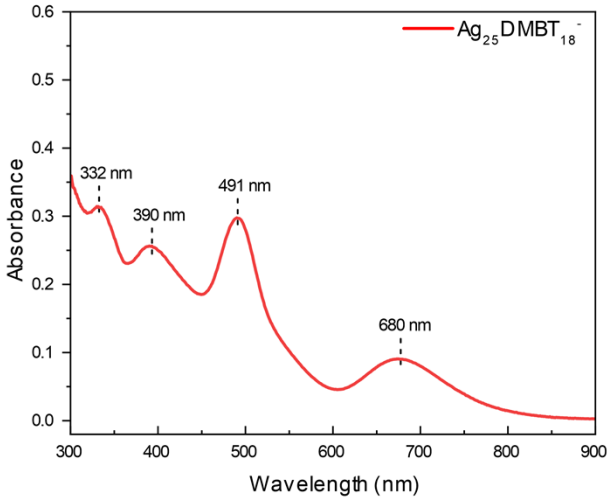

Figure S1. UV-vis absorption spectrum of a solution of $[Ag_{25}(DMBT)_{18}][TOA]$ ([C] = 0.05 mg/ml, DCM) normalised at 400 nm (A = 0.25) for better comparison.

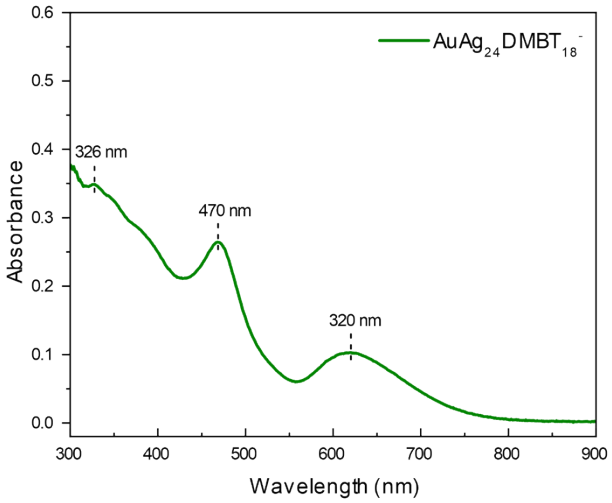

Figure S2. UV-vis absorption spectrum of a solution of $[Ag_{24}Au(DMBT)_{18}][TOA]$ ([C] = 0.05 mg/ml, DCM) normalised at 400 nm (A = 0.25) for better comparison.

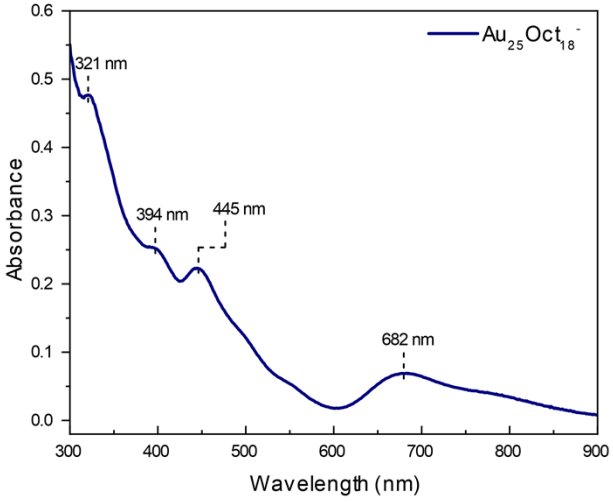

Figure S3. UV-vis absorption spectrum of a solution of $[Au_{25}(Oct)_{18}][TOA]$ ([C] = 0.05 mg/ml, DCM) normalised at 400 nm (A = 0.25) for better comparison.

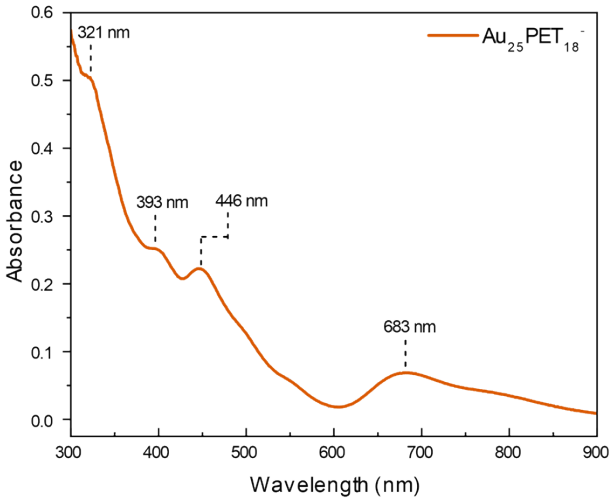

Figure S4. UV-vis absorption spectrum of a solution of $[Au_{25}(PET)_{18}][TOA]$ ([C] = 0.05 mg/ml, DCM) normalised at 400 nm (A = 0.25) for better comparison.

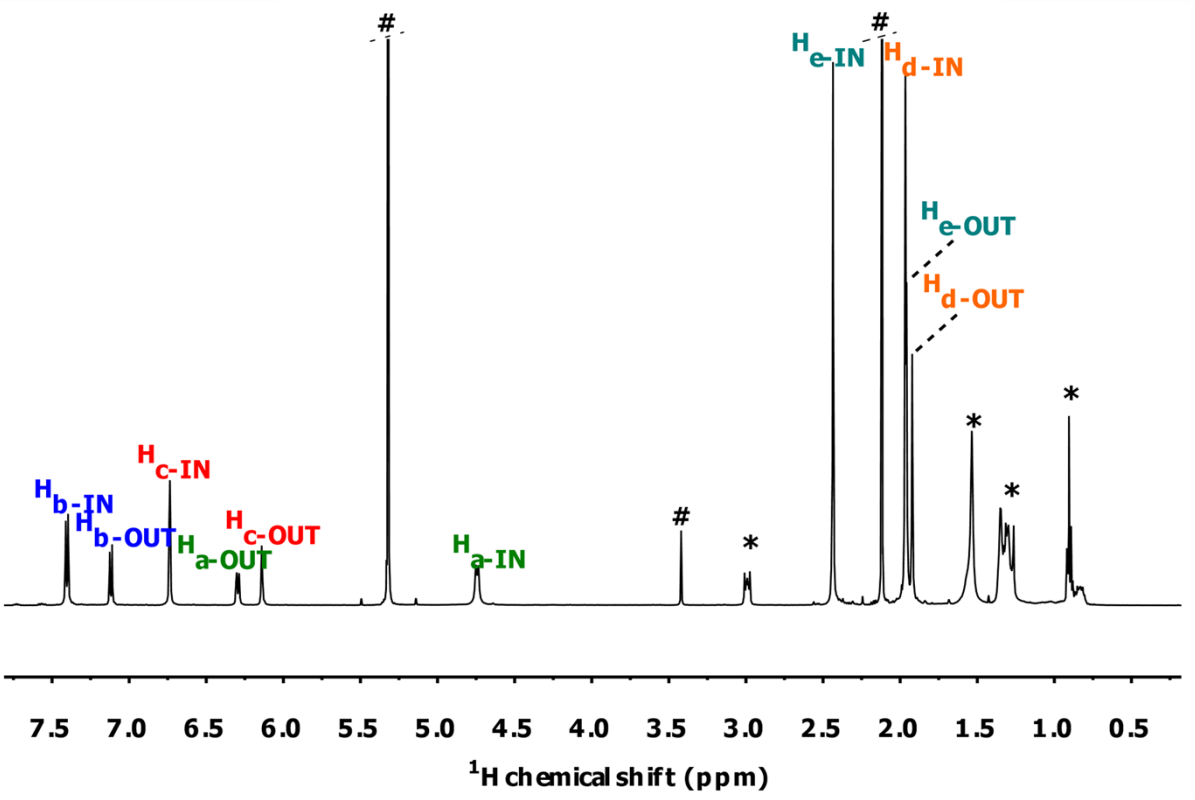

Figure S5. Complete ^1H of $[Ag_{25}(DMBT)_{18}][TOA]$ in dichloromethane-d_2. * Indicates the TOA^+ counterion peaks. # Indicates the deuterated solvent residual peaks or impurities. The chemical structure of the of the ligand with proton labelling is reported in the main text or in Fig. S13.

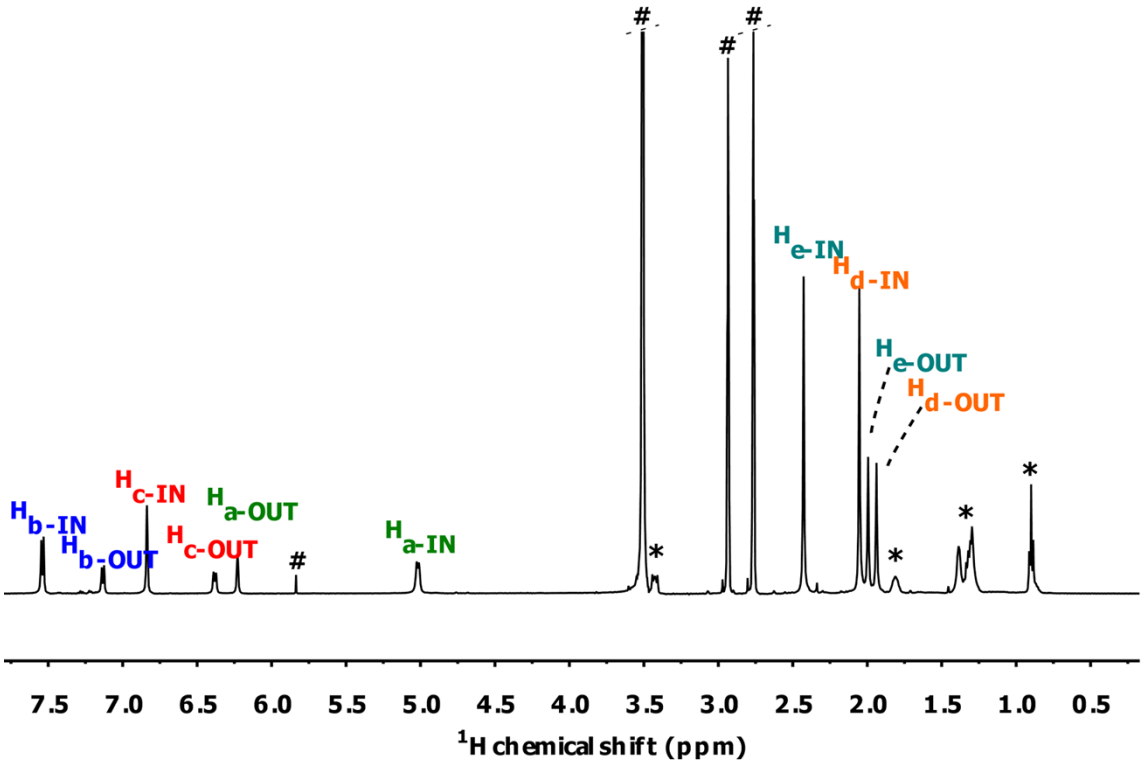

Figure S6. Complete ^{1}H of $[Ag_{24}Au(DMBT)_{18}][TOA]$ in dimethylformamide-d_7. * Indicates the TOA^{+} counterion peaks. # Indicates the deuterated solvent residual peaks or impurities. The chemical structure of the of the ligand with proton labelling is reported in the main text or in Fig. S13.

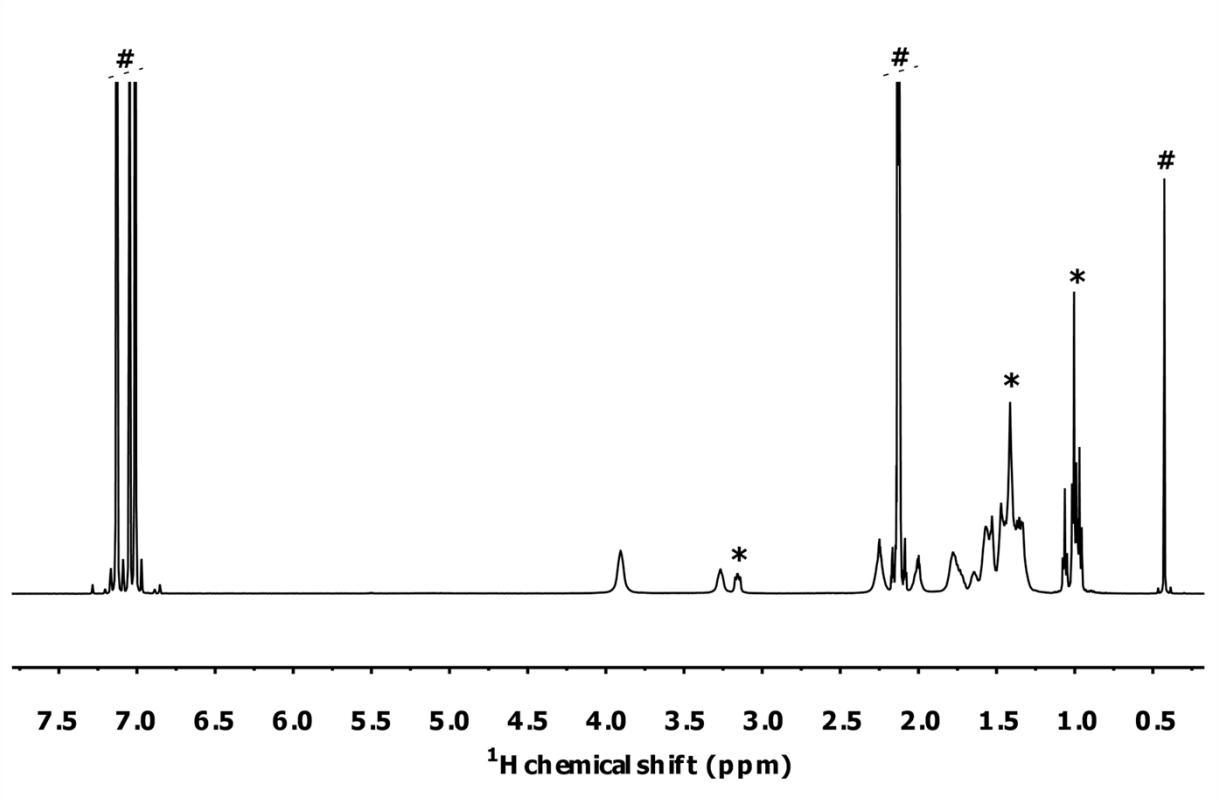

Figure S7. Complete ^{1}H of $[Au_{25}(Oct)_{18}][TOA]$ in toluene-d_7. * Indicates the TOA^{+} counterion peaks. # Indicates the deuterated solvent residual peaks or impurities.

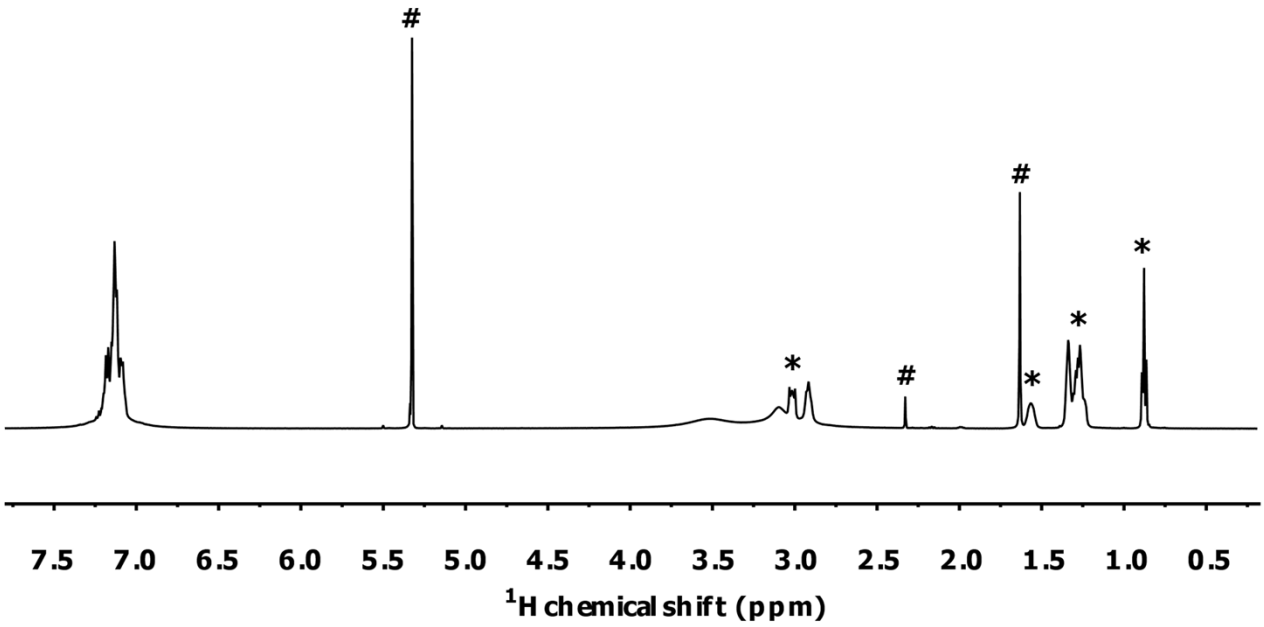

Figure S8. Complete ^{1}H of $[Au_{25}(PET)_{18}][TOA]$ in dichloromethane-d_2. * Indicates the TOA^{+} counterion signals. # Indicates the deuterated solvent residual peaks or impurities. Complete assignation in Fig. S9.

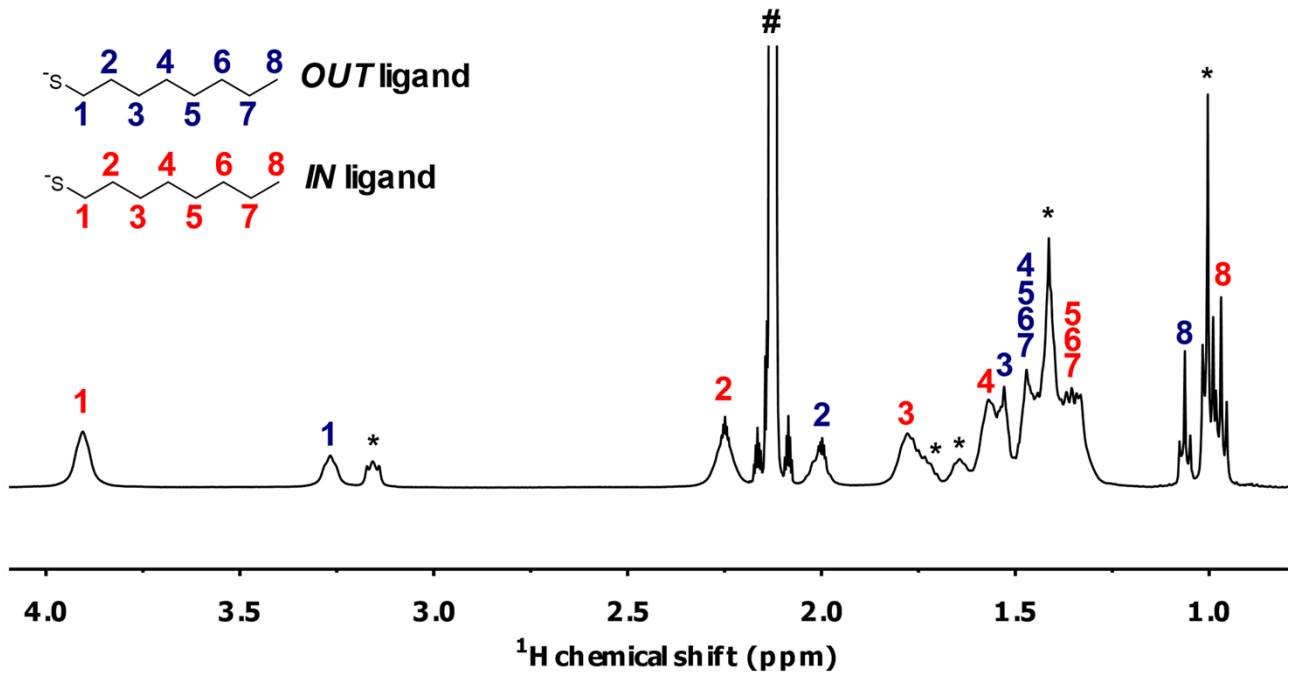

Figure S9. Assignation of the signals in the ^{1}H NMR spectrum of $[Au_{25}(Oct)_{18}][TOA]$ in toluene-d_8. Alifatic region detail. * Indicates the TOA^{+} counterion signals. # Indicates the deuterated solvent residual peaks or impurities.

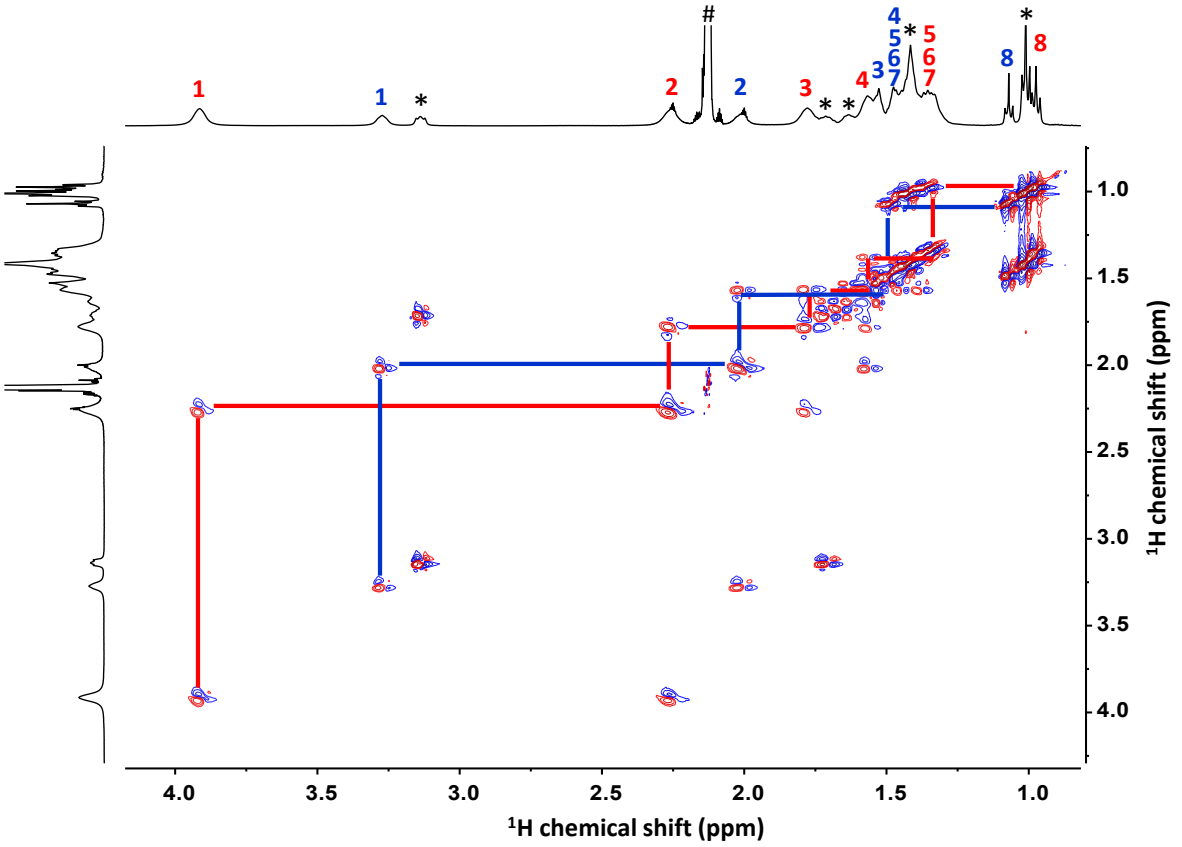

Figure S10. Detail of the alifatic region of the ^{1}H-^{1}H COSY spectrum of $[Au_{25}(Oct)_{18}][TOA]$ in toluene-d_8 used for signal assignation. Color code as in Fig S9. * Indicates the TOA^{+} counterion signals. # Indicates the deuterated solvent residual peaks or impurities.

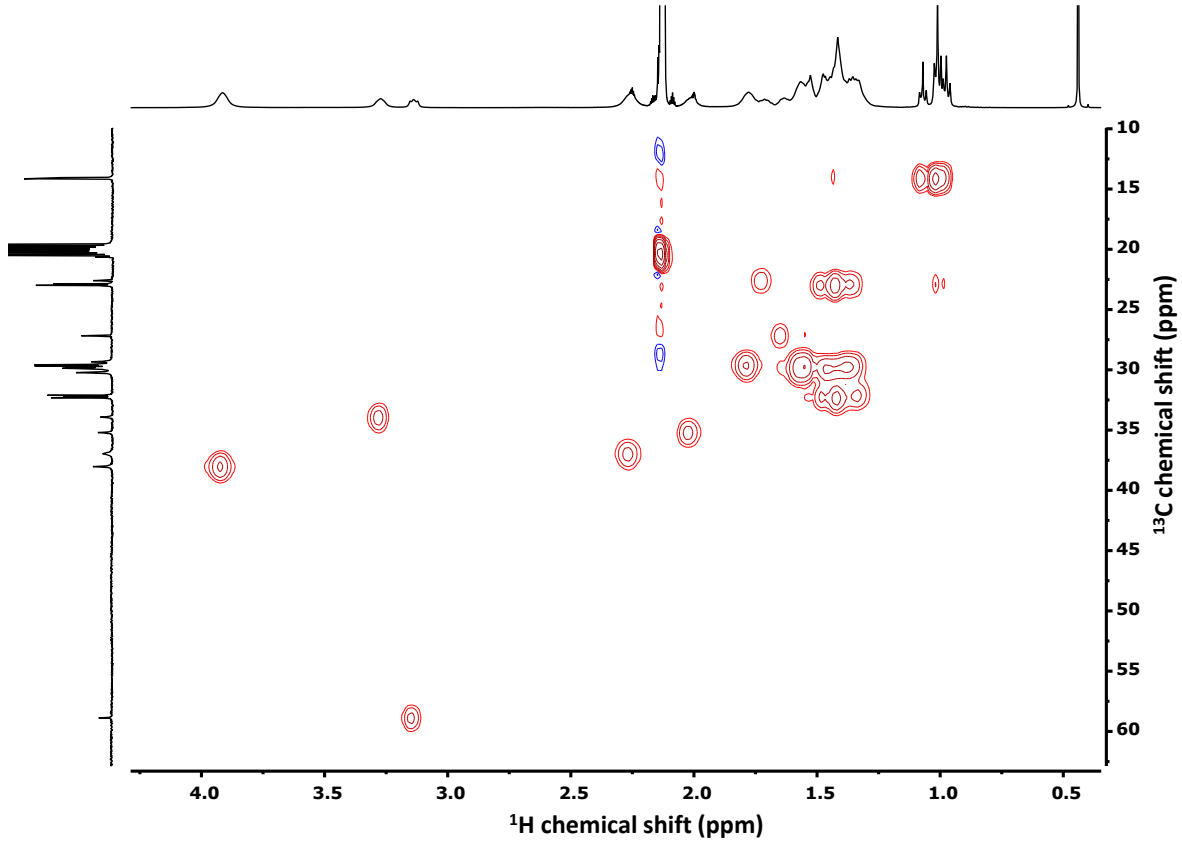

Figure S10. Detail of the alifatic region of the ^{1}H-^{13}C HSQC spectrum of $[Au_{25}(Oct)_{18}][TOA]$ in toluene-d_8 used for signal assignation.

3. DNMR simulations

3.1 General workflow

To calculate the variable temperature (VT) spectra we used the DNMR envinroment in the Topspin® Bruker suite. The spectrum of the cluster was divided in one (or more) fitting regions, carfully chosen in a way to include all and only the signals of the cluster under analysis (solvent residual peaks and the counterion signals were conveniently left out of those regions).
The signal of each proton (H_a, H_b, …) was set as a separate "spin system". Each spin system was composed of two nuclei, corresponding to the *IN* (nucleus 1) and *OUT* (nucleus 2) symmetry non-equivalent positions of the same proton in the cluster . The exchange reaction between the *IN* and *OUT* positions (and viceversa) was therefore set for each spin system between nucleus 1 and nucleus 2. Stoichiometric coefficients of 0.67 and 0.33 were used to take into account that the two positions are differently populated (12 vs 6 thiolates). The starting value for the exchange rate *k* was set accordingly to previously published results, when available.[1] When visible, coupling constants were measured directly from the spectrum, and the experimental *J* value obtained was inserted as starting value of the optimization. Intensity and LB of the signals were roughly matched to the experimental ones using the interactive graphical interface of the program. The values obtained were used as starting values.
The quality of the simulation was measured through the *FIT* value (eqn. 1):

$$FIT = 100 \cdot \left(1 - \frac{\sum_{v} |Y_{calc}(v) - Y_{exp}(v)|}{2\sum_{v} Y_{exp}(v)} \right) \quad (1)$$

Where $Y_{calc}(v)$ and $Y_{exp}(v)$ are respectively the calculated and experimental spectrum intensity at a given frequency *v*. A FIT value > 90 was set as decisional limit to include (or exclude) the extrapolated k_r values in the thermodynamic analysis. The fitting was performed by successive steps of 1000 iterations each and considered converged when two conditions were met: *FIT* >90 and $|\Delta FIT| < 0.1$ upon extra 1000 iterations.

3.2 Complete DNMR data

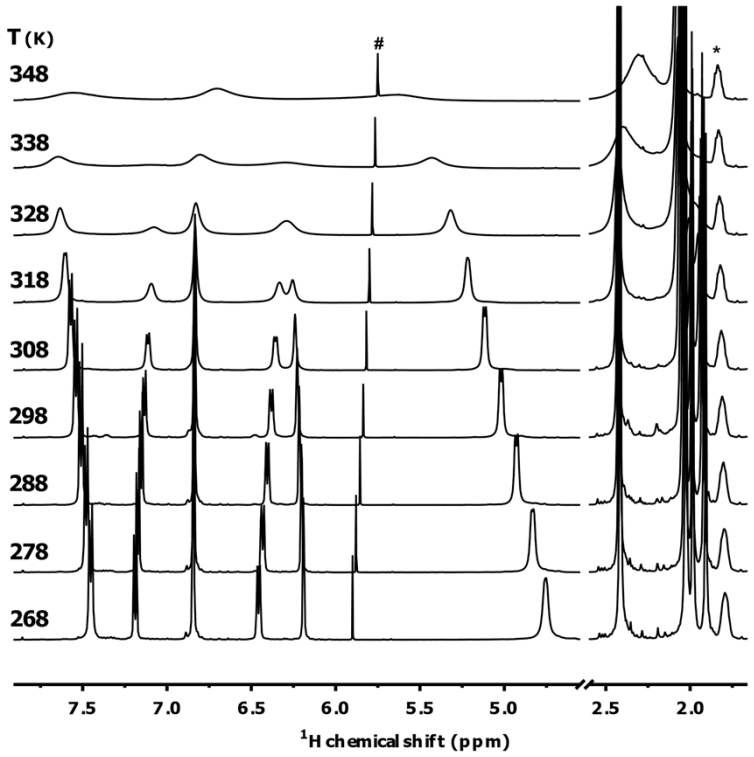

Figure S11: ^{1}H-NMR (400 MHz) spectra in dimethylformamide-d_7 of the variable temperature experiment extended to the aliphatic region (268 to 348 K with 10 K increments) for a 20.0 mM solution of $[Ag_{25}(DMBT)_{18}][TOA]$.

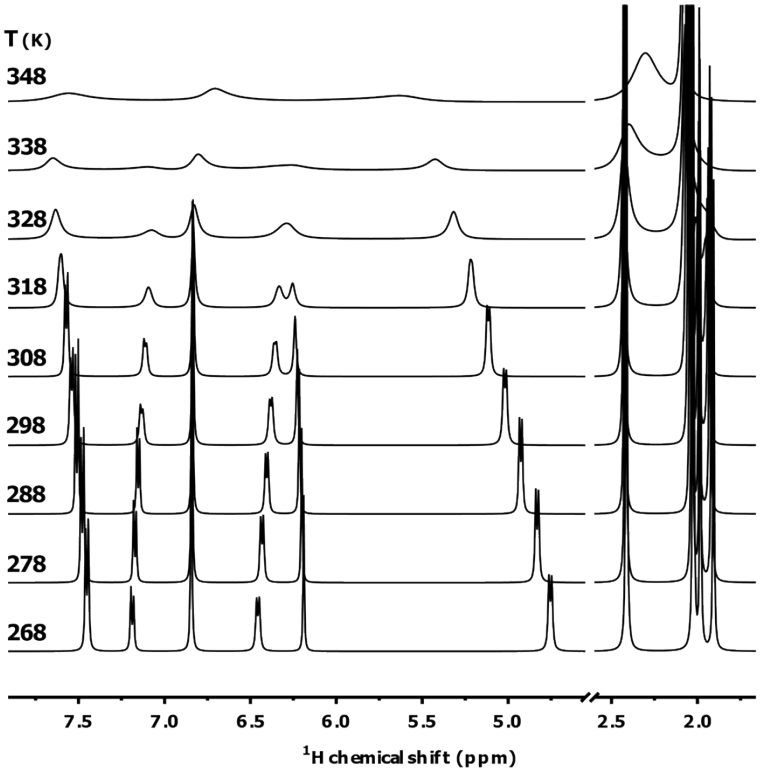

Figure S12: result of the DNMR lineshape analysis of the ^{1}H-NMR spectra of Figure S10 used to extract the values of exchange rate for each corresponding temperature.

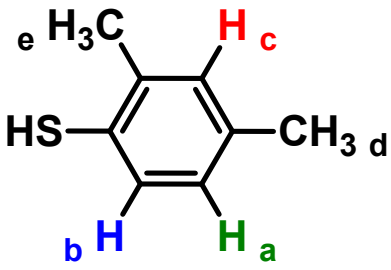

Figure S13: Proton assignation used in the manuscript for the DMBT resonances.

Table S1: Exchange rate values obtained from the spectra simulations for each of the DMBT protons of $[Ag_{25}(DMBT)_{18}][TOA]$ 20 mM

		H_a		H_b		H_c		H_d		H_e		fitting match (%)
T (K)	1/T (K^{-1})	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	
278	0.00360	0.49	-6.33	0.39	-6.56	0.43	-6.48	0.38	-6.59	0.36	-6.64	92.9
288	0.00347	1.53	-5.24	1.43	-5.31	1.39	-5.33	1.36	-5.36	1.49	-5.26	93.3
298	0.00336	3.46	-4.46	3.414	-4.47	3.59	-4.42	3.69	-4.39	3.86	-4.35	92.8
308	0.00325	10.16	-3.41	11.88	-3.26	10.98	-3.33	12.39	-3.21	11.57	-3.28	95.4
318	0.00314	30.00	-2.36	22.42	-2.65	22.78	-2.64	25.90	-2.51	22.64	-2.64	96.5
328	0.00305	60.00	-1.70	60.00	-1.70	60.00	-1.70	54.28	-1.80	62.11	-1.66	98.3
338	0.00296	132.36	-0.94	157.17	-0.77	137.73	-0.90	136.19	-0.91	149.93	-0.81	95.9
348	0.00287	306.84	-0.13	302.52	-0.14	314.33	-0.10	315.42	-0.10	298.53	-0.15	97.5

Table S2: Average exchange rate of H_a, H_b, H_c, H_d and H_e values obtained from the data in *Table S1*.

T (K)	k_r (Hz)	ln(k_r /T)	dev. St
278	0.41	-6.52	0.12
288	1.44	-5.30	0.05
298	3.60	-4.42	0.05
308	11.40	-3.30	0.08
318	24.75	-2.56	0.13
328	59.28	-1.71	0.05
338	142.68	-0.86	0.07
348	307.53	-0.12	0.02

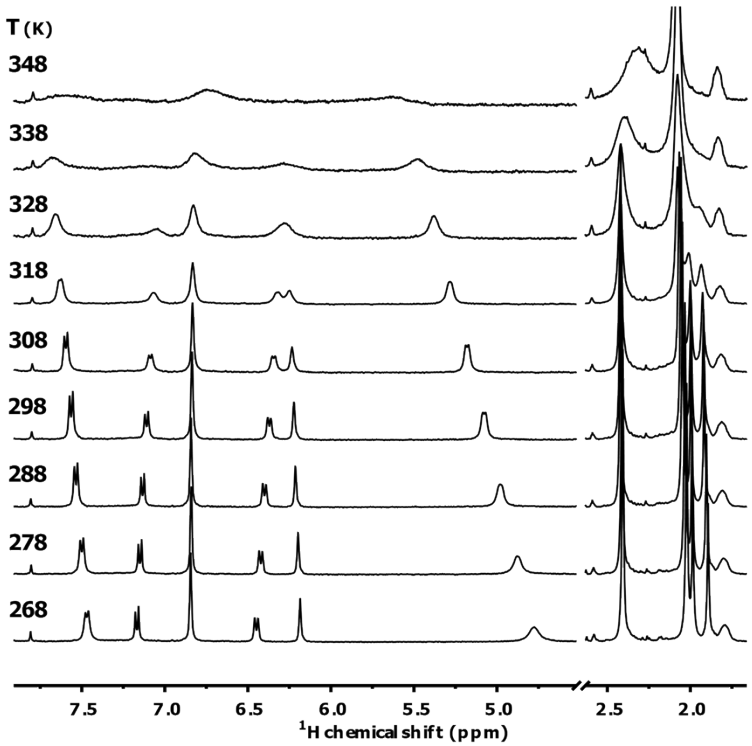

Figure S14: ^{1}H-NMR (400 MHz) spectra in dimethylformamide-d_7 of the variable temperature experiment (268 to 348 K with 10 K increments) for a 2 mM solution of $[Ag_{24}Au(DMBT)_{18}][TOA]$;

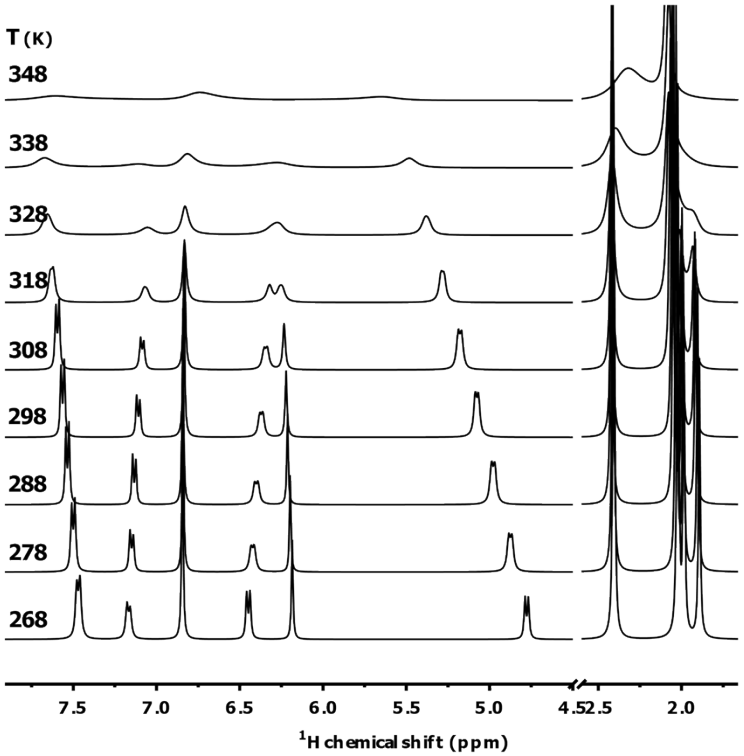

Figure S15: result of the DNMR lineshape analysis of the ^{1}H-NMR spectra of Figure S14 used to extract the values of exchange rate for each corresponding temperature.

Table S3: Exchange rate values obtained from the spectra simulations for each of the DMBT protons of $[Ag_{24}Au(DMBT)_{18}][TOA]$ 2 mM.

		H_a		H_b		H_c		H_d		H_e		fitting match (%)
T (K)	1/T (K^{-1})	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	
278	0.00360	0.54	-6.24	0.44	-6.46	0.55	-6.22	0.61	-6.12	0.39	-6.56	91.8
288	0.00347	1.62	-5.18	1.64	-5.17	1.53	-5.24	1.40	-5.32	1.14	-5.53	92.2
298	0.00336	4.28	-4.24	4.109	-4.28	3.58	-4.42	4.35	-4.23	3.92	-4.33	92.5
308	0.00325	12.24	-3.23	12.17	-3.23	10.67	-3.36	9.73	-3.45	9.88	-3.44	92.3
318	0.00314	24.52	-2.56	24.37	-2.57	19.32	-2.80	23.20	-2.62	24.15	-2.58	93.8
328	0.00305	54.17	-1.80	66.10	-1.60	55.26	-1.78	51.92	-1.84	47.26	-1.94	95.4
338	0.00296	98.04	-1.24	141.17	-0.87	111.17	-1.11	145.27	-0.84	123.94	-1.00	97.5
348	0.00287	277.06	-0.23	328.55	-0.06	272.91	-0.24	215.09	-0.48	303.16	-0.14	96.2

Table S4: Average exchange rate of H_a, H_b, H_c, H_d and H_e values obtained from the data in *Table S3*

T (K)	k_r (Hz)	ln(k_r /T)	dev. St
278	0.51	-6.32	0.18
288	1.47	-5.29	0.15
298	4.05	-4.30	0.08
308	10.94	-3.34	0.11
318	23.11	-2.63	0.10
328	54.94	-1.79	0.12
338	123.92	-1.01	0.16
348	279.35	-0.23	0.16

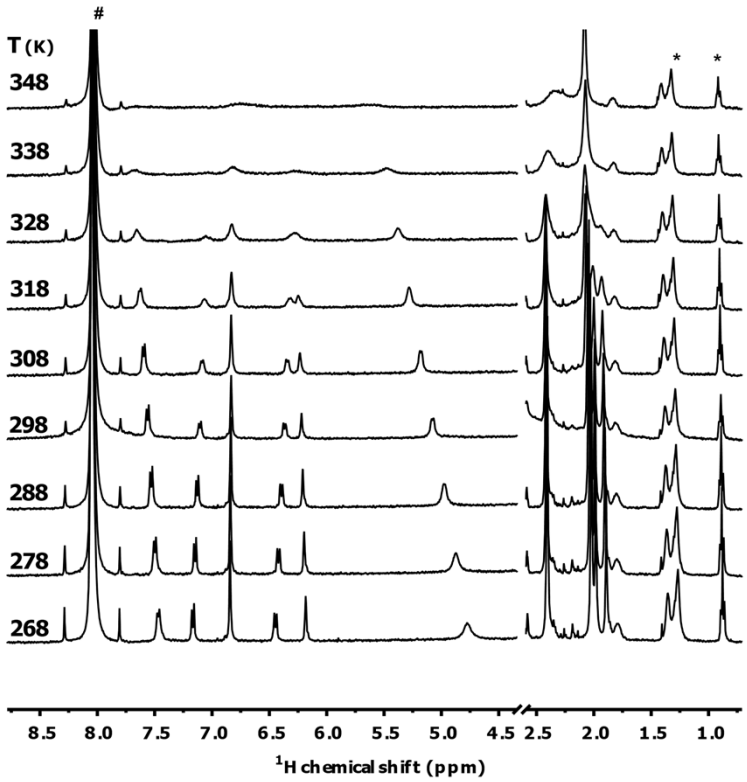

Figure S16: ^{1}H-NMR (400 MHz) spectra in dimethylformamide-d_7 of the variable temperature experiment (268 to 348 K with 10 K increments) for a 0.67 mM solution of $[Ag_{24}Au(DMBT)_{18}][TOA]$.

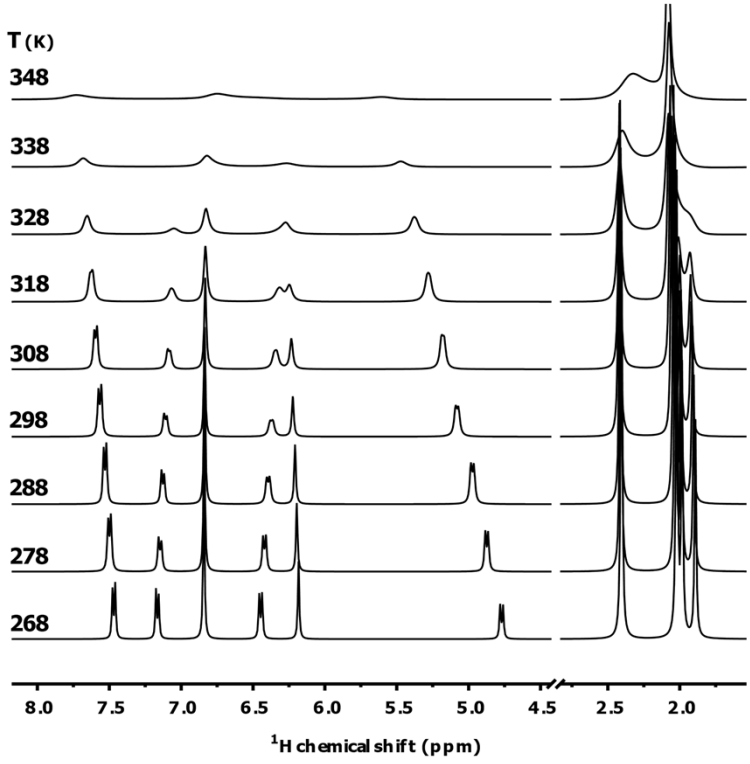

Figure S17: result of the DNMR lineshape analysis of the ^{1}H-NMR spectra of Figure S16 used to extract the values of exchange rate for each corresponding temperature.

Table S5: Exchange rate values obtained from the spectra simulations for each of the DMBT protons of $[Ag_{24}Au(DMBT)_{18}][TOA]$ 0.67 mM.

		H_a		H_b		H_c		H_d		H_e		fitting match (%)
T (K)	1/T (K^{-1})	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	k_r (Hz)	ln(k_r /T)	
278	0.00360	0.43	-6.47	0.56	-6.20	0.51	-6.30	0.43	-6.48	0.55	-6.22	91.0
288	0.00347	1.48	-5.27	1.51	-5.25	1.47	-5.28	1.65	-5.16	1.61	-5.18	91.4
298	0.00336	5.03	-4.08	4.589	-4.17	4.56	-4.18	5.20	-4.05	4.51	-4.19	90.0
308	0.00325	9.01	-3.53	9.94	-3.43	9.97	-3.43	10.15	-3.41	9.80	-3.45	92.3
318	0.00314	20.66	-2.73	22.37	-2.65	22.52	-2.65	23.08	-2.62	21.04	-2.72	92.2
328	0.00305	44.33	-2.00	44.15	-2.01	40.43	-2.09	55.52	-1.78	51.97	-1.84	92.7
338	0.00296	94.87	-1.27	94.21	-1.28	83.78	-1.39	120.05	-1.04	100.41	-1.21	92.0
348	0.00287	241.31	-0.37	252.73	-0.32	249.27	-0.33	263.58	-0.28	254.15	-0.31	92.1

Table S6: Average exchange rate of H_a, H_b, H_c, H_d and H_e values obtained from the data in *Table S5*

T (K)	k_r (Hz)	ln(k_r /T)	dev. St
278	0.50	-6.33	0.13
288	1.54	-5.23	0.05
298	4.78	-4.13	0.06
308	9.78	-3.45	0.05
318	21.93	-2.67	0.05
328	47.28	-1.94	0.13
338	98.66	-1.24	0.13
348	252.21	-0.32	0.03

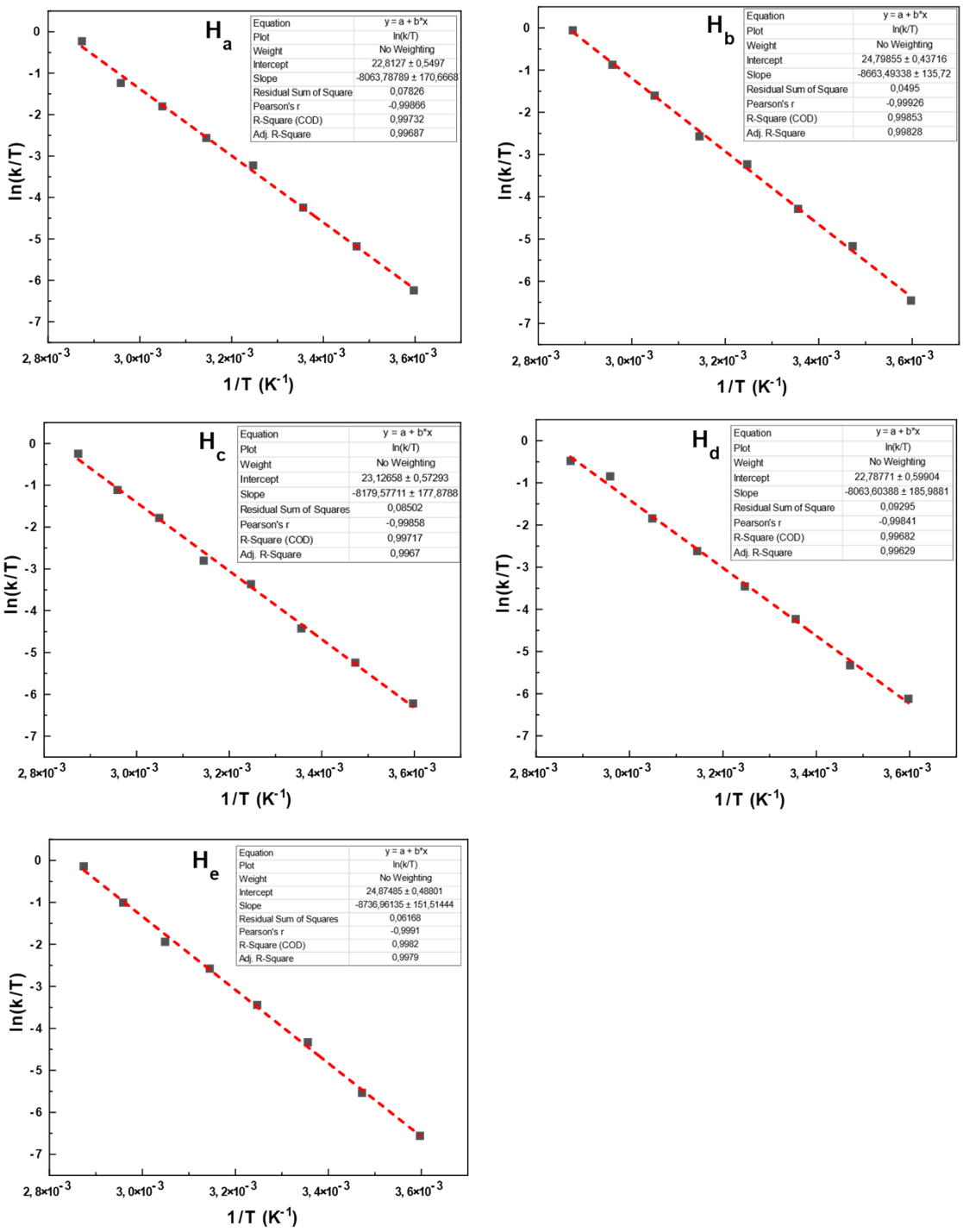

Figure S18: Eyring plot for each of the DMBT signals of $[Ag_{25}(DMBT)_{18}]^-$. Data from *Table S1.*

Table S7: Fitting parameters obtained from the graphs reported in *Figure S18.*

	intercept		slope		R^2
	value	error	value	error	
H_b	22.81	0.58	-8063.79	170.67	0.9973
H_c	24.80	0.44	-8663.49	135.73	0.9985
H_a	23.13	0.57	-8179.57	177.88	0.9972
H_d	22.79	0.60	-8063.60	185.99	0.9968
H_e	24.87	0.49	-8736.96	151.51	0.9982

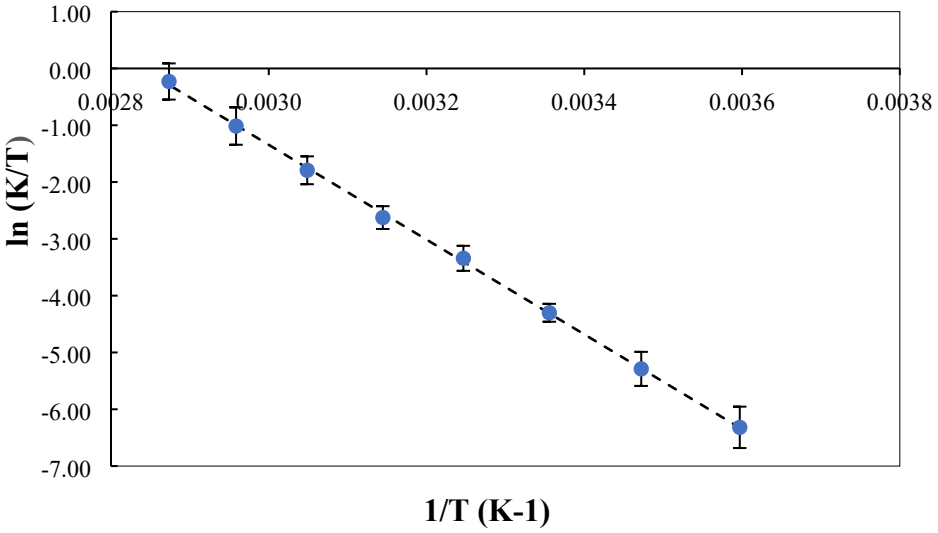

Figure S19: Eyring plot obtained for a 2 mM solution of $[Ag_{24}Au(DMBT)_{18}]^-$ for temperatures ranging between 278 to 348 K and the average exchange rates extrapolated from the simulated VT spectra (Fig. S13, Table S3 and S4). The regression shown in the graph is $ln\frac{k}{T}$ = -8.341.5 $\frac{1}{T}$ + 23.68 with R^2 = 0.9995. Error bars represent the standard deviation (average on all the 5 DMBT proton signals). The data for each individual signal is reported in the *Table S8.*

Table S8: Fitting parameters for each of the DMBT protons in $[Ag_{24}Au(DMBT)_{18}]^-$ 2 mM.

	intercept		slope		R^2	$\Delta H^‡$ (kcal·mol^{-1})	$\Delta S^‡$ (kcal·mol^{-1}·K^{-1})
	value	error	value	error			
H_b	22.81	0.58	-8063.79	170.67	0.9973	-16.02	-1.88
H_c	24.80	0.44	-8663.49	135.73	0.9985	-17.22	2.06
H_a	23.13	0.57	-8179.57	177.88	0.9972	-16.25	-1.26
H_d	22.79	0.60	-8063.60	185.99	0.9968	-16.02	-1.93
H_e	24.87	0.49	-8736.96	151.51	0.9982	-17.36	2.21

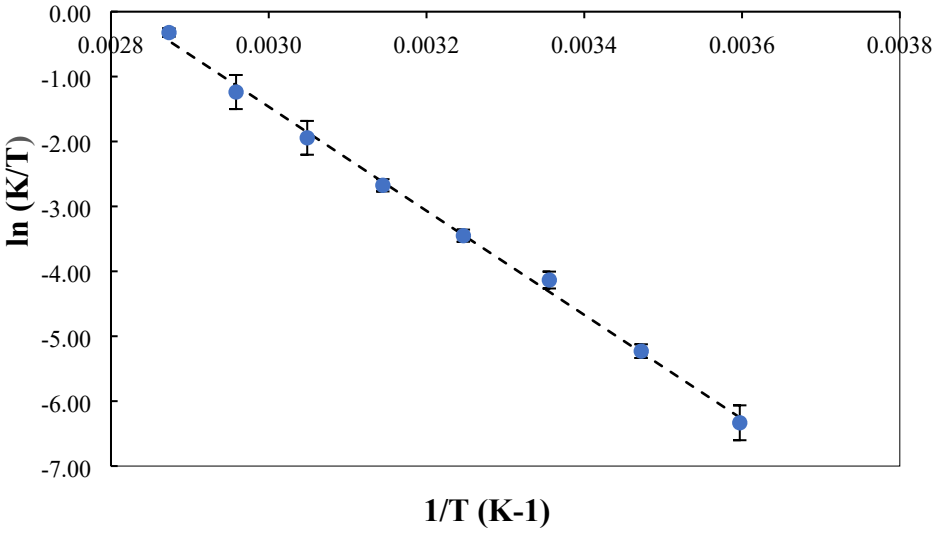

Figure S20: Eyring plot obtained for a 0.67 mM solution of $[Ag_{24}Au(DMBT)_{18}]^-$ for temperatures ranging between 278 to 348 K and the average exchange rates extrapolated from the simulated VT spectra (Fig. S15, Table S5 and S6). The regression shown in the graph is $ln\frac{k}{T} = -8014.8\frac{1}{T} + 22.579$ with $R^2 = 0.9973$. Error bars represent the standard deviation (average on all the 5 DMBT proton signals). The data for each individual signal is reported in the *Table S9.*

Table S9: Fitting parameters for each of the DMBT protons in $[Ag_{24}Au(DMBT)_{18}]^-$ 0.67 mM.

	intercept		slope		R^2	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (kcal·mol^{-1}·K^{-1})
	value	error	value	error			
H_b	22.70	0.76	-8066.98	236.94	0.9949	16.03	-2.11
H_c	22.16	0.54	-7885.20	169.16	0.9972	15.67	-3.17
H_a	22.09	0.73	-7876.14	227.30	0.9950	15.65	-3.31
H_d	23.51	0.66	-8285.68	203.68	0.9964	16.46	-0.49
H_e	22.43	0.43	-7959.98	134.69	0.9983	15.82	-2.65

4. Other NMR experiments

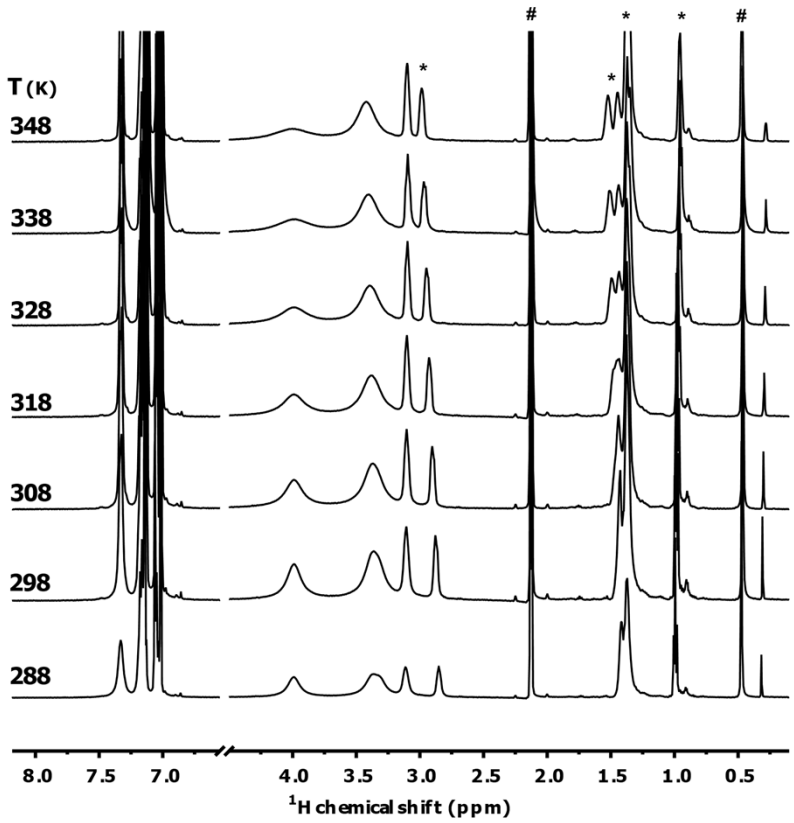

Figure S21: ^{1}H NMR (400 MHz) in toluene-d_8 of the variable temperature experiment (288 to 348 K with 10 K increments) for a 2 mM solution of $[Au_{25}(PET)_{18}]^{-}$. Like in the case of $[Au_{25}(Oct)_{18}]^{-}$ presented in the main text, no peak coalescence is detectable during the VT experiment suggesting no ligand rearrangement (in fast exchange regime).

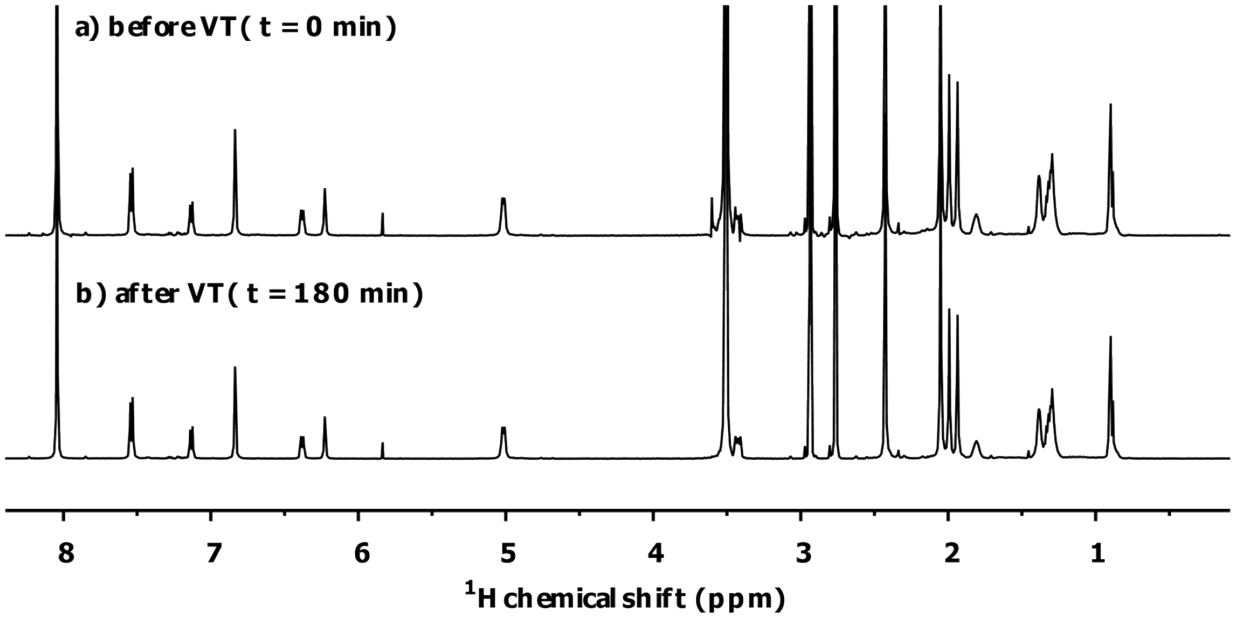

Figure S22: ^{1}H NMR (400 MHz) spectra in of $[Ag_{25}(DMBT)_{18}][TOA]$] in dimethylformamide-d_7 acquired at 298 K before (a, t = 0 min) and after (b, t = 180 min) the VT experiment. Stability test.

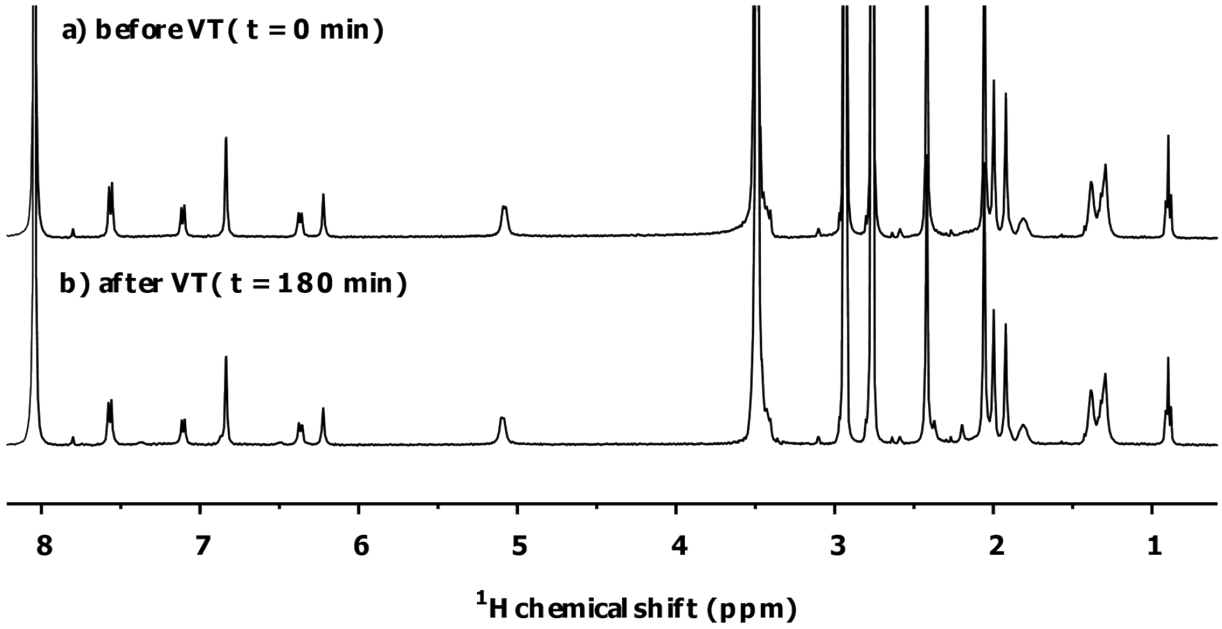

Figure S23: ^{1}H NMR (400 MHz) spectra of $[Ag_{24}Au(DMBT)_{18}][TOA]$ in dimethylformamide-d_7 acquired at 298 K before (a, t = 0 min) and after (b, t = 180 min) the VT experiment. Stability test.

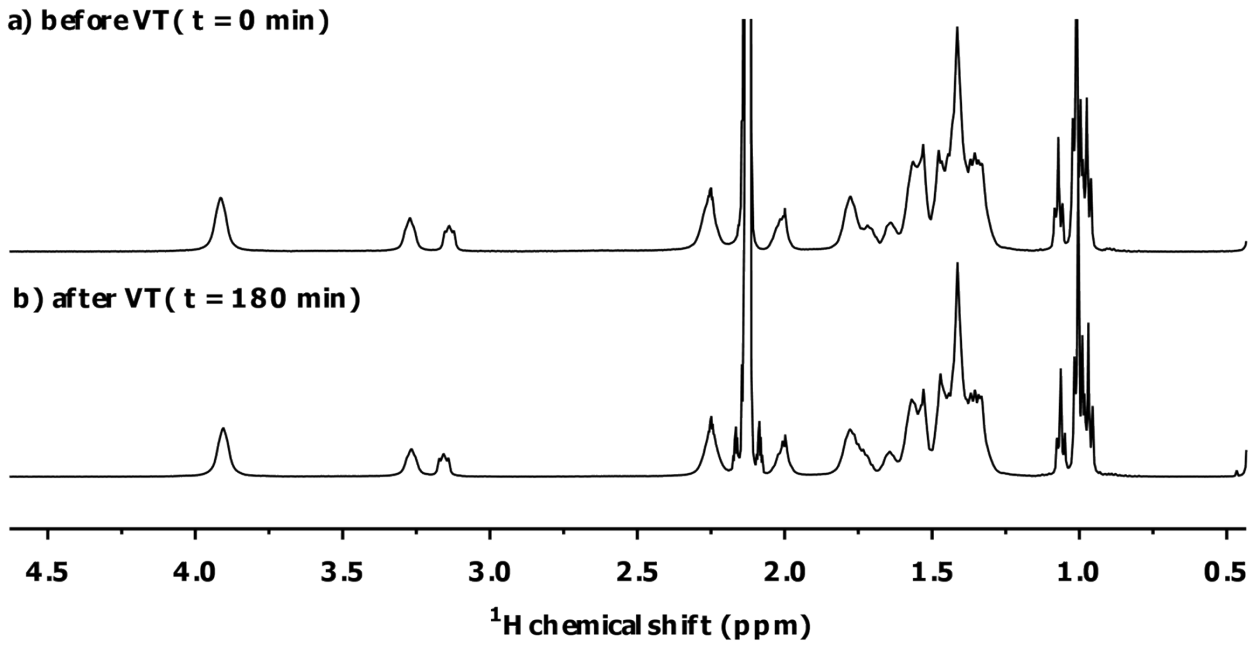

Figure S24: ^{1}H NMR (400 MHz) spectra of $[Au_{25}(Oct)_{18}][TOA]$ in toluene-d_8 acquired at 298 K before (a, t = 0 min) and after (b, t = 180 min) the VT experiment. Stability test.

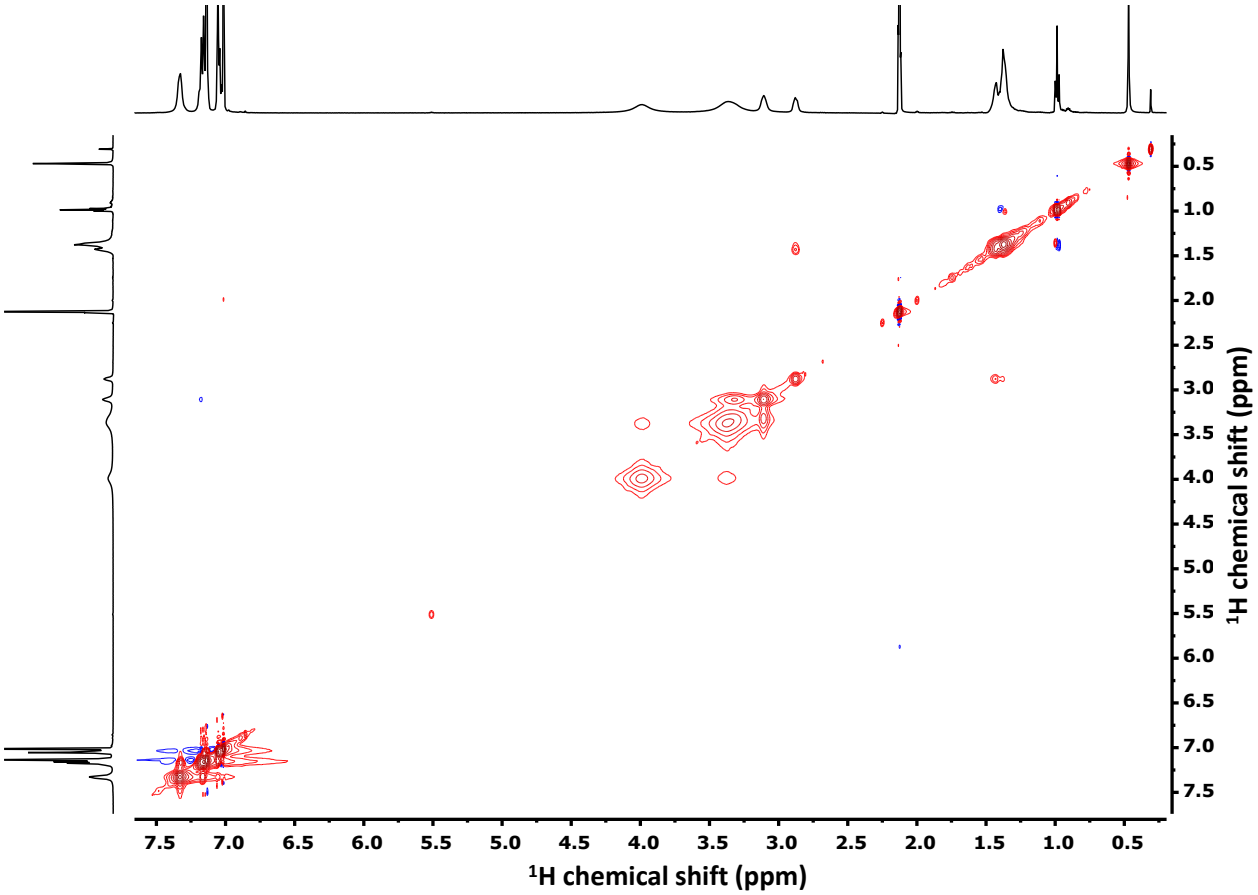

Figure S25: ^{1}H-^{1}H NMR (500 MHz) spectra in of $[Au_{25}(PET)_{18}][TOA]$ in toluene-d_8 acquired at 298 K showing no cross peaks between the *IN* and *OUT* positions, therefore no exchange.

5. Bibliography

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