SUPPLEMENTARY MATERIAL

Experimental part:

General

Reagents and solvents were commercially available and were used as received. K_2PtCl_4, purchased from Strem Chemicals. Elemental analyses were performed at LCC on a Perkin-Elmer 2400 Serie II. Infra-red spectra were obtained with a Perkin Elmer GX 2000 spectrometer.

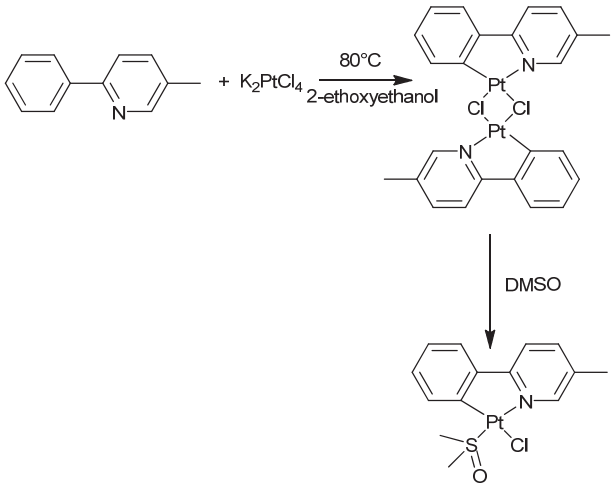
Mass spectrometry: Positive-ion electrospray mass spectra were obtained by MS by using an API 365 Sciex PerkinElmer instrument. The detection was scan mode (total ionic current) with a step size of 0.10 atomic units (amu) and scan range of 600-2500.

Electron Paramagnetic Resonance (EPR): EPR data were recorded using an Elexsys E 500 Bruker spectrometer, operating at a microwave frequency of approximately 9.5 GHz. All spectra were recorded using a microwave power of 80 mW across a sweep width of 150 mT (centred at 310 mT) with a modulation amplitude of 2 mT. Experiments were carried out at 110 K using a liquid nitrogen cryostat.

Nuclear Magnetic Resonance (RMN). 1D ^1H were recorded on a Bruker Avance 500 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI 1H, 31P, BB). Suppression of the water signal was achieved with WATERGATE or presaturation sequences. Diffusion measurements were made using the stimulated echo pulse sequence with bipolar gradient pulses.

Synthesis

Ligand : 2-Phenyl-5-methylpyridine was prepared as previously reported.[1]



Scheme 1.

We used the synthesis described by Gobbert et al.[2] for the Platinum complex.

(2-phenyl-5-methylpyridine)Pt(DMSO) Cl

^{1}H ($CDCl_3$): 9.46(s, 1H, J_{PtH} 34Hz); 8.36(dd, 1H, J_{HH} 6Hz J_{HH} 2Hz, J_{PtH} 42Hz); 7.71(dd, 1H, J_{HH} 8.2Hz, J_{HH} 1.5Hz); 7.66(d,1H, J_{HH} 8.2Hz); 7.50(dd, 1H, J_{HH} 6.8Hz, J_{HH} 1.4Hz); 7.24-7.21(m, 2H); 3.67(s, 6H, J_{PtH} 22Hz); 2.42(s, 3H).

^{13}C(DMSO d6): 163.0; 149.2; 145.0; 142.5; 140.2; 133.9; 133.0; 130.0; 125.4; 124.4; 119.5; 40.9; 18.4

Microanalysis: Found C 35.50; H 3.30; N 3.24. Calc. for C14H16NOSClPt: C 35.26; H 3.38; N 2.94%.

IR (ATR, cm^{-1}): 3054(w), 3003(w), 2917(w), 1609(m), 1583(m), 1496(m),1439(m), 1407(m), 1381(m), 1314(m), 1243(m), 1127(vs), 1018(s), 980(s), 941(m), 923(m), 830(s), 771(vs), 726(vs), 690(s);

Crystals were obtained after slow evaporation of a concentrated DMSO solution of the complex.

Crystallographic data collection.

Molecular structure of complex III is shown in Figure S1 and selected bond lengths and angles are listed in Table 1. Complex III crystallises in the triclinic P-1 space group and the asymmetric unit contains eigth independent molecules that differ mainly in the planarity of the ligand. Indeed, the dihedral angles between the two aromatic rings of the ligand, for

different molecules, vary in the range 4.26°-16.16. The platinum is located in a slightly distorded square-planar environnement and is surrounded by the nitrogen ligand bound trans to the sulfur atom of the solvent molecule.

The crystallographic data were collected at low temperature 180(2)K on a Bruker Kappa APEX II diffractometer using Mo Kα radiation (λ=0.71073 Å) and equipped with an Oxford Cryosystems cooler device. The structure was solved by direct methods using SHELXS97 [3] and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL-97.[4] All hydrogens atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $W = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$. Molecular structure was drawn using ORTEP.[5] Crystal data and details of collection and refinement are given in table S1.

Similar structures on cycloplatinated complexes with the phenylpyridine ligand have been reported.[2] In fact the presence of the methyl group on the pyridine ting has no influence on the geometry around the metal.[6]

Table S1. Crystal data for complex **1**

	Complex 1
Chemical formula	C14H16NOPtSCl
Formula weight	476,88
Crystal system	triclinic
Space group	*P-1*
a (Å)	17.388(2)
b (Å)	18.740(2)
c (Å)	20.159(2)
α (°)	100.511(5)
β (°)	113.597(4)
γ (°)	90.274(5)
V ($Å^3$)	5896.5(11)
Z	16
ρcalc (Mgm^{-3})	2.149
θ range (°)	5.1 - 26,37
μ (mm^{-1})	9.832
Reflections collected	105032
Independent reflections	23731
R*int*	0.0307
Goodness of fit	1.003
R1 (I>2σ(I))	0.0222
wR^2 (all data)	0.0411
Largest difference peak and hole ($eÅ^{-3}$)	1,272 and -1,273

$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR^2 = [\Sigma w(|Fo^2|-|Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

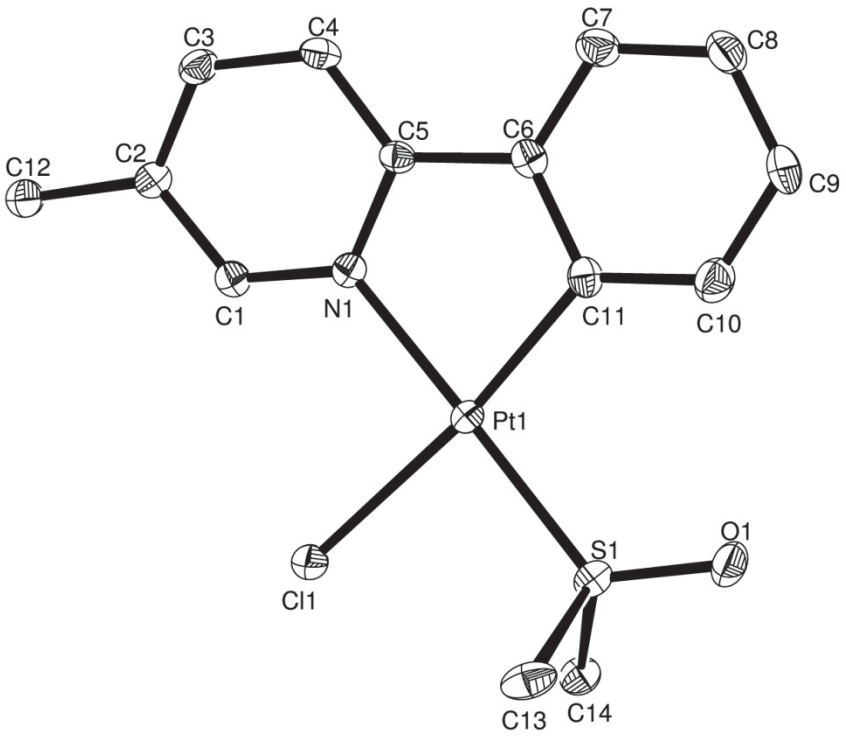


Figure S1. ORTEP view of one of the eight independent molecules of complex III present in the asymmetric unit. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.Selected distances (Å): Pt-C11: 1.994(4)-2.014(4); Pt-N: 2.043(3)-2.068(3); Pt-Cl: 2.395(1)-2.409(1); Pt-S: 2.211(1)-2.222(1). Selected angles (°): C11-Pt-N: 80.45(15)-80.91(14); C11-Pt-S: 98.06(12)-99.55(11); C11-Pt-Cl: 172.37(14)-173.65(12); N-Pt-S: 174.32(9)-178.52(9).

CCDC-853886 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

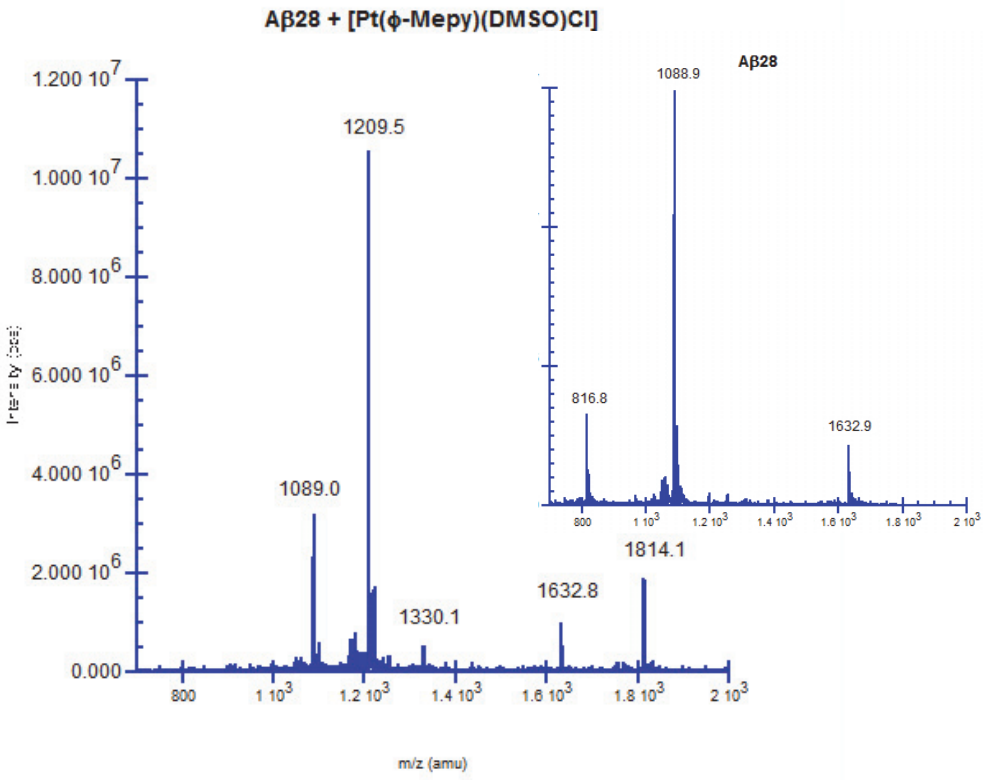


Figure S2. ESI-MS spectra of $A\beta_{28}$ (inset) and $A\beta_{28}$ + complex **1**. The aqueous mixture of $A\beta_{28}$ was prepared by mixing equivalent amounts of $A\beta_{28}$ and complex **1** in $(NH_4)H_2PO_4$ 0.8mM, after adjustment of pH to 7.4 with a final concentration of 0.05 mM. The mixture was incubated at 8°C for 12 hours.

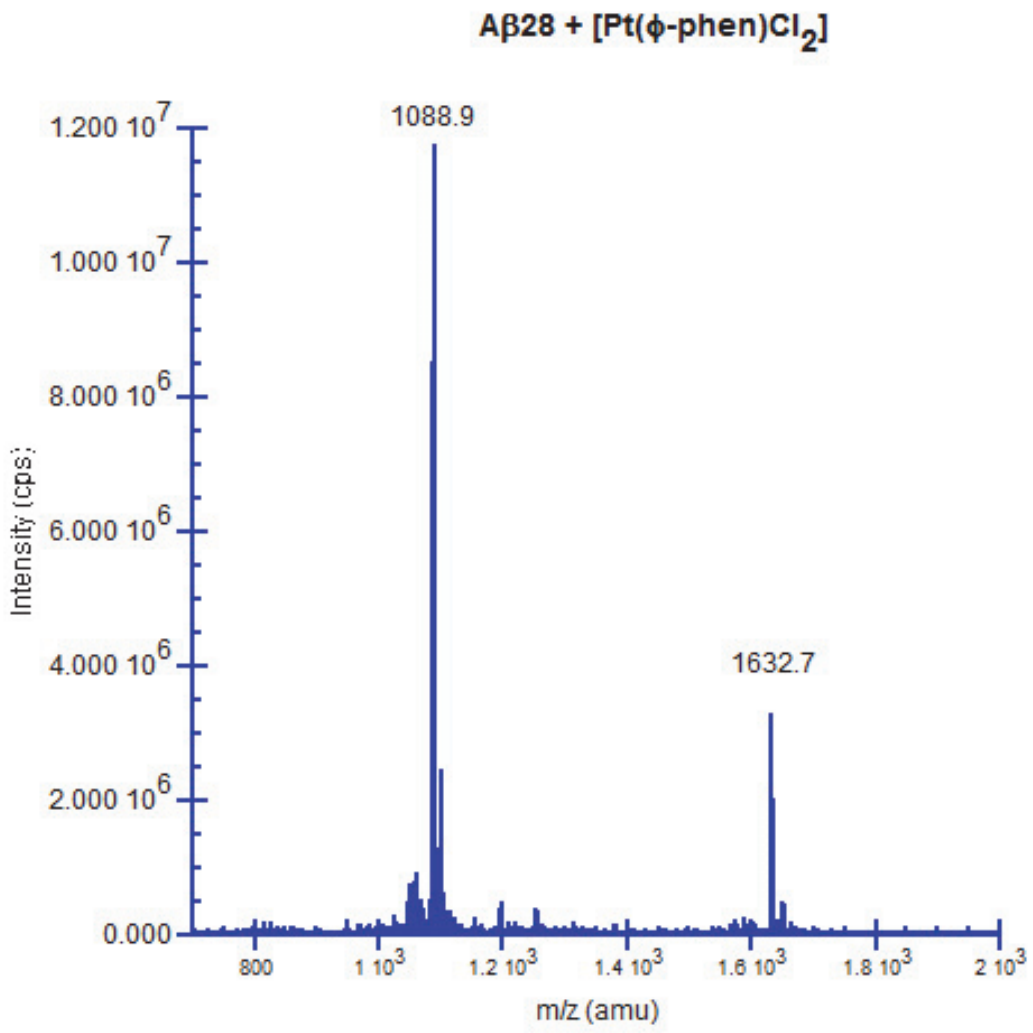


Figure S3. ESI-MS spectra of $A\beta_{28}$ + complex **2**. The aqueous mixture of $A\beta_{28}$ was prepared by mixing equivalent amounts of $A\beta_{28}$ and complex **2** in $(NH_4)H_2PO_4$ 0.8mM, after adjustment of pH to 7.4 with a final concentration of 0.05mM. The mixture was incubated at 8°C for 12 hours.

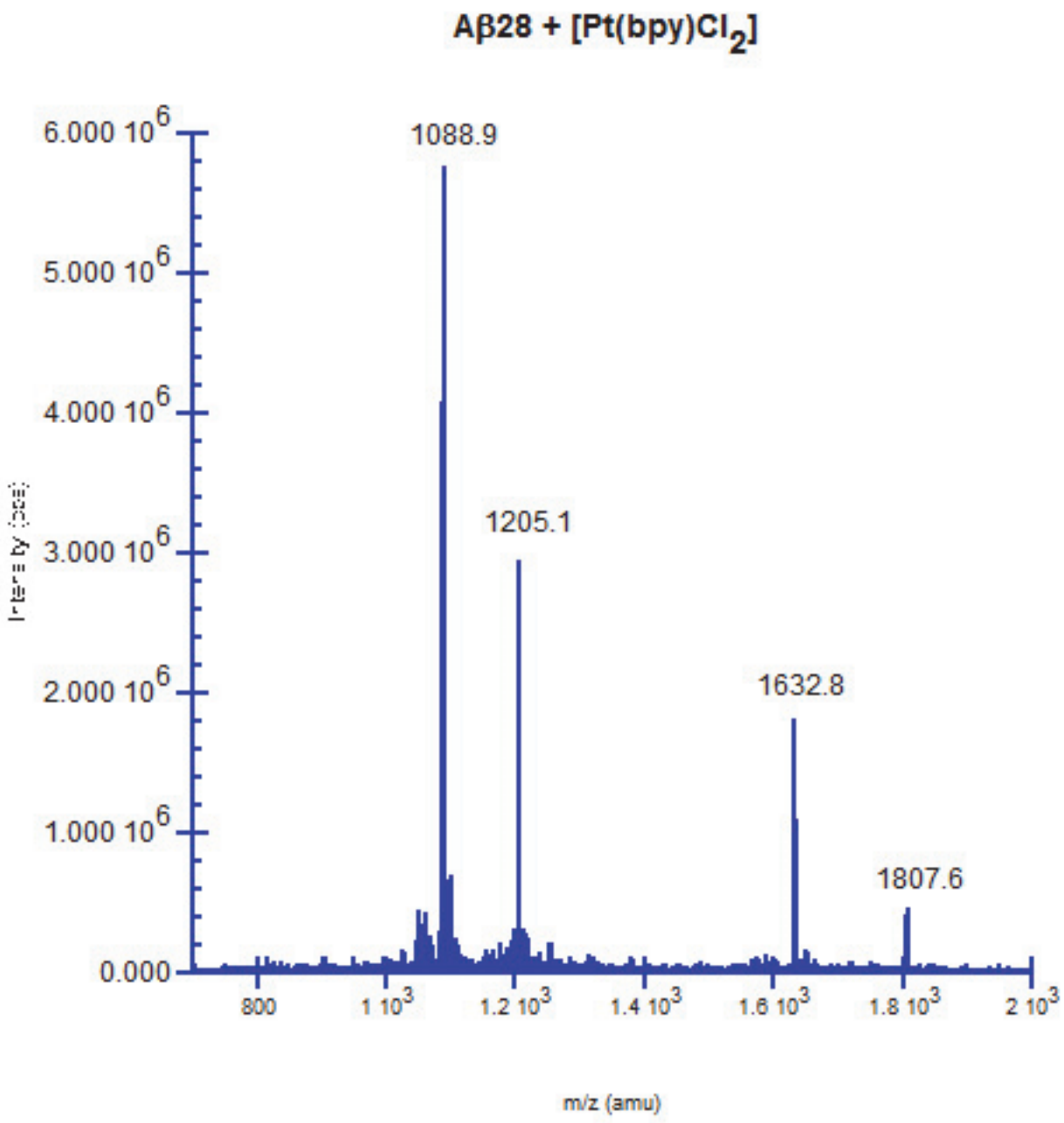


Figure S4. ESI-MS spectra of $A\beta_{28}$ + complex **3**. The aqueous mixture of $A\beta_{28}$ was prepared by mixing equivalent amounts of $A\beta_{28}$ and complex **3** in $(NH_4)H_2PO_4$ 0.8mM, after adjustment of pH to 7.4 with a final concentration of 0.05mM. The mixture was incubated at 8°C for 12 hours.

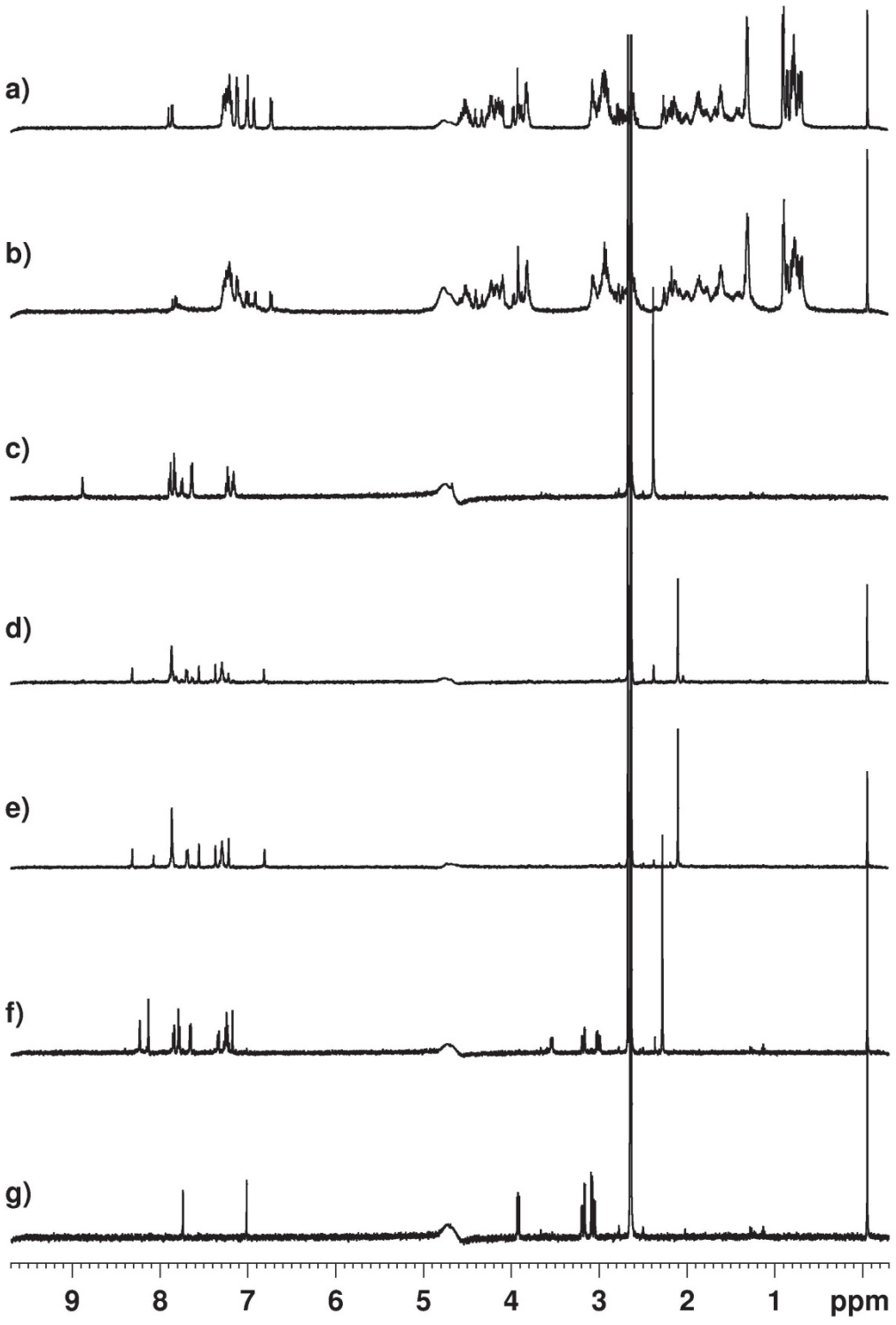


Figure S5. ^{1}H NMR spectra of (a) $A\beta_{28}$; (b) $A\beta_{28}$ after addition of one equiv. of complex **1**; (c) complex **1**; (d) complex **1** + 0.9 equiv. of imidazole; (e) complex **1** + 2 equiv. of imidazole; (f) complex **1** + 1 equiv. of L-histidine; (g) L-histidine at pH 7.4 in phosphate buffer 20 mM, T = 298K.

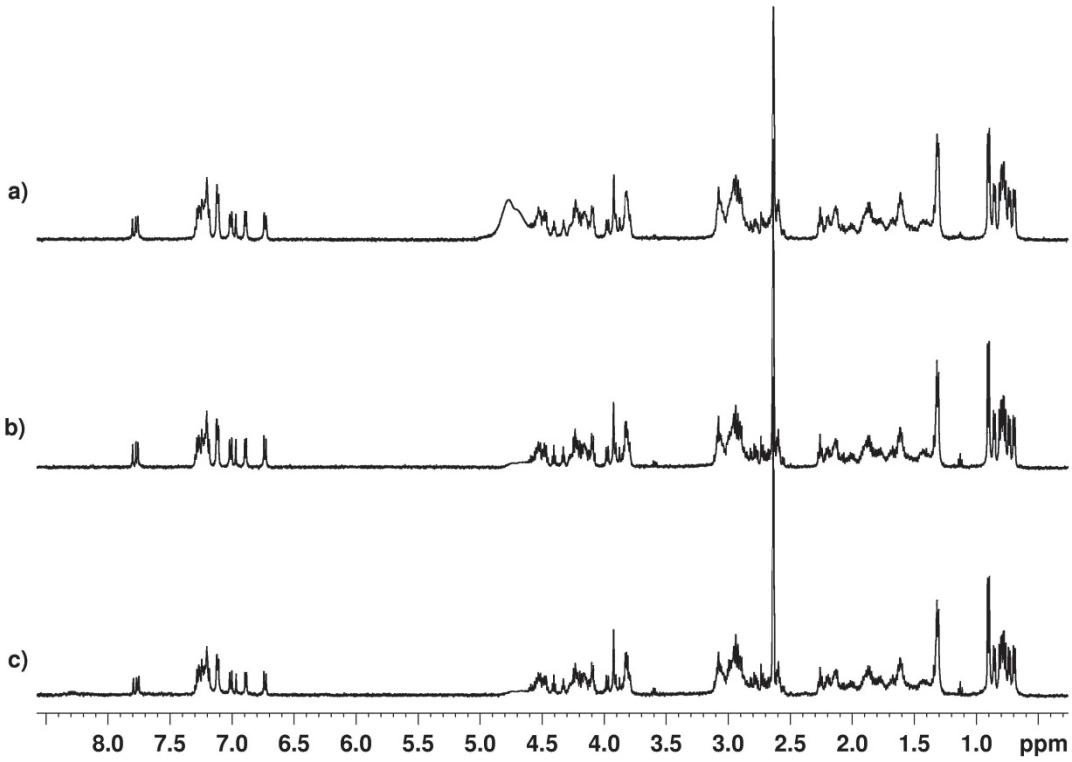


Figure S6. ^{1}H NMR spectrum of $A\beta_{28}$ (a) after addition of one equiv. of the different complexes at pH 7.4 in phosphate buffer 20 mM, T = 298K. From top to bottom: (a) 0.20mM $A\beta_{28}$; (b) after addition of 1.0 equiv. of complex **2**; (c) after addition of 1.0 equiv of complex **3**.

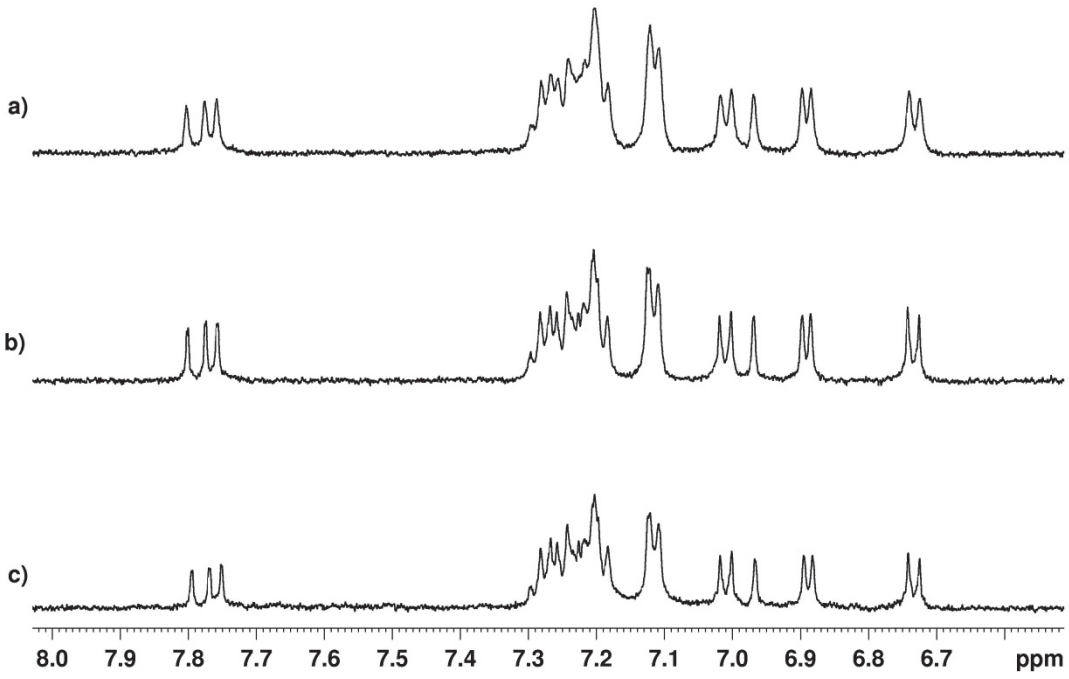


Figure S7. ^{1}H NMR spectrum of Aβ_{28} (a) after addition of one equiv. of the different complexes at pH 7.4 in phosphate buffer 20 mM, T = 298K. From top to bottom: (a) 0.20mM Aβ_{28}; (b) after addition of 1.0 equiv. of complex **1**; (c) after addition of 1.0 equiv of complex **2**; (d) after addition of 1.0 equiv. of complex **3**. Aromatic region.

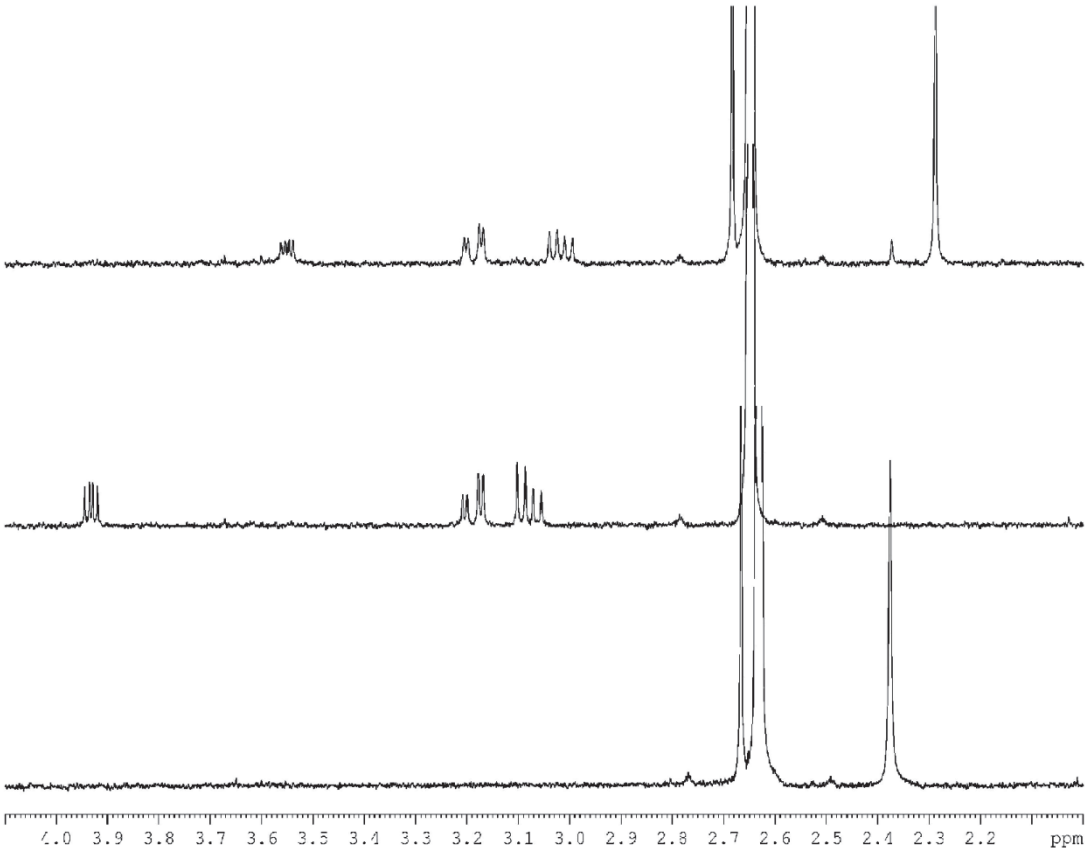


Figure S8. ^{1}H NMR spectrum of complex **1** at pH 7.4 in phosphate buffer 20 mM, T = 298K, NaCl 150mM, after addition of one equivalent of L-histidine (final concentration 0.2mM). Bottom: complex **1**; middle: L-histidine; top: complex **1** immediately after addition of one equivalent of L-histidine.

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Electronic Supplementary Material (ESI) for Dalton Transactions