Supporting Information

Peptide-coated, self-assembled $M_{12}L_{24}$ coordination spheres and their immobilization onto an inorganic surface

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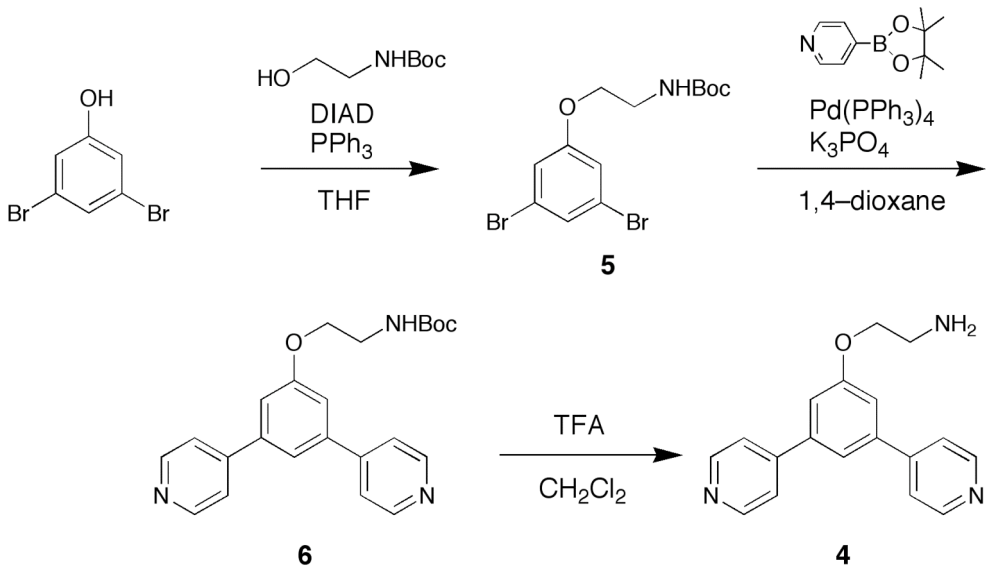
1. General procedure

NMR spectra were recorded on a Bruker DRX-500 equipped with 5 mm BBO gradient probe, on a Bruker AV-500 equipped with TCI gradient CryoProbe, on a JEOL JNM-ECA300 spectrometer equipped with TH5 probe with a z-field gradient coil, or on a JEOL JNM-ECA600 spectrometer equipped with HCN Cold Probe with a z-field gradient coil (53040HCNVC). ^{1}H NMR spectra were referenced internally to tetramethylsilane as a standard unless otherwise noted. ^{13}C NMR spectra were referenced to the solvent resonance, and methyl, methylene, and methyne signals were assigned by DEPT spectra. MALDI-TOF MS (Matrix-Assisted Laser Desorption Ionization time-of-flight Mass Spectrometry) was performed on an Applied Biosystems BioSpectrometry Workstation model Voyager-DE STR spectrometer. IR measurements were carried out as KBr pellets using a DIGILAB FTS-7000 instrument. Melting points were determined on a Yanaco MP-500V melting-point apparatus. Elemental analyses were performed on a Yanaco MT-6. Solvents and reagents were purchased from TCI Co., Ltd., and WAKO Pure Chemical Industries Ltd. Fmoc amino acids and some reagents for the peptide synthesis were purchased from Watanabe Chemical Industries Ltd. All chemicals were used without any further purification. Automated peptide synthesis was performed on a Applied Biosystems ABI 433A. Peptides were purified on a reversed phase HPLC system equipped with a Develosil ODS preparative column (ODS-15/30 (50 × 500 mm), *NOMURA CHEMICAL*). High resolution ESI-TOF MS (ElectroSpray Ionization time-of-flight Mass Spectrometry) and MS/MS analyses for peptide derivatives were performed on a Bruker maXis®. The data analyses of the high resolution mass spectra were processed on a Bruker DataAnalysis (Version 4.0 SP 2) software and the simulations were performed on a Bruker IsotopePattern software. The data analyses of the MS/MS spectra were processed on a Bruker BioTools (Version 3.1). QCM (quartz crystal microbalance) measurements were performed on a Q-Sense AB QCM-D300 instrument using a Ti sputter-coated QCM sensor. UV/Ozone surface treatment was performed on a BioForceNanosciences Inc. ProCleaner. AFM images on a single-crystalline TiO_2 plate (1 × 1 cm^2 from K & R Creation) were collected on an Asylum Research MFP-3D-Bio microscope.

2. Materials and methods

· Syntheses and physical properties of compounds 4–6

Ligand 4 was synthesized as follows:



Synthesis of *tert*-butyl 2-(3,5-dibromophenoxy)ethylcarbamate 5:

To a mixture of 3,5-dibromophenol (254 mg, 1.01 mmol), *tert*-butyl 2-hydroxyethylcarbamate (277 mg, 1.72 mmol), and triphenylphosphine (346 mg, 1.32 mmol) in tetrahydrofuran (30 mL), diisopropyl azodicarbonate (236 μL, 1.20 mmol) was added at 0 ºC under argon atmosphere. The reaction mixture was stirred at r. t. for 18 h. The reaction mixture was evaporated, diluted with chloroform, washed with water and saturated brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution from hexane:ethyl acetate = 10:1 to 5:1) to give the title compound as colorless oil (332 mg, 0.840 mmol) in 84% yield. Elemental Analysis, Found: C, 39.6; H, 4.4; N, 3.4. Calc. for $C_{13}H_{17}Br_2NO_3$: C, 39.5; H, 4.3; N, 3.55%; IR (KBr, cm^{-1}) 2979, 2935, 2876, 1692, 1528, 1453, 1393, 1367, 1281, 1252, 1173, 1069, 867, 778; ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 7.24 (s, 1H), 6.97 (s, 2H), 5.06 (s, NH, 1H), 3.98 (t, J = 4.9 Hz, 2H), 3.51 (d, J = 4.7 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K) δ 159.70 (C), 155.78 (C), 126.74 (CH), 123.13 (C), 116.92 (CH), 79.65 (C), 67.78 (CH_2), 39.87 (CH_2), 28.37 (CH_3).

Synthesis of *tert*-butyl 2-(3,5-di(pyridin-4-yl)phenoxy)ethylcarbamate 6:

A mixture of *tert*-butyl 2-(3,5-dibromophenoxy)ethylcarbamate **5** (1.58 g, 4.00 mmol), 4-pyridylboronic acid pinacol ester (2.30 g, 11.2 mmol), Tetrakis(triphenylphosphine)palladium(0) (463 mg, 0.400 mmol), and potassium phosphate (6.76 g, 31.8 mmol) in 1,4-dioxane (100 mL) was stirred at 90 ºC for 3 days under argon atmosphere. The reaction mixture was diluted with chloroform and filtered. The filtrate was evaporated, diluted with chloroform, washed with water and saturated brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution from chloroform:methanol = 100:1 to 25:1) and by phase separation (chloroform /hexane) to give the title compound as yellow powder (1.40 g, 3.57 mmol) in 89% yield. Elemental Analysis, Found: C, 70.0; H, 6.6; N, 10.2. Calc. for $C_{23}H_{25}N_3O_3 \cdot 0.3H_2O \cdot 0.1$Hexane: C, 69.9; H, 6.7; N, 10.4%; mp 164–166 ºC; IR (KBr, cm^{-1}) 3036, 2978, 2935, 1707, 1690, 1594, 1548, 1501, 1441, 1404, 1366, 1348, 1274, 1254, 1202, 1171, 1078, 1056, 994, 954, 872, 814, 674, 611; MALDI-TOF MS (matrix: dithranol) *m/z* Calcd. for $[M + H]^+$: 392.20 Found: 392.44; ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 8.70 (d, *J* = 4.7 Hz, 4H), 7.53 (d, *J* = 5.2 Hz, 4H), 7.46 (s, 1H), 7.22 (s, 2H), 5.12 (s, -NH, 1H), 4.18 (t, *J* = 4.6 Hz, 2H), 3.61 (d, *J* = 4.6 Hz, 2H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K) δ 159.84 (C), 155.93 (C), 150.44 (C), 147.68 (C), 140.72 (C), 121.74 (CH), 118.62 (CH), 113.77 (CH), 79.73 (C), 67.65 (CH_2), 40.11 (CH_2), 28.41 (CH_3).

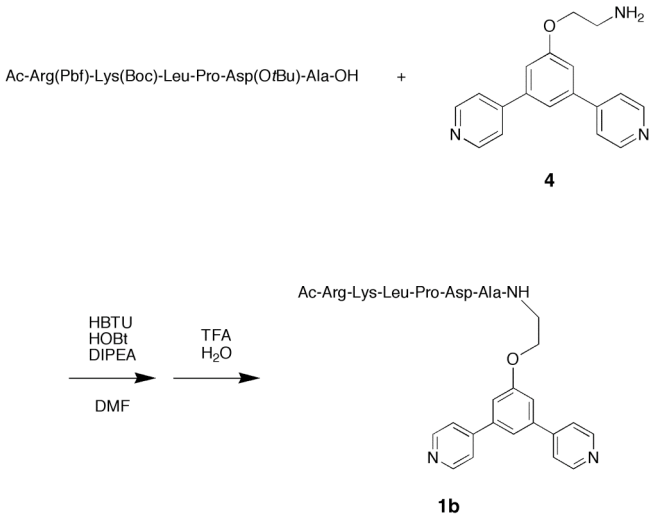
Synthesis of 2-(3,5-di(pyridin-4-yl)phenoxy)ethanamine 4:

A mixture of *tert*-butyl 2-(3,5-di(pyridin-4-yl)phenoxy)ethylcarbamate **6** (586 mg, 1.50 mmol) in trifluoroacetic acid (3 mL) and dichloromethane (12 mL) was stirred at r. t. for 2 h. The reaction mixture was neutralized with aqueous solution of potassium carbonate, diluted with chloroform and washed with saturated brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give the title compound as yellow powder (392 mg, 1.35 mmol) in 90% yield. Elemental Analysis, Found: C, 73.4; H, 6.0; N, 13.9. Calc. for $C_{18}H_{17}N_3O \cdot 0.25H_2O$: C, 73.1, ; H, 6.0; N, 14.2%; mp 189–190 ºC; IR (KBr, cm^{-1}) 3025, 1593, 1549, 1442, 1404, 1342, 1335, 1206, 1078, 1013, 994, 942, 917, 878, 814, 611; ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 8.70 (d, *J* = 6.2 Hz, 4H), 7.53 (d, *J* = 6.2 Hz, 4H), 7.45 (t, *J* = 1.4 Hz, 1H), 7.24 (d, *J* =

1.3 Hz, 2H), 4.14 (t, *J* = 5.2 Hz, 2H), 3.17 (t, *J* = 5.4 Hz, 2H), 1.39 (s, NH, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K) δ 160.17 (C), 150.43 (CH), 147.79 (C), 140.69 (C), 121.76 (CH), 118.47 (CH), 113.80 (CH), 70.70 (CH_2), 41.54 (CH_2)

· Synthesis and physical properties of ligands 1b,c

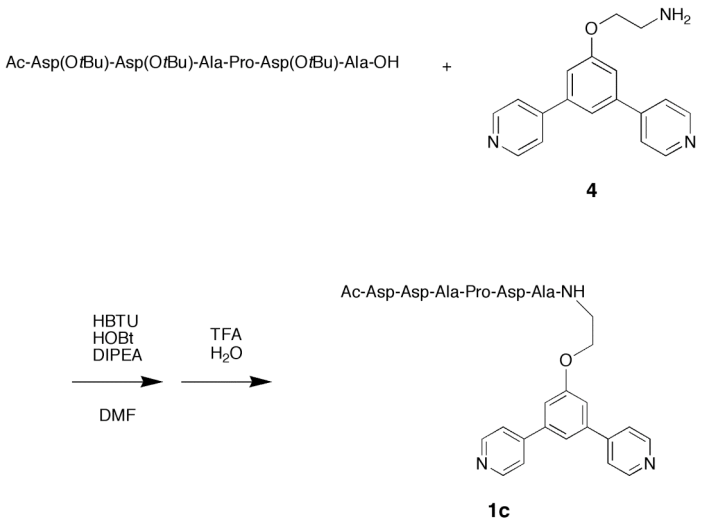
Ligand 1b was synthesized as follows:



Protected peptide was synthesized on an automated peptide synthesizer using the standard Fmoc-based FastMoc coupling chemistry in a 0.25 mmol scale. Protected peptides were cleaved from the resin with 5 mL of a mixture of acetic acid/trifluoroethanol/dichloromethane (2:2:6) at r. t. for 2 h. The cleaved protected peptides were filtrated and separated from the resin using the cleavage solution. The filtrate was diluted with a large amount of hexane and evaporated. The residue was dissolved with chloroform and washed with saturated brine. The protected peptide was used in the following reaction without further purification. To a mixture of the protected peptide, HBTU (114 mg, 0.300 mmol), HOBt (41 mg, 0.30 mmol), *N*,*N*-diisopropylethylamine (174 μL, 1.00 mmol) in *N*,*N*-dimethylformamide (10 mL) was added compound **4** (87 mg, 0.300 mmol). The reaction mixture was stirred for 1 day at r. t. and evaporated, diluted with chloroform, washed with 4% sodium hydrogen carbonate aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. To the residue was added trifluoroacetic acid (TFA, 10 mL containing 5% (v/v) water) to cleave the protecting groups of peptides at r. t. for 1.5 h. To the residue, about 20 mL of ether was added, and the precipitate was collected by filtration. The crude product was purified by reversed phase HPLC using aqueous 0.1% TFA and

methanol in a gradient elution method, and white powder of ligand **1b** as TFA salt (209 mg, 0.206 mmol) was obtained by lyophilization in 57% yield. Elemental Analysis, Found: C, 45.15; H, 5.6; N, 11.75. Calc. for $C_{50}H_{71}N_{13}O_{10}$·4TFA·4H_2O: C, 45.2; H, 5.4; N, 11.8%; mp 145–147 ºC; IR (KBr, cm^{-1}) 3080, 2970, 1673, 1640, 1546, 1529, 1513, 1431, 1347, 1202, 1132, 1080, 992, 882, 800, 722, 610; High Resolution ESI-TOF MS *m/z* Calcd. for $[M + 2H]^{2+}$: 507.7796 Found: 507.7792 (error = 0.8 ppm); The sequence of amino acids was confirmed by MS/MS fragmentation patterns (Fig. S15); 4,4-Dimethyl-4-silapentane-1-sulfonic acid, sodium salt (DSS) was used as an external standard. ^{1}H NMR (D_2O, 600 MHz, 300 K) δ 8.87 (d, *J* = 6.4 Hz, 4H), 8.41 (d, *J* = 6.2 Hz, 4H), 8.01 (s, 1H), 7.72 (s, 2H), 4.60 (dd, *J* = 3.5, 3.7 Hz, 1H), 4.54 (t, *J* = 6.7 Hz, 1H), 4.39–4.31 (m, 4H), 4.28–4.23 (m, 2H), 3.85–3.60 (m, 4H), 3.20 (t, *J* = 4.7, 6.9 Hz, 2H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.80–2.67 (m, 2H), 2.30–2.20 (m, 1H), 2.03 (s, 3H), 2.02–1.95 (m, 2H), 1.90–1.83 (m, 1H), 1.82–1.50 (m, 12H), 1.48–1.40 (m, 2H), 1.38 (d, *J* = 8.1 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (D_2O, 75 MHz, 300 K) δ 175.85 (C), 175.13 (C), 175.10 (C), 174.82 (C), 174.57 (C), 174.24 (C), 173.59 (C), 172.74 (C), 160.68 (C), 157.79 (C), 157.56 (C), 142.22 (CH), 138.43 (C), 125.86 (CH), 121.39 (CH), 118.16 (CH), 67.97 (CH_2), 61.37 (CH), 54.27 (CH), 53.85 (CH), 51.08 (CH), 51.05 (CH), 50.99 (CH), 48.61 (CH_2), 41.40 (CH_2), 40.00 (CH_2), 39.70 (CH_2), 39.61 (CH_2), 36.28 (CH_2), 31.04 (CH_2), 30.03 (CH_2), 28.95 (CH_2), 26.99 (CH_2), 25.45 (CH_2), 25.21 (CH), 25.18 (CH_2), 23.20 (CH_3), 22.81 (CH_2), 22.39 (CH_3), 21.20 (CH_3), 17.38 (CH_3)

Ligand 1c was synthesized as follows:



Protected peptide was synthesized by an automated peptide synthesizer using the standard Fmoc-based FastMoc coupling chemistry in a 0.25 mmol scale. Protected peptides were cleaved from the resin with 5 mL of a mixture of acetic acid/trifluoroethanol/dichloromethane (2:2:6) at r. t. for 2 h. Protected peptides were filtered and separated from the resin with the cleavage solution. The filtrate was diluted with a large amount of hexane and evaporated. The residue was dissolved with chloroform and washed with saturated brine. The protected peptide was used in the following reaction without further purification. To a mixture of the protected peptide, HBTU (114 mg, 0.300 mmol), HOBt (41 mg, 0.30 mmol), *N*,*N*-diisopropylethylamine (174 μL, 1.00 mmol) in *N*,*N*-dimethylformamide (10 mL) was added compound **4** (87 mg, 0.300 mmol). The reaction mixture was stirred for 1 day at r. t., evaporated, diluted with chloroform, washed with 4% sodium hydrogen carbonate aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. To the residue was added TFA 10 mL containing 5% (v/v) water to cleave the protecting groups of peptides at r. t. for 1.5 h. To the residue, about 20 mL of ether was added, and the precipitate was collected by filtration. The crude product was purified by reversed phase HPLC using aqueous 0.1% TFA and methanol in a gradient elution method, and white powder of ligand **1c** as TFA salt (144 mg, 0.126 mmol) which contains its diastereomer was obtained by lyophilization in 50% yield. Elemental Analysis, Found: C, 45.95; H, 4.9; N, 10.45. Calc. for $C_{43}H_{51}N_9O_{14}$·2TFA·4.5H_2O : C, 46.0; H, 5.1; N, 10.3; mp 155–157 ºC; IR (KBr, cm^{-1}) 3094, 1723, 1666, 1638, 1547, 1526, 1514, 1429, 1347, 1200, 1135, 826, 800, 719; High resolution ESI-TOF MS *m*/*z* Calcd. for $[M + H]^+$: 918.3628: Found: 918.3637 (error = 1.0 ppm); ^{1}H NMR (D_2O, 600 MHz, 300 K) The $CDCl_3$ solution of tetramethylsilane (TMS) was used as an external standard. δ 8.87 (d, *J* = 6.6 Hz, 4H), 8.42 (d, *J* = 6.6 Hz, 4H), 8.01 (d, *J* = 5.6 Hz, 1H), 7.72 (s, 2H), 4.72–4.63 (m, 2H), 4.58–4.48 (m, 2H), 4.39–4.22 (m, 4H), 3.83–3.47 (m, 4H), 2.93–2.66 (m, 6H), 2.24–2.14 (m, 1H), 2.02 (d, *J* = 3.6 Hz, 3H), 1.99–1.93 (m, 1H), 1.86–1.80 (m, 1H), 1.79–1.71 (m, 1H), 1.44–1.26 (m, 6H); ^{13}C NMR (D_2O, 125 MHz, 300 K) δ 175.44 (C), 175.26 (C), 174.69 (C), 174.47 (C), 174.43 (C), 174.31 (C), 174.24 (C), 174.23 (C), 174.21 (C), 174.18 (C), 174.11 (C), 173.14 (C), 173.97 (C), 172.63 (C), 172.62 (C), 171.98 (C), 171.87 (C), 171.75 (C), 171.74 (C), 160.16 (C), 160.12 (C), 157.00 (C), 141.62 (CH), 141.59 (CH), 137.66 (C), 137.65 (C), 125.16 (CH), 120.66 (CH), 120.62 (CH), 117.52 (CH), 117.50 (CH), 67.29 (CH_2), 67.22 (CH_2),

61.06 (CH), 61.04 (CH), 50.66 (CH), 50.46 (CH), 50.39 (CH), 50.37 (CH), 50.26 (CH), 49.99 (CH), 48.38 (CH), 48.32 (CH), 47.86 (CH_2), 39.15 (CH_2), 39.02 (CH_2), 35.39 (CH_2), 35.38 (CH_2), 35.11 (CH_2), 35.07 (CH_2), 29.30 (CH_2), 29.13 (CH_2), 24.91 (CH_2), 24.87 (CH_2), 21.92 (CH_3), 16.75 (CH_3), 16.53 (CH_3), 15.54 (CH_3), 15.53 (CH_3)

· Synthesis and physical properties of spheres 2b,c

Synthesis of sphere 2b: Ligand **1b** (15.4 mg, 10.5 μmol) was treated with $Pd(NO_3)_2$ (1.69 mg, 7.35 μmol) in DMSO (1.05 mL) at 70 ºC for 24 h. The quantitative formation of sphere **2b** was confirmed by ^{1}H NMR. By addition of 8 mL of a mixture of ethyl acetate and ether (1/1) to the solution of sphere **2b**, precipitated white solid was separated by centrifugation, washed with ether, and dried in vacuo to give the title complex in 74% yield. Elemental Analysis, Found: C, 43.95; H, 6.2; N, 12.0. Calc. for $C_{1200}H_{1704}N_{336}O_{312}Pd_{12}$·48TFA·96$H_2O$·48DMSO: C, 43.9; H, 5.9; N, 12.4%; mp > 230 ºC (decomposed); IR (KBr, cm^{-1}) 3070, 2962, 1665, 1545, 1410, 1381, 1202, 1178, 1132, 1024, 953, 833, 801, 719; NMR spectra were referenced to the solvent resonance. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.52 (br, 96H), 8.39 (br, 96H), 8.21 (br, NH), 8.09 (br, NH), 8.07 (br, 24H), 8.00 (br, NH), 7.95 (br, NH), 7.73 (br, NH), 7.64 (br, 48H), 7.59 (br, NH), 4.48 (br, 48H), 4.24 (br, 144H), 3.08 (br, 48H), 2.74 (br, 96H), 2.02 (br, 24H), 1.92 (br, 24H), 1.85 (s, 72H), 1.83 (br, 48H), 1.63 (br, 72H), 1.48 (br, 144H), 1.28 (br, 48H), 1.21 (t, J = 7.9, 7.3 Hz, 48H), 1.17 (d, J = 6.3 Hz, 72H), 0.87 (t, J = 7.1, 6.9 Hz, 144H); ^{13}C NMR (DMSO-d_6, 150 MHz, 300 K) δ 172.33 (C), 171.97 (C), 171.78 (C), 171.47 (C), 171.33 (C), 170.64 (C), 169.95 (C), 169.66 (C), 159.81 (C), 156.83 (C), 151.10 (CH), 149.01 (C), 136.33 (C), 124.28 (CH), 119.24 (CH), 115.72 (CH), 66.86 (CH_2), 59.50 (CH), 52.31 (CH), 51.96 (CH), 49.38 (CH), 48.78 (CH), 48.29 (CH), 46.74 (CH_2), 40.46 (CH_2), 40.04 (CH_2), 38.75 (CH_2), 36.04 (CH_2), 35.65 (CH_2), 31.28 (CH_2), 29.00 (CH_2), 28.95 (CH_2), 26.50 (CH_2), 25.04 (CH_2), 24.44 (CH_2), 24.01 (CH), 23.23 (CH_3), 22.45 (CH_3), 22.15 (CH_2), 21.34 (CH_3), 18.31 (CH_3).

Synthesis of sphere 2c: Ligand **1c** (42.3 mg, 36.9 μmol) was treated with $Pd(NO_3)_2$ (5.10 mg, 22.1 μmol) in DMSO (1.17 mL) at 70 ºC for 24 h. The quantitative formation of sphere **2c** was confirmed by ^{1}H NMR. By addition of 8 mL of a mixture of ethyl acetate and ether (1/1) to the solution of sphere **2c**, precipitated white solid was

separated by centrifugation, washed with ether, and dried in vacuo to give the title complex in 62 % yield. Elemental Analysis, Found: C, 44.7; H, 5.9; N, 10.4. Calc. for $C_{1032}H_{1224}N_{240}O_{408}Pd_{12}\cdot 96H_2O\cdot 60DMSO$: C, 44.3; H, 5.7; N, 10.8%; mp > 225 ºC (decomposed); IR (KBr, cm^{-1}) 3070, 3000, 1721, 1659, 1642, 1615, 1547, 1531, 1513, 1414, 1383, 1350, 1201, 1021, 951, 834, 699, 644; NMR spectra were referenced to the solvent resonance. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.47 (br, 96H), 8.39 (br, 96H), 8.33 (br, NH), 8.22 (t, J = 6.5 Hz, NH), 8.13 (br, NH), 8.09 (br, NH), 8.06 (br, 24H), 7.89 (br, NH), 7.82 (br, NH), 7.80 (br, NH), 7.66 (br, NH), 7.56 (br, 48H), 4.48 (br, 72H), 4.37 (br, 24H), 4.20 (br, 72H), 4.09 (br, 24H), 3.47 (br, 96H), 2.67 (br, 96H), 2.48–2.41 (m, 48H), 1.99 (br, 24H), 1.82 (d, J = 6.7 Hz, 72H), 1.74 (br, 72H), 1.25–1.08 (m, 144H); ^{13}C NMR (DMSO-d_6, 150 MHz, 300 K) δ 172.42(C), 172.35 (C), 172.27 (C), 171.97 (C), 171.85 (C), 171.82 (C), 171.78 (C), 170.84 (C), 170.71 (C), 170.02 (C), 169.92 (C), 169.78 (C), 169.59 (C), 159.79 (C), 151.06 (CH), 149.09 (C), 136.35 (C), 124.31 (CH), 118.54 (CH), 115.44 (CH), 66.59 (CH_2), 60.00 (CH), 49.96 (CH), 49.74 (CH), 49.71 (CH), 49.61 (CH), 49.56 (CH), 49.32 (CH), 49.23 (CH), 48.63 (CH), 48.45 (CH), 46.63 (CH), 40.06 (CH_2), 38.12 (CH_2), 35.96 (CH_2), 35.84 (CH_2), 35.67 (CH_2), 35.53 (CH_2), 28.90 (CH_2), 28.79 (CH_2), 24.50 (CH_2), 24.38 (CH_2), 22.51 (CH_3), 18.07 (CH_3), 17.66 (CH_3), 16.63 (CH_3), 16.48 (CH_3).

· QCM measurement

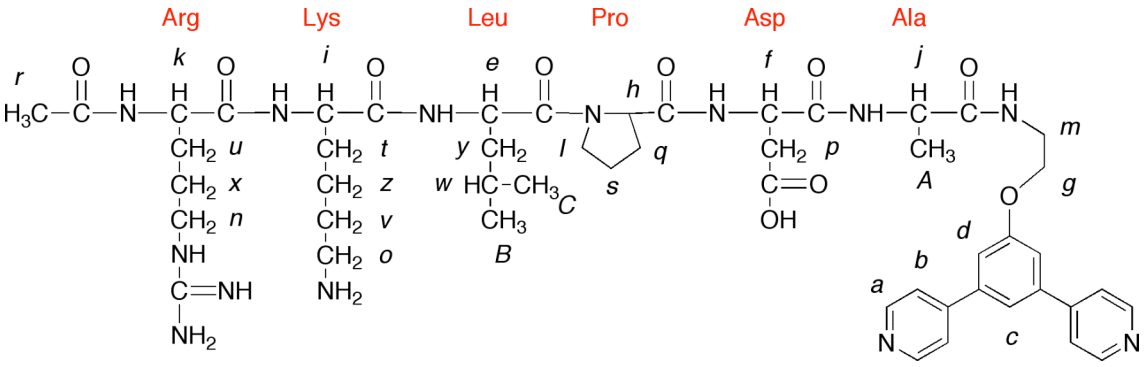
Prior to measurements, the sensor was cleaned for 10 min using a UV/ozone surface treatment system. The measurements were carried out at 25 ºC, and the analytical data were collected at 14.8 MHz. The sensor was first equilibrated with 100 mM HEPES (pH 7.5) buffer and an aqueous solution (H_2O:DMSO = 95:5 (v/v)) buffered with 9.5 mM HEPES (pH 7.5), successively, followed by the injection of an aqueous solution of an analytical sample (H_2O:DMSO = 95:5 (v/v)) buffered with 9.5 mM HEPES (pH 7.5). Energy dissipation accompanying association of sphere **2b** with the Ti sensor is shown in Fig. S16.

· AFM measurement

The microscope was operated in AC mode on aqueous conditions at r. t., using silicon nitride cantilevers (BL-AC40TS-C2, Olympus) with resonance frequencies of approximately 110 kHz, a force constant of about 0.1 N/m, and tip radii less than 10 nm. The images were obtained at scan rate of 1 Hz over a 250 nm × 250 nm scan area with 256 points × 256 lines. Before measurement, a single-crystalline TiO_2 plate was cleaned for 10 min using a UV/ozone surface treatment system. The plate was contacted with a 200 μL diluted solution of sphere **2b** (1 μM) for 5 min and rinsed with water 5 times. The measurements were performed with the cantilever dipped in the water.

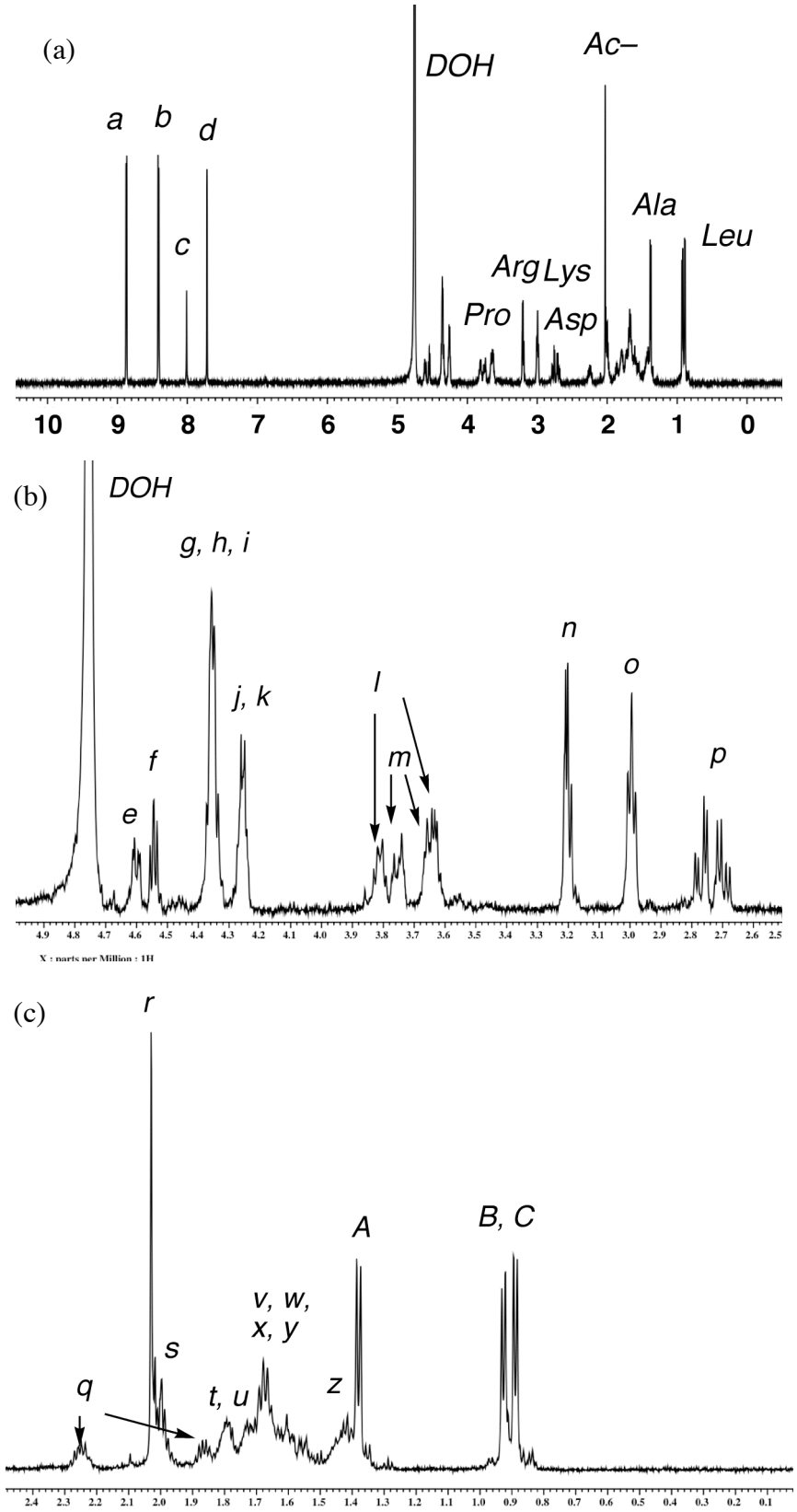
3. NMR spectra of ligands **1b**,**c** and spheres **2b**,**c**

All the signals of ligand 1b were assigned as follows:

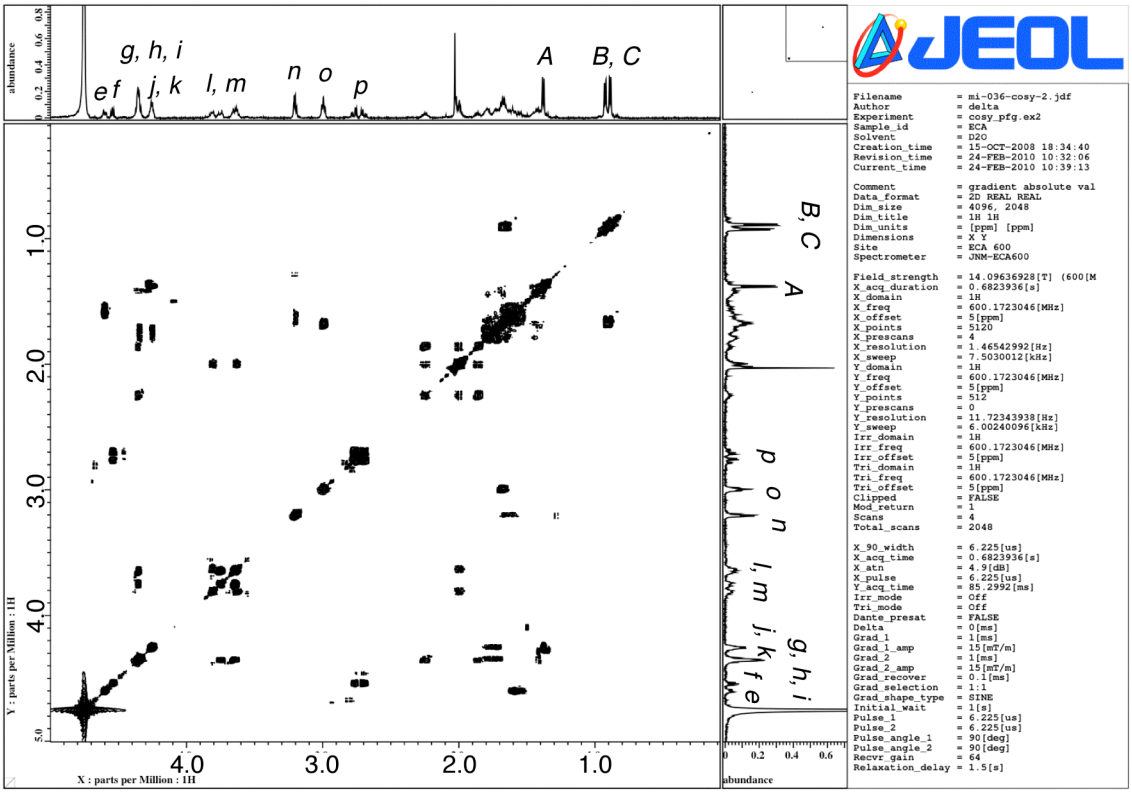


The structure of ligand **1b** and alphabetical labeling of ^{1}H nuclei.

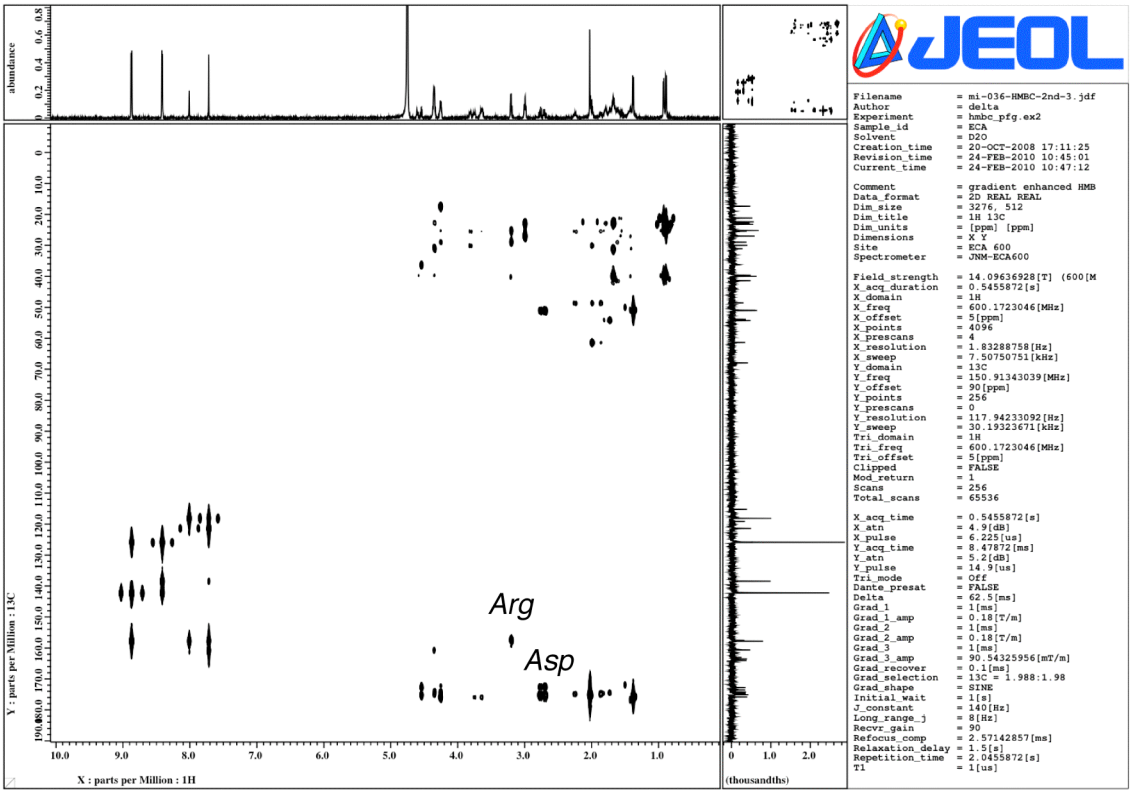
The ^{1}H signal of *p* on Asp residue and that of *n* on Arg residue were assigned by HMBC measurement (Fig. S3). ^{1}H signals of *a*, *b*, *c*, *d*, *g*, *r*, *o*, *A*, *B*, and *C* were assigned by edit–HSQC measurement (Fig. S4). Edit–HSQC–TOCSY spectrum (Fig. S5) and COSY spectrum (Fig. S2) indicated the *J*-coupled correlations of Asp (*p*–*f*), Lys (*o*–*v*–*z*–*t*–*i*), Arg (*n*–*x*–*u*–*k*), Leu (*B*–*w*–*y*–*i* and *C*–*w*–*y*–*i*), Ala (*A*–*j*), Pro (*l*–*s*–*q*–*h*), and (*g*–*m*).



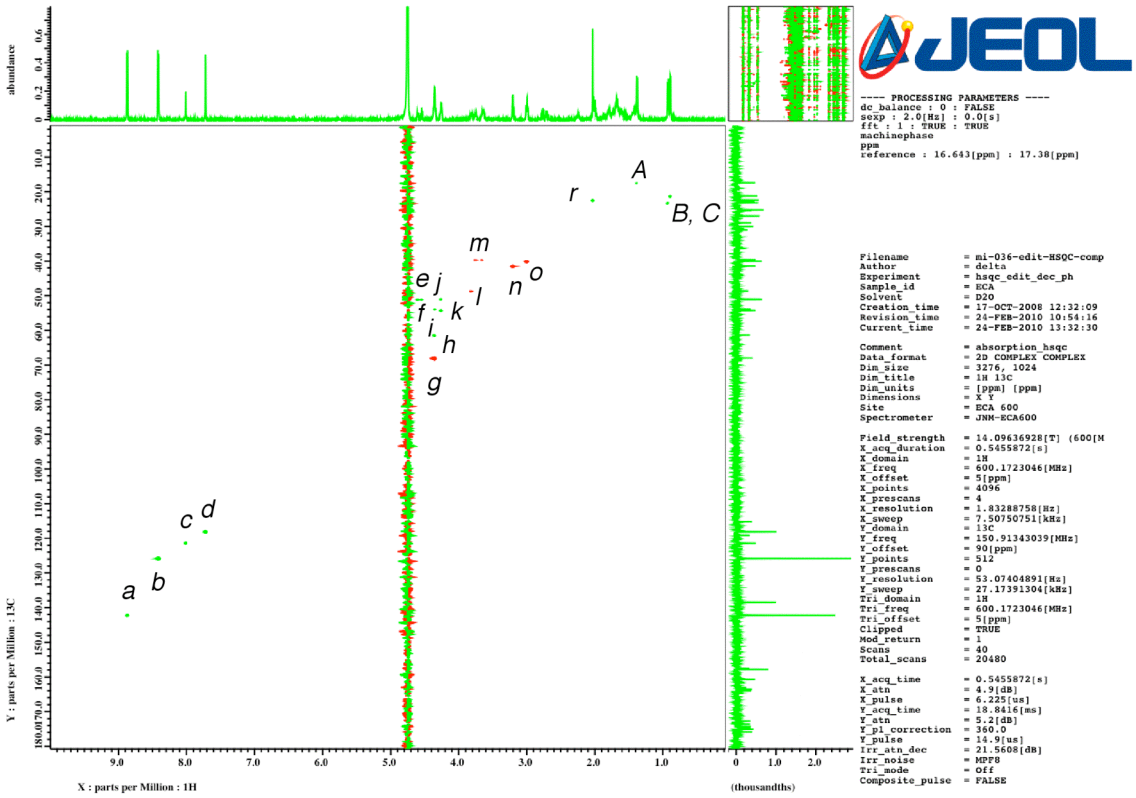
· Fig. S1. ^{1}H NMR spectra of ligand **1b** (a) in a full range, (b) expanded in 5–2.5 ppm, and (c) expanded in 2.5–0 ppm (600 MHz, 300 K, D_2O).



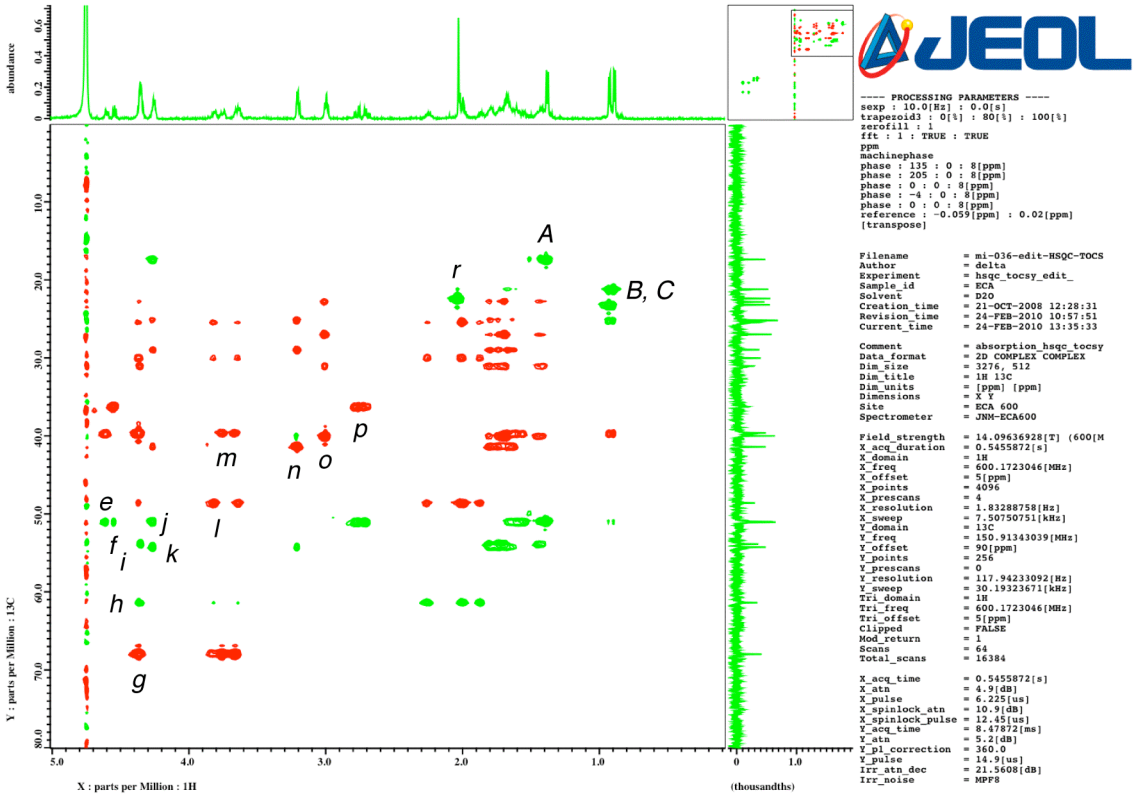
· Fig. S2. ^{1}H–^{1}H COSY spectrum of ligand **1b** (600 MHz, 300 K, D_2O).



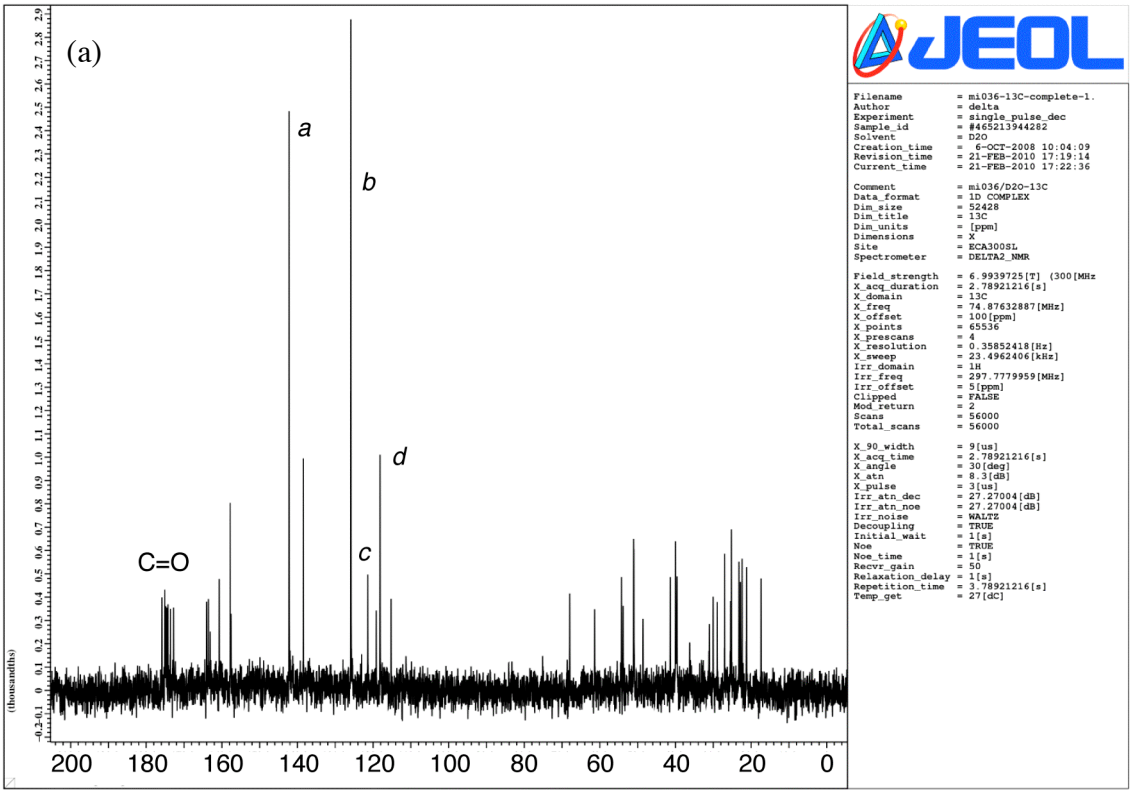
· Fig. S3. ^{1}H–^{13}C HMBC spectrum of ligand **1b** (600 MHz, 300 K, D_2O).

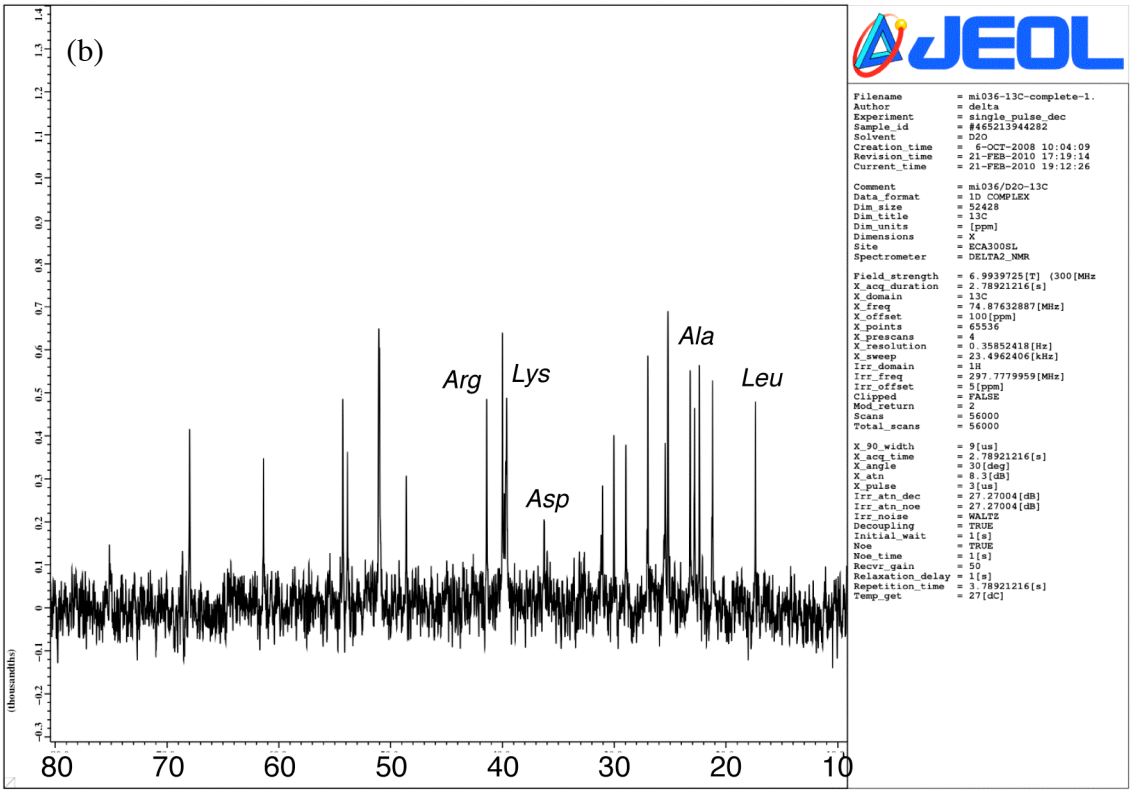


· Fig. S4. Edit–^{1}H–^{13}C HSQC spectrum of ligand **1b** (600 MHz, 300 K, D_2O).

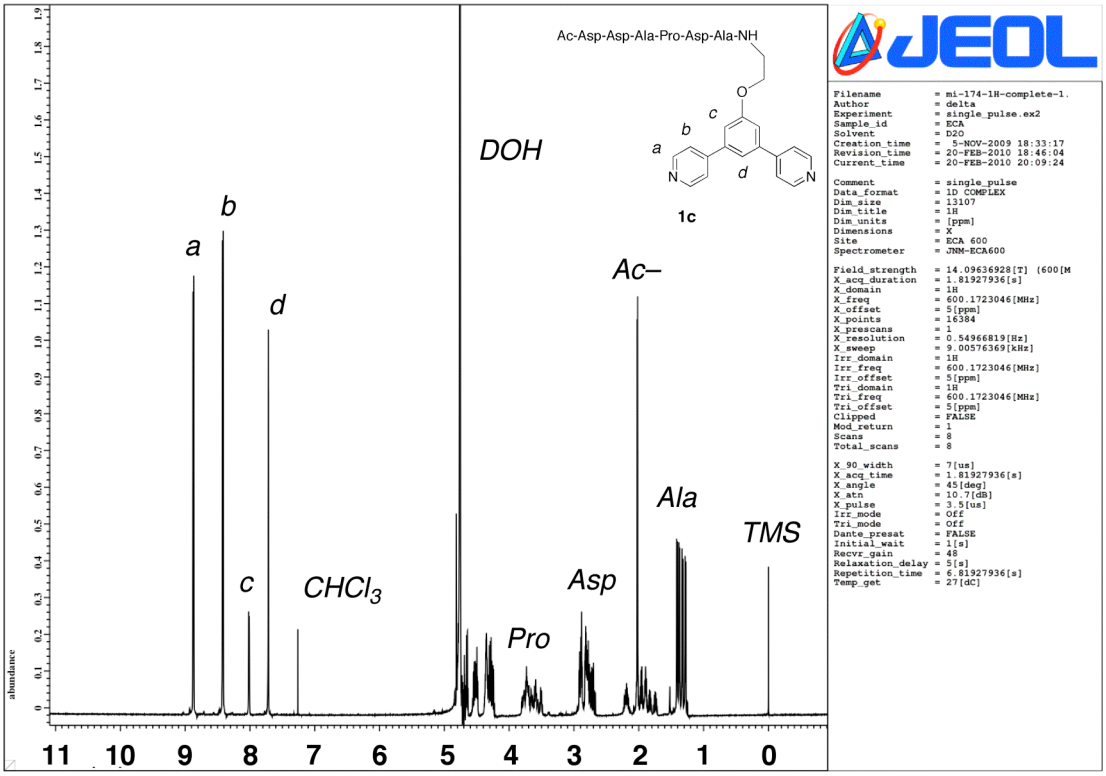


· Fig. S5. Edit–^{1}H–^{13}C HSQC–TOCSY spectrum of ligand **1b** (600 MHz, 300 K, D_2O).

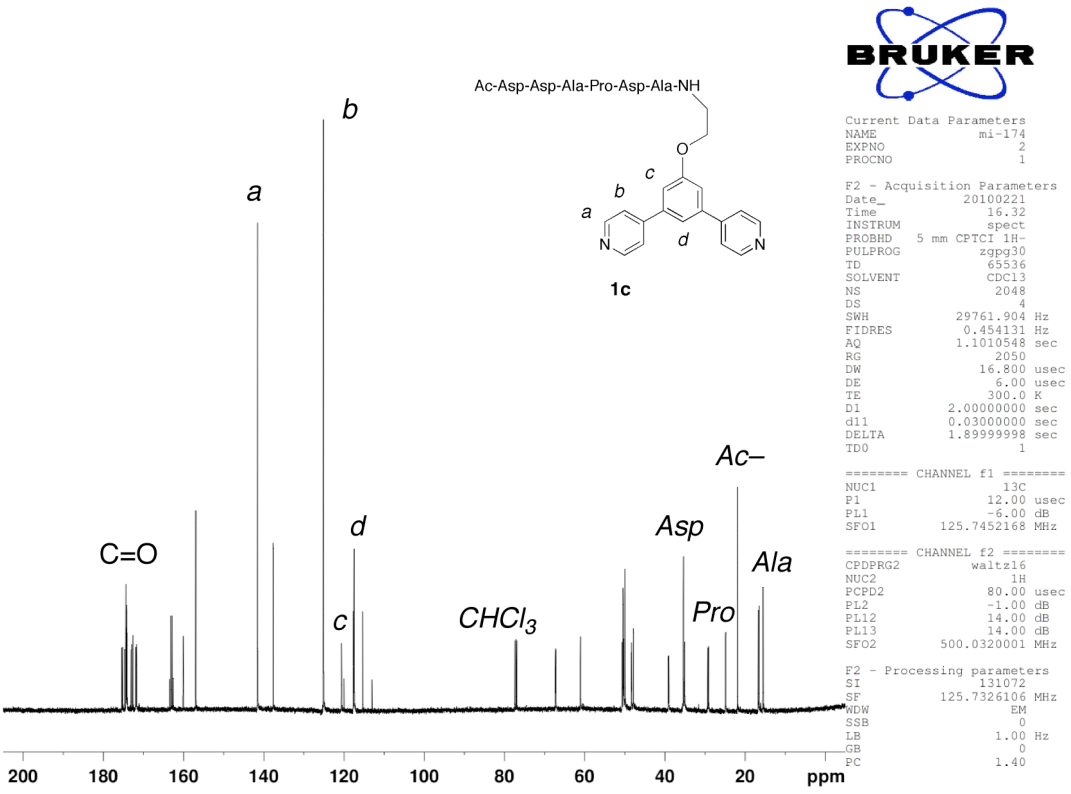




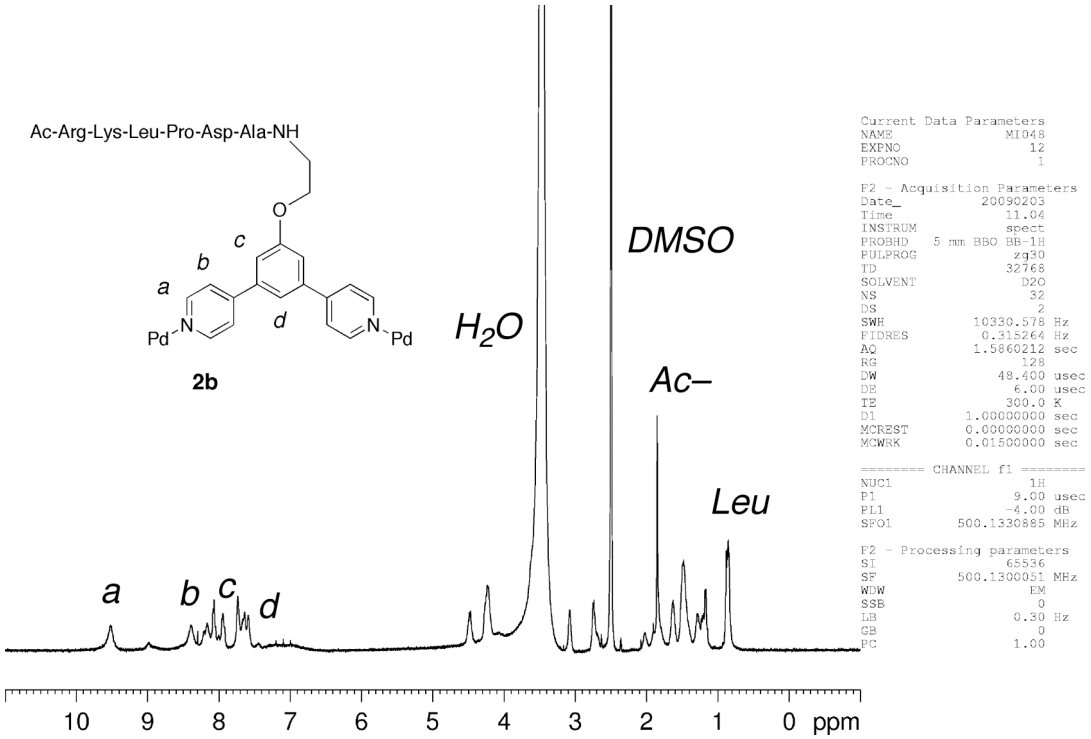
· Fig. S6. ^{13}C NMR spectra of ligand **1b** (a) in a full range and (b) expanded in 80–10 ppm (75 MHz, 300 K, D_2O).



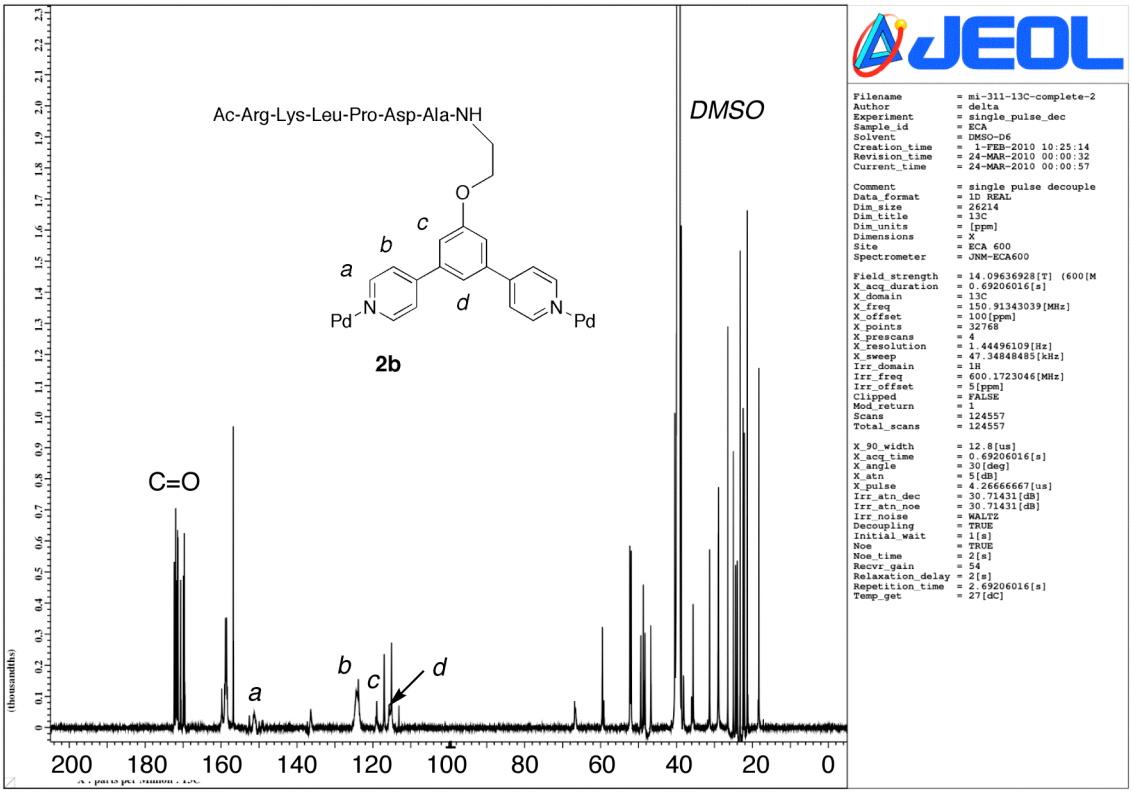
· Fig. S7. ^{1}H NMR spectrum of ligand **1c** (600 MHz, 300 K, D_2O).



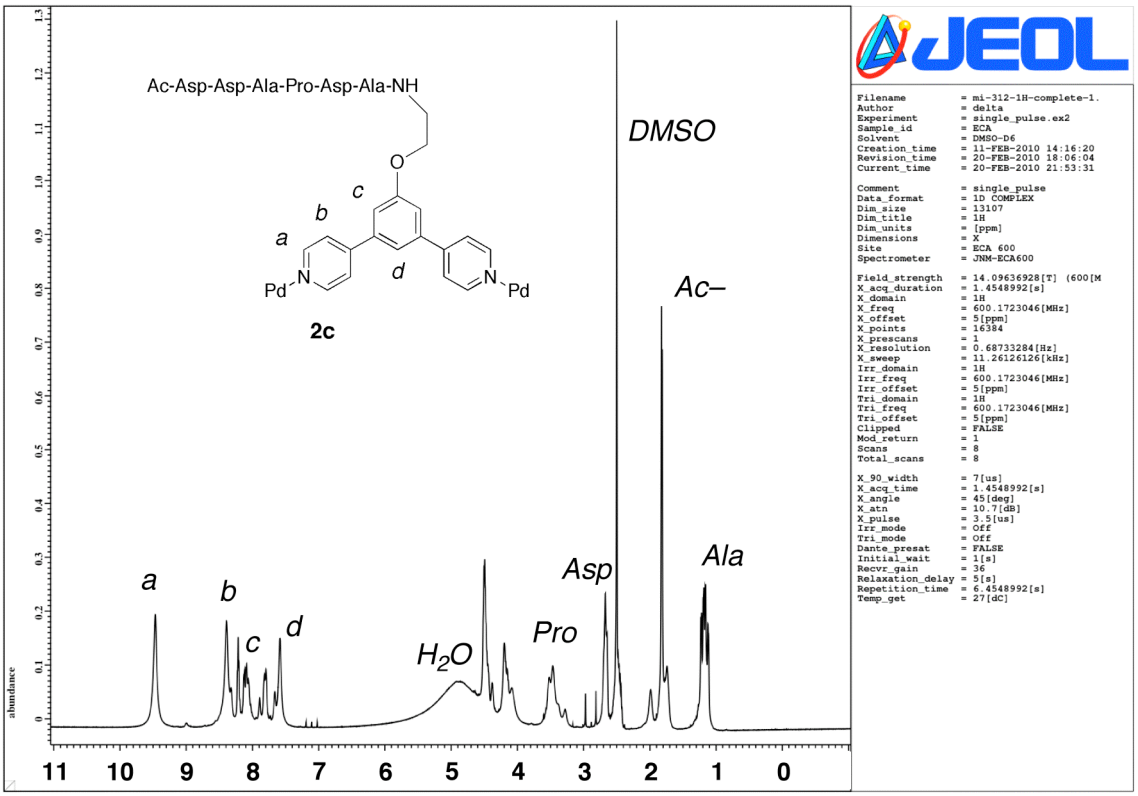
· Fig. S8. ^{13}C NMR spectrum of ligand **1c** (125 MHz, 300 K, D_2O).



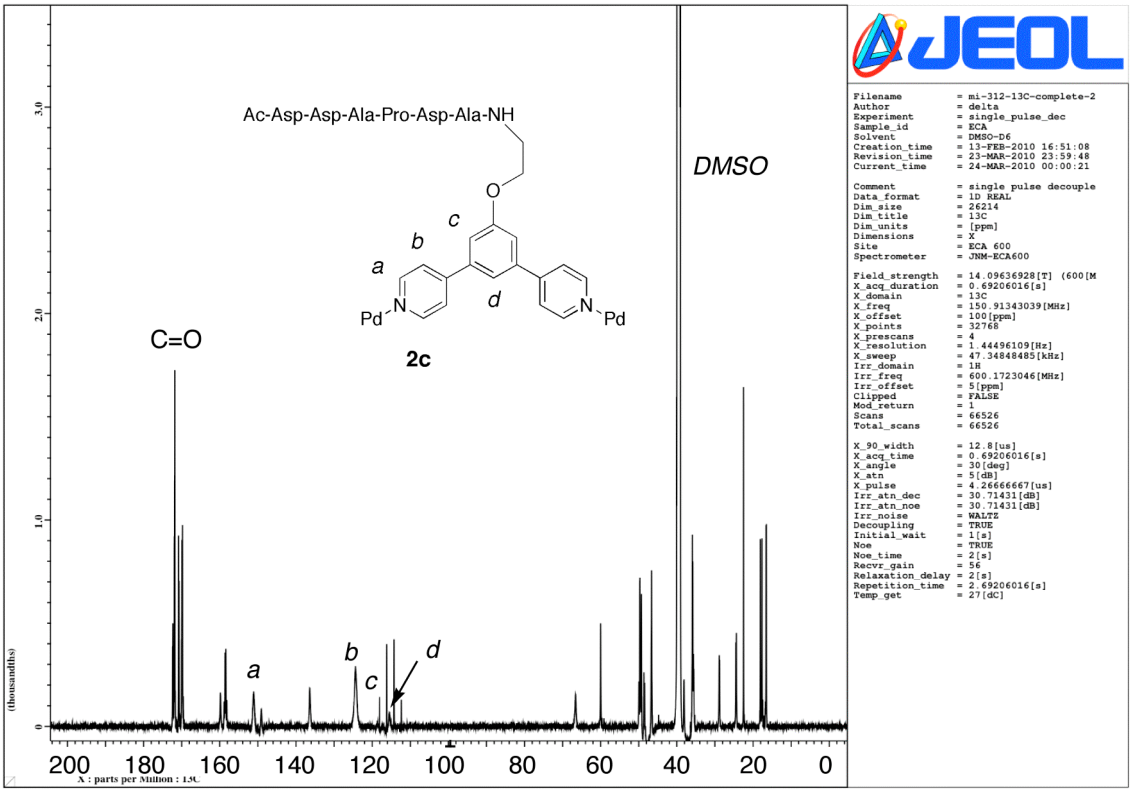
· Fig. S9. ^{1}H NMR spectrum of sphere **2b** (500 MHz, 300 K, DMSO–d_6).



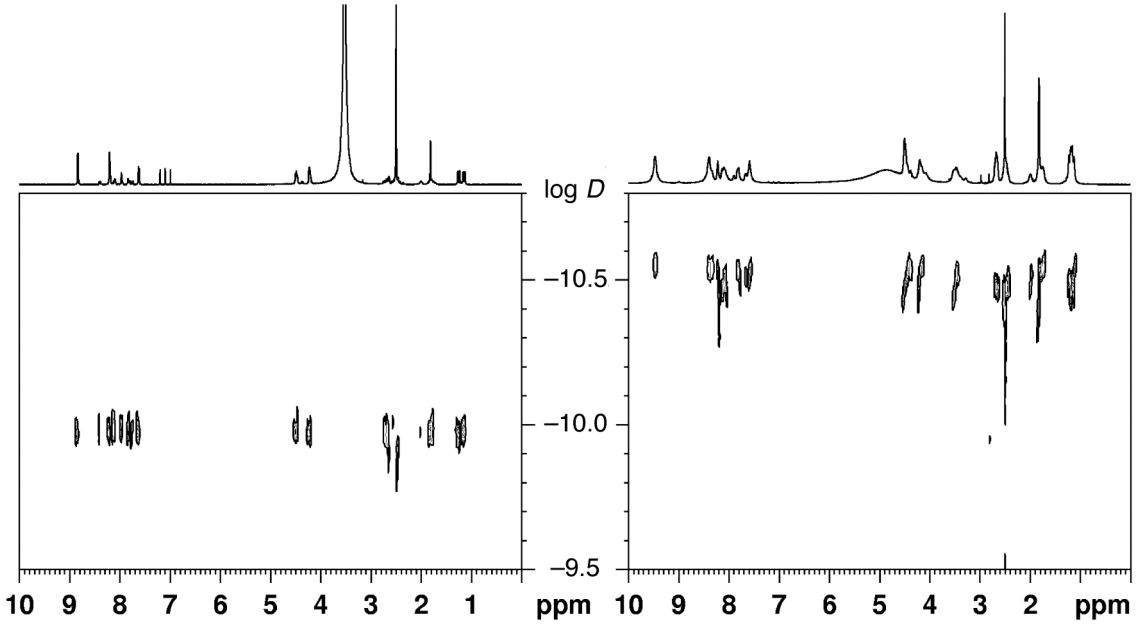
· Fig. S10. ^{13}C NMR spectrum of sphere **2b** (150 MHz, 300 K, DMSO–d_6).



· Fig. S11. ^{1}H NMR spectrum of sphere **2c** (600 MHz, 300 K, DMSO–d_6).

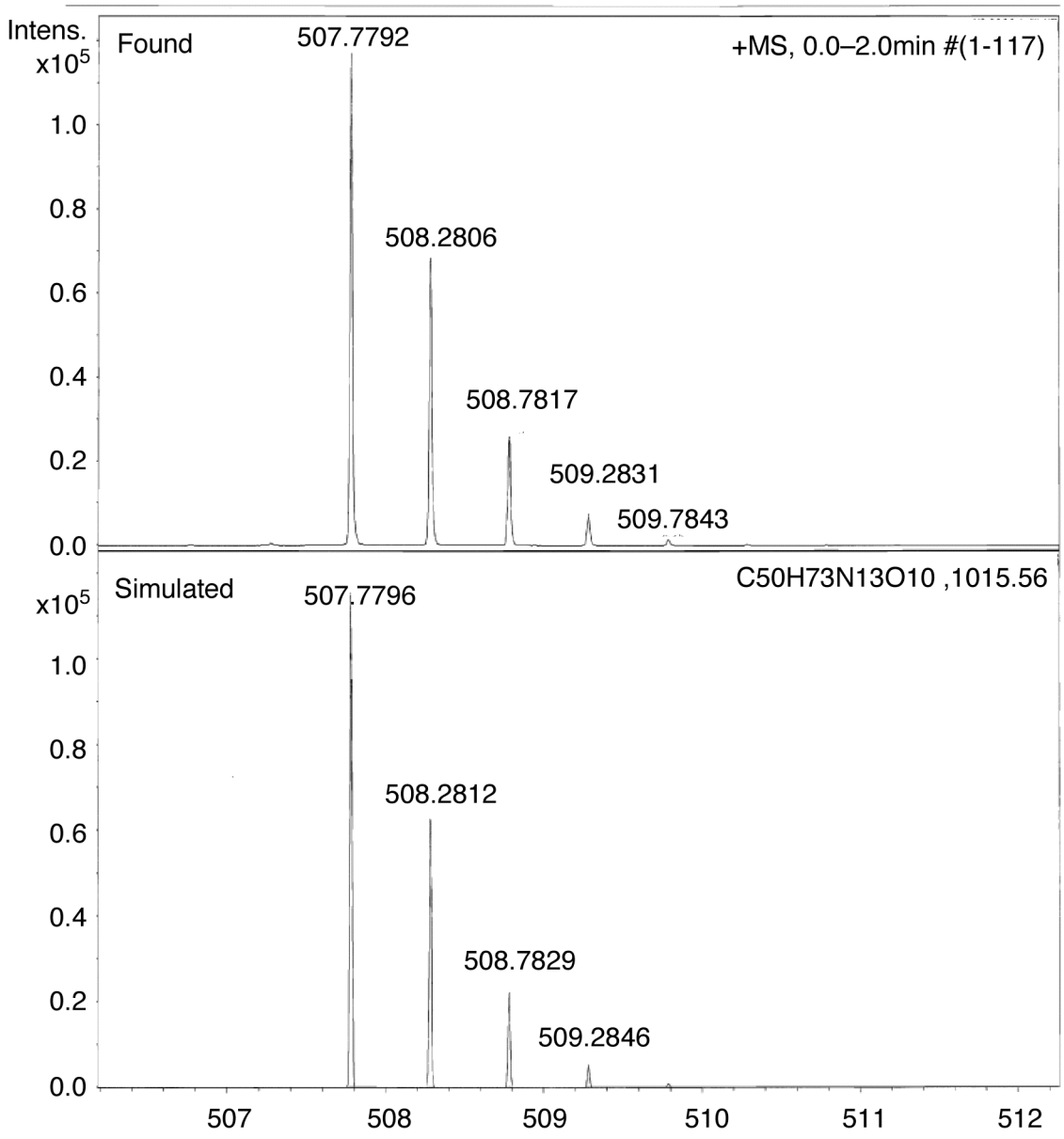


· Fig. S12. ^{13}C NMR spectrum of sphere **2c** (150 MHz, 300 K, DMSO–d_6).

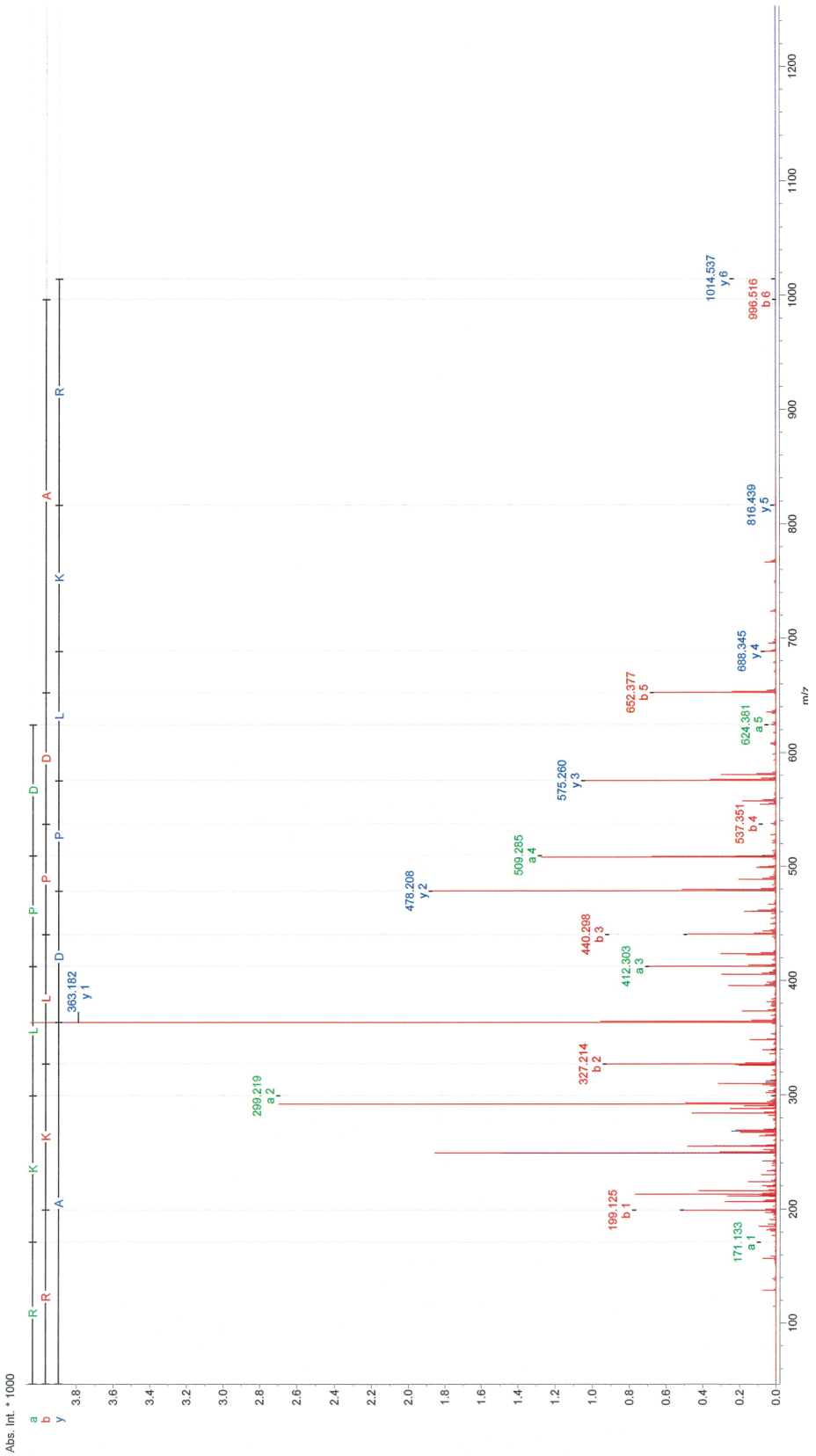


· Fig. S13. ^{1}H DOSY spectra of (left) ligand **1c** and (right) sphere **2c** (500 MHz, 300 K, DMSO–d_6).

4. Mass spectrometric data

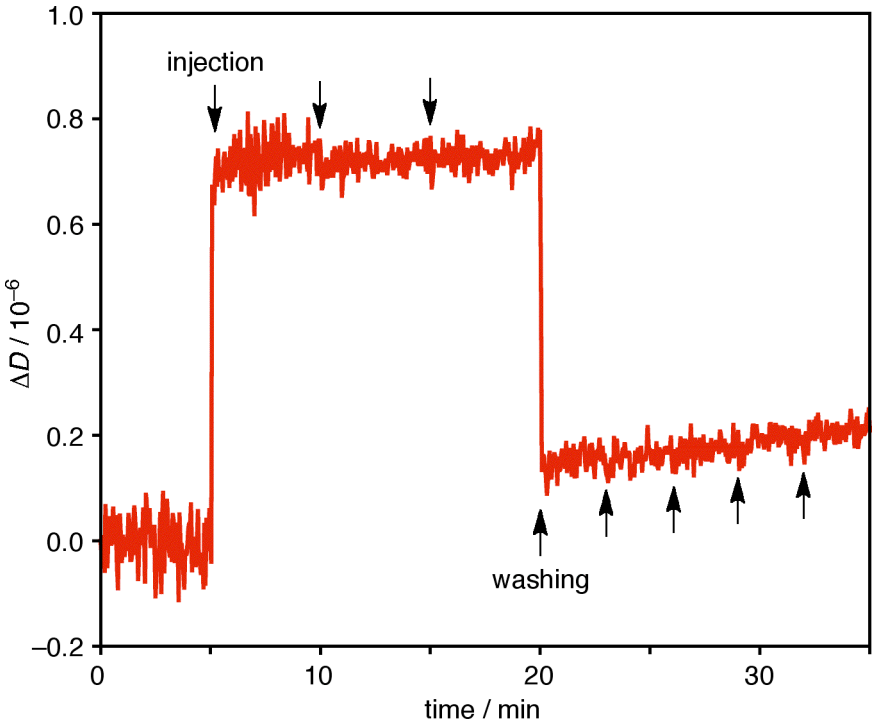


· Fig. S14. High resolution ESI-TOF mass spectrum of ligand **1b**.



· Fig. S15. MS/MS spectrum of ligand **1b**.

5. QCM data



· Fig. S16. Energy dissipation accompanying association of sphere **2b** with the Ti sensor. At 5, 10, and 15 min (indicated with down-pointing arrows), the sample solution of sphere **2b** was injected for three times. From 20 min, the sensor was washed with blank buffer solution for five times (indicated with up-pointing arrows).