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Supporting Information

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Title: Solvato-Controlled Assembly of Pd_3L_6 and Pd_4L_8 Coordination "Boxes"

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General

NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. The chemical shift values reported here are with respect to an internal TMS standard. CSI-MS (cold-spray ionization mass spectroscopy) spectra were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source. Melting points were determined on a Yanaco MP-500V melting-point apparatus. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Yanaco MT-6. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. X-ray crystallographic analyses were done on the Bruker

APEX2 or Bruker AXS SMART 1000. Single crystal X-ray diffraction data were collected on a Siemens SMART/CCD diffractmeter equipped with a 173 K, and cell refinement and data reduction were performed using the Bruker SAINT program. Structural solution was performed using the SHELXS-97 (Sheldrick, 1990) program, and structural refinement was performed using the SHELXL-97 (Sheldrick, 1997) program. Solvents and reagents were, unless otherwise noted, purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co.

1. Procedure

Synthesis of 1,2-bis[2-(pyridin-4-yl)ethynyl]benzene (1) Tri-*t*-butylphosphine (0.038 mL, 0.13 mmol; 10% solution in hexane) and diisopropylamine (1.0 mL, 7.1 mmol) were added to a mixture of 1,2-dibromobenzene (300 mg, 1.27 mmol), 4-ethynylpyridine hydrochloride (497 mg, 3.56 mmol), $Pd(PhCN)_2Cl_2$ (25.3 mg, 0.0659 mmol) and copper (I) iodide (8.6 mg, 0.045 mmol), and the mixture was stirred in dioxane (2 mL) at 40 ˚C for 12 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and filtered. After dilution with water (100 mL), the mixture was washed with ethylenediamine (2 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$:MeOH = 2:1) to give the title compound as a white solid (329 mg, 1.17 mmol) in 92% yield. mp 92-93 ˚C. ^{1}H NMR (500 MHz, DMSO-d_6, 27 ˚C) 8.66 (d, J = 6.0 Hz, 4H, H_a), 7.76 (dd, J = 3.6, 5.8 Hz, 2H, H_c), 7.57 (dd, J = 3.2, 5.7, Hz, 2H, H_d), 7.53 (d, J = 6.0 Hz, 4H, H_b). ^{1}H NMR (500 MHz, CD_3CN, 27 ˚C) 8.61 (d, J = 5.7 Hz, 4H, H_a), 7.67 (dd, J = 3.5, 5.7 Hz, 2H, H_c), 7.49 (dd, J = 3.4, 5.7, Hz, 2H, H_d), 7.45 (d, J = 5.9 Hz, 4H, H_b). ^{13}C NMR (125 MHz, DMSO-d_6, 27 ˚C) 150.1 (CH), 132.4 (CH), 129.9 (CH), 129.7 (C), 125.2 (CH), 123.9 (C), 91.6 (C), 90.9 (C). ^{13}C NMR (125 MHz, CD_3CN, 27 ˚C) 151.2 (CH), 133.4 (CH), 131.5 (C), 130.6 (CH), 126.4 (CH), 125.7 (C), 92.5 (C), 91.8 (C). Diffusion coefficient (DMSO-d_6, 27 °C) $D = 2.7 \times 10^{-10}$ m^2s^{-1}. Diffusion coefficient (CD_3CN, 27 °C) $D = 1.7 \times 10^{-9}$ m^2s^{-1}. IR (KBr, cm^{-1}) 2219, 1593, 1535, 1494, 1445, 1407, 1218, 989, 835, 816, 768, 676. MS (EI, *m/z*) Calcd for

$C_{20}H_{12}N_2$ (M^+) 280.1, found 280. Elemental Analysis Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.59; H, 4.44; N, 9.77.

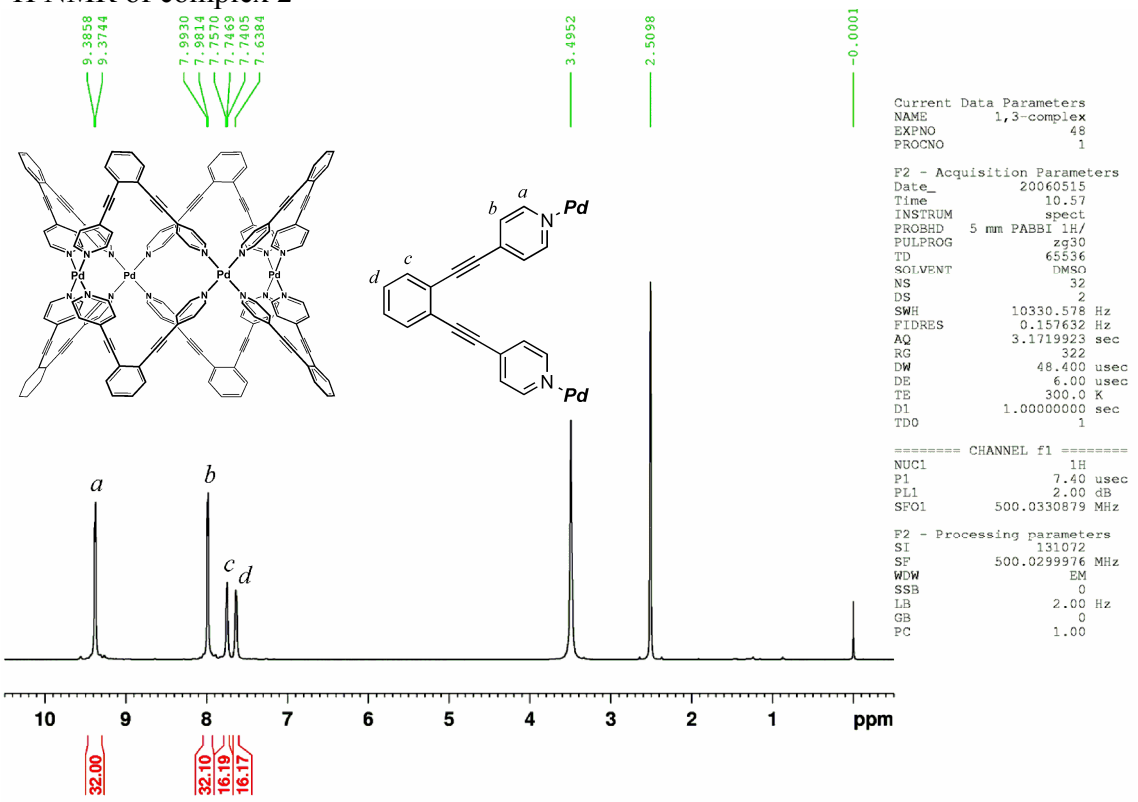
Synthesis of complex 2 (M_4L_8) Compound **1** (5.6 mg, 0.02 mmol) was treated with $Pd(NO_3)_2$ (2.3 mg, 0.01 mmol) in dimethyl sulfoxide (1.0 mL) at 60 °C for 4 h. The quantitative formation of **2** was confirmed by ^{1}H NMR. Slow diffusion of ethyl acetate into a DMSO solution of **2** gave pale yellow crystals. Isolated yield was 75% (NMR yield 100%). mp >176 ˚C (decomposed). ^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) 9.38 (d, J = 6.0 Hz, 32H, H_a), 7.98 (d, J = 6.0 Hz, 32H, H_b), 7.75 (br, 16H, H_c), 7.64 (br, 16H, H_d). ^{13}C NMR (125 MHz, DMSO-d_6, 27 °C) 151.1 (CH), 133.8 (C), 132.8 (CH), 130.8 (CH), 128.9 (CH), 123.1 (C), 95.5 (C), 89.2 (C). Diffusion coefficient (DMSO-d_6, 27 °C) D = 6.3 × 10^{-11} m^2s^{-1}. IR (KBr, cm^{-1}) 2223, 1611, 1503, 1428, 1385, 1342, 1273, 1215, 1061, 1041, 839, 765. CSI-MS (DMSO:acetone = 1:3): *m/z* 1520.8 $[M–2(NO_3^–)]^{2+}$, 993.0 $[M–3(NO_3^–)]^{3+}$, 729.2 $[M–4(NO_3^–)]^{4+}$, 571.2 $[M–5(NO_3^–)]^{5+}$. Elemental Analysis Calcd for $C_{160}H_{96}N_{24}O_{24}Pd_4$·5.5DMSO·$4H_2O$, C, 56.30; H, 3.73; N, 9.21. Found: C, 56.14; H, 3.68; N, 9.32.

Synthesis of complex 3 (M_3L_6) Compound **1** (2.8 mg, 0.01 mmol) was treated with $Pd(NO_3)_2$ (1.2 mg, 0.05 mmol) in acetonitrile (5.0 mL) at 60 °C for 4 h. The quantitative formation of **3** was confirmed by ^{1}H NMR. Slow diffusion of tetrahydrofuran into a acetonitrile solution of **3** gave pale yellow crystals. Isolated yield was 65% (NMR yield 100%). mp >198 ˚C (decomposed). ^{1}H NMR (500 MHz, CD_3CN, 27 °C) 9.25 (d, J = 6.0 Hz, 24H, H_a), 7.67 (d, J = 6.0 Hz, 24H, H_b), 7.67 (br, 12H, H_c), 7.55 (br, 12H, H_d). ^{13}C NMR (125 MHz, CD_3CN, 27 °C) 153.0 (CH), 136.1 (C), 133.5 (CH), 131.8 (CH), 129.6 (CH), 125.4 (C), 97.6 (C), 90.5 (C), 18.7 (CH_3). Diffusion coefficient (CD_3CN, 27 °C) D = 5.0 × 10^{-10} m^2s^{-1}. IR (KBr, cm^{-1}) 2223, 1612, 1503, 1434, 1385, 1344, 1215, 1062, 1042, 838, 762. CSI-MS (CH_3CN): *m/z* 1124.5 $[M–2(NO_3^–)]^{2+}$, 728.9 $[M–3(NO_3^–)]^{3+}$, 530.9 $[M–4(NO_3^–)]^{4+}$. Elemental Analysis Calcd for $C_{120}H_{72}N_{18}O_{18}Pd_3$·1$CH_3CN$·11$H_2O$·3THF, C, 56.90; H, 4.31; N, 9.41. Found: C, 56.56; H, 3.99; N, 9.05.

2. NMR and MS data

Self-assembly of complex 2

^{1}H NMR of complex **2**

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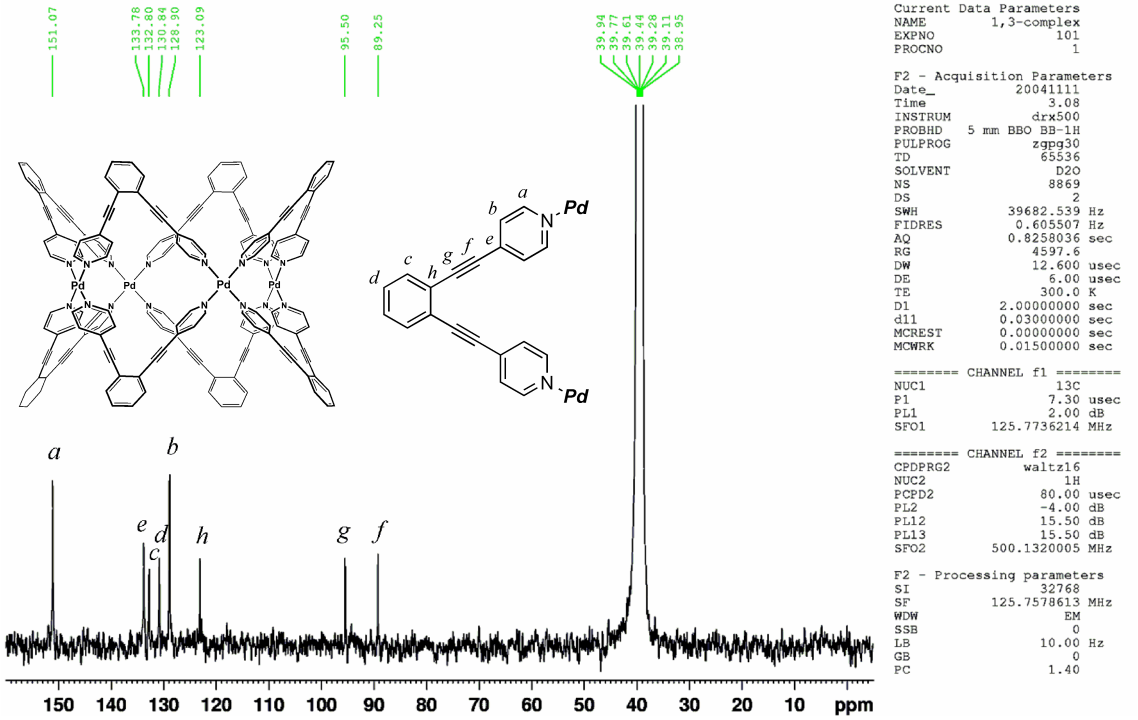
^{13}C NMR of complex **2**

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PL13              15.50 dB
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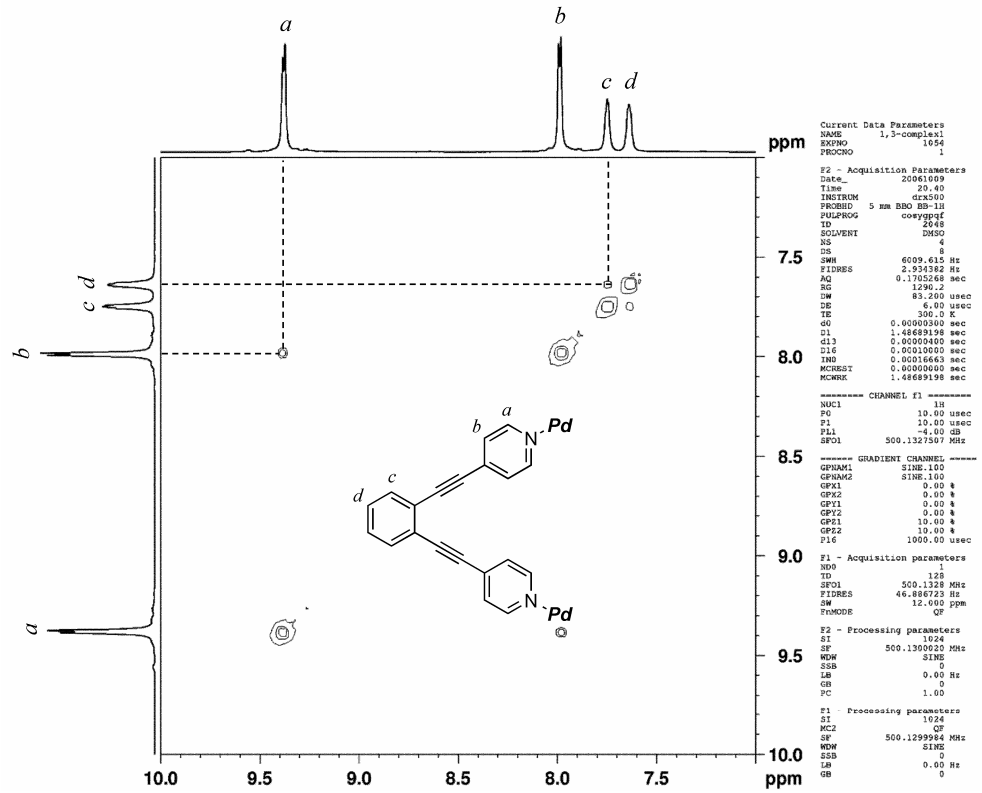
H-H COSY of complex **2**



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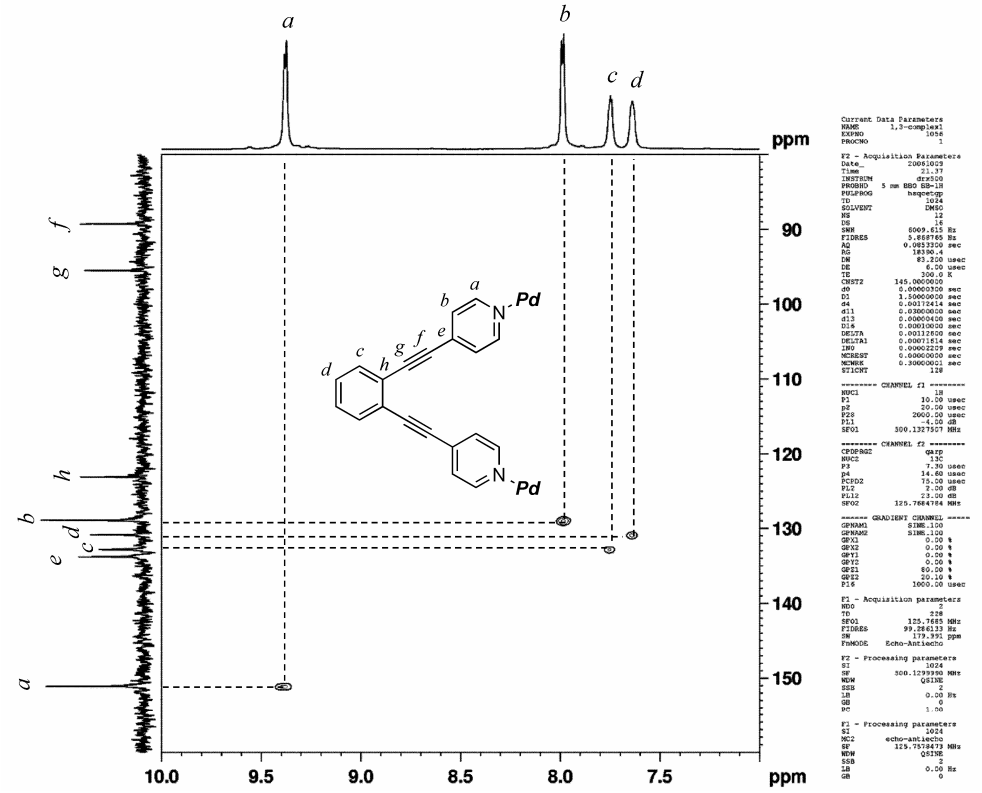
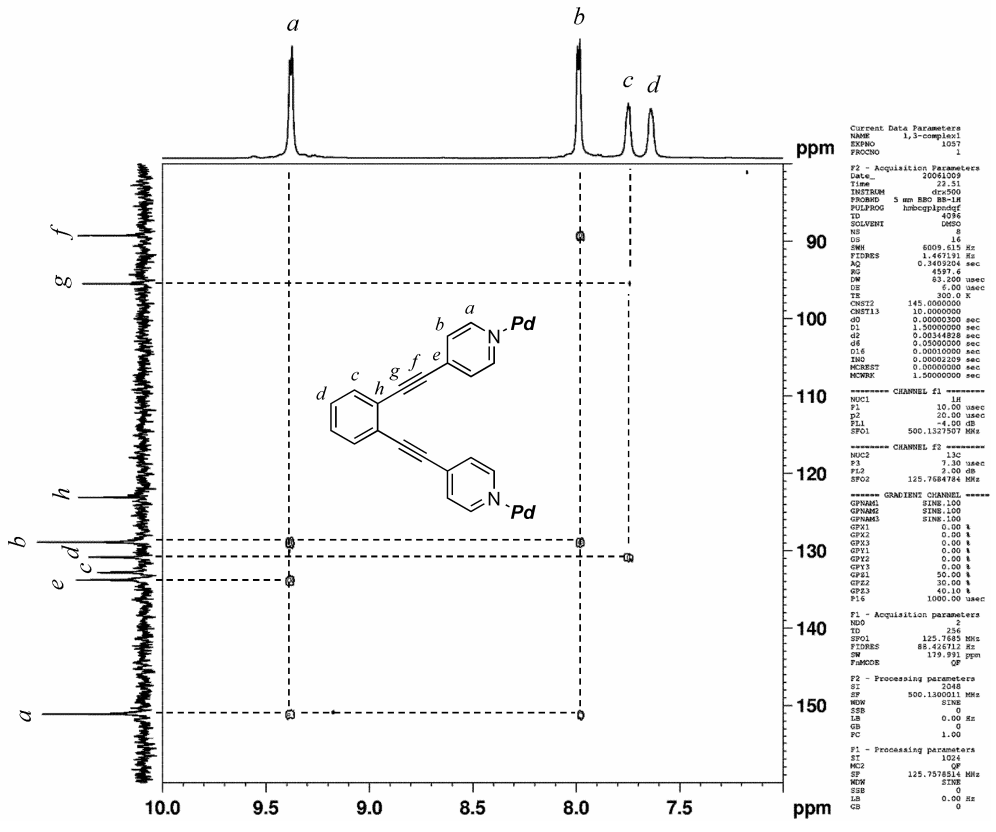


HMBC of complex **2**



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p2 20.00 usec
PL1 -4.00 dB
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PL2 2.00 dB
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====== GRADIENT CHANNEL =====
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GPNAM2 SINE.100
GPNAM3 SINE.100
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GPX2 0.00 %
GPX3 0.00 %
GPY1 0.00 %
GPY2 0.00 %
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GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 usec

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SW 179.991 ppm
FnMODE QF

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SSB 0
LB 0.00 Hz
GB 0
PC 1.00

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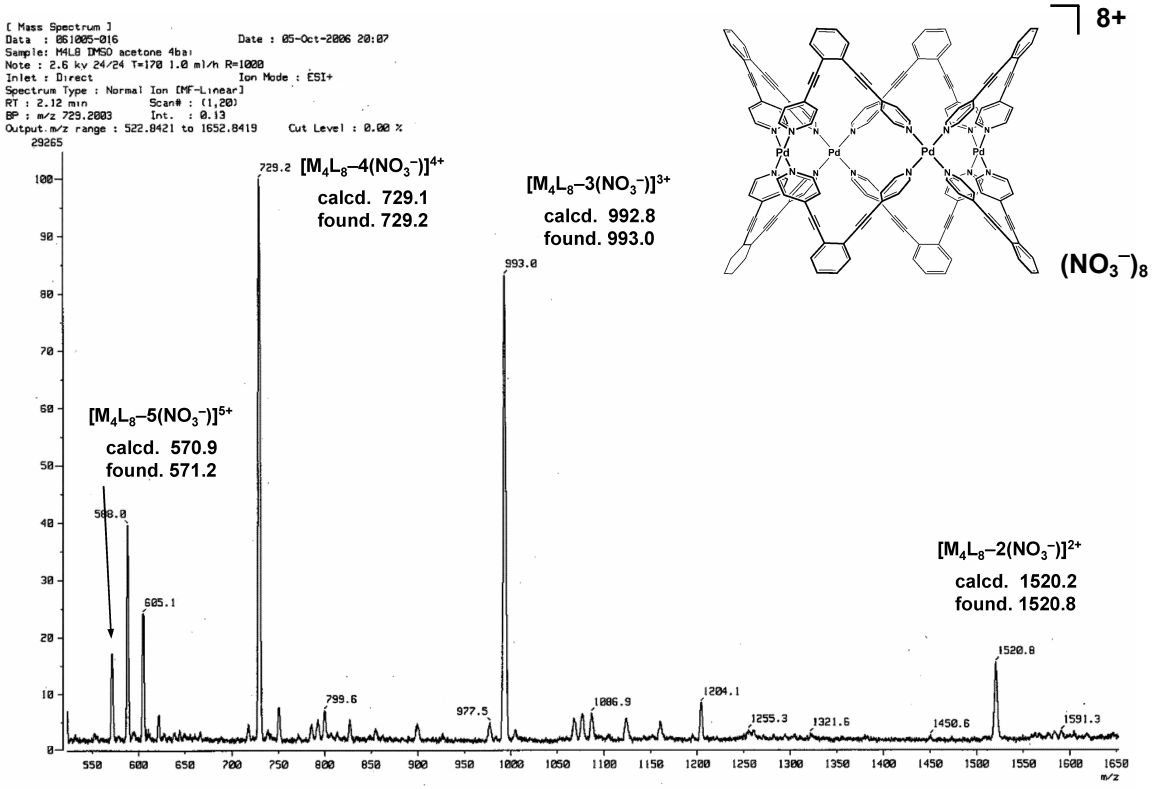
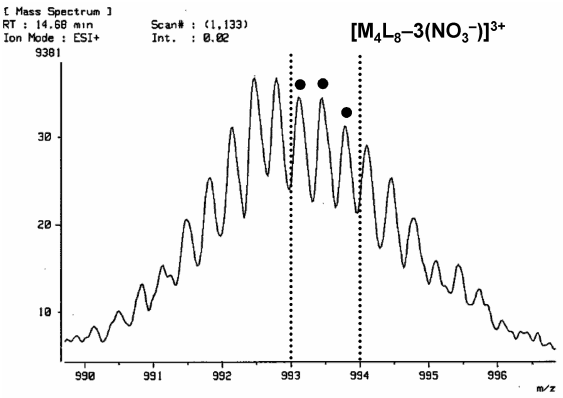
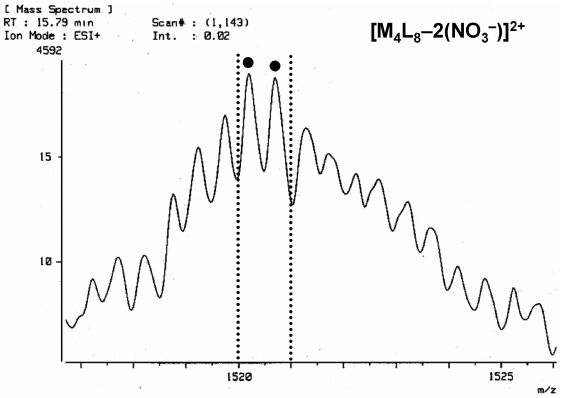
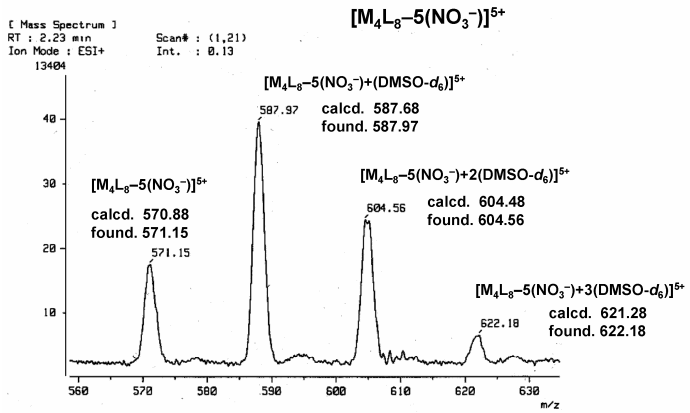
CSI-MS of complex **2** (DMSO:acetone = 1:3)



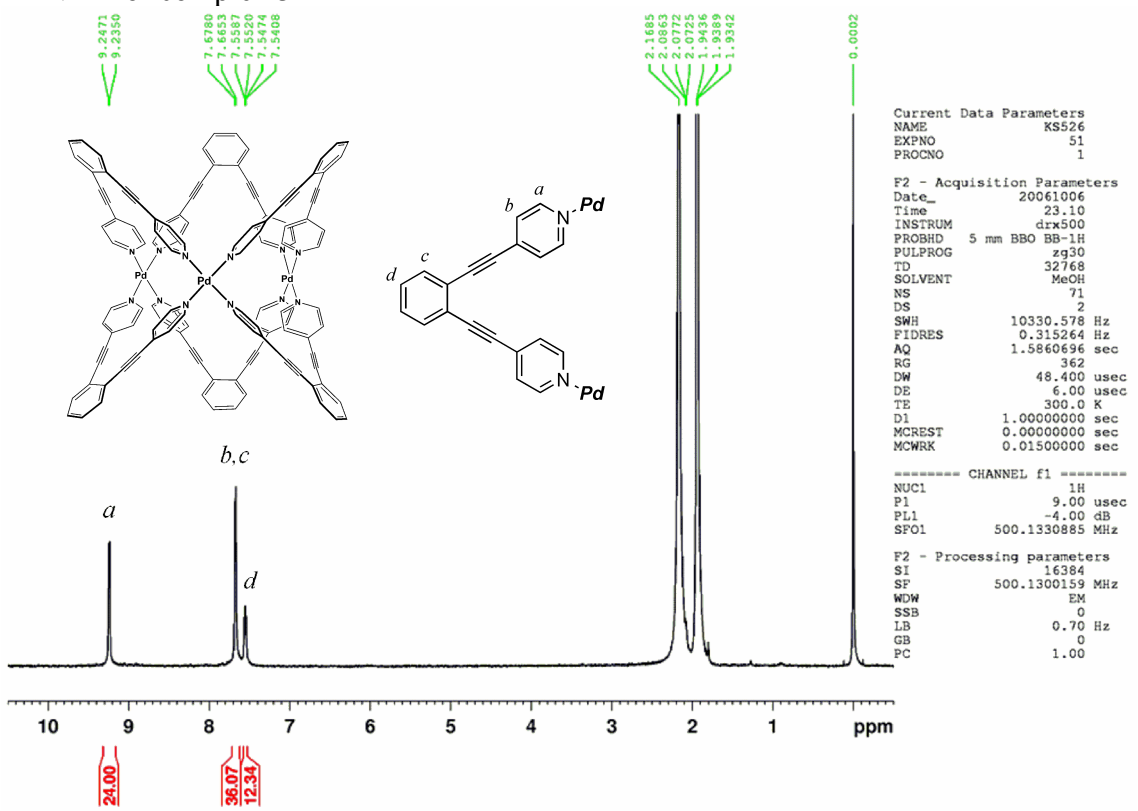




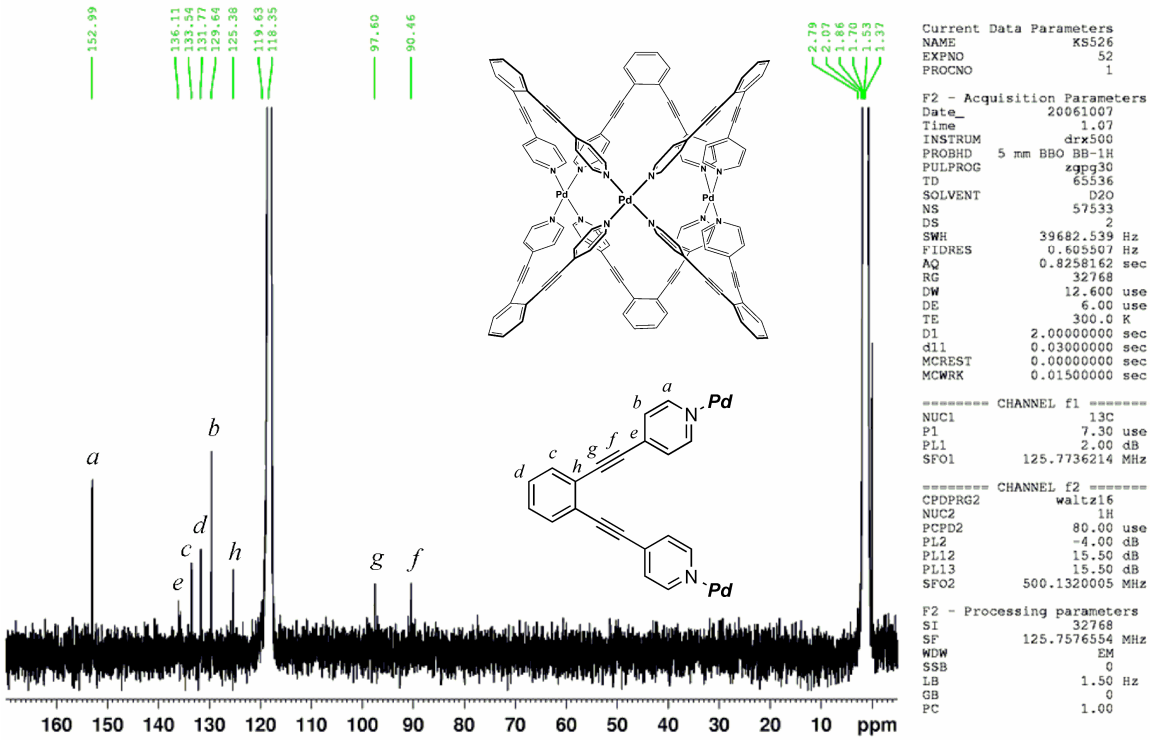


Self-assembly of complex 3

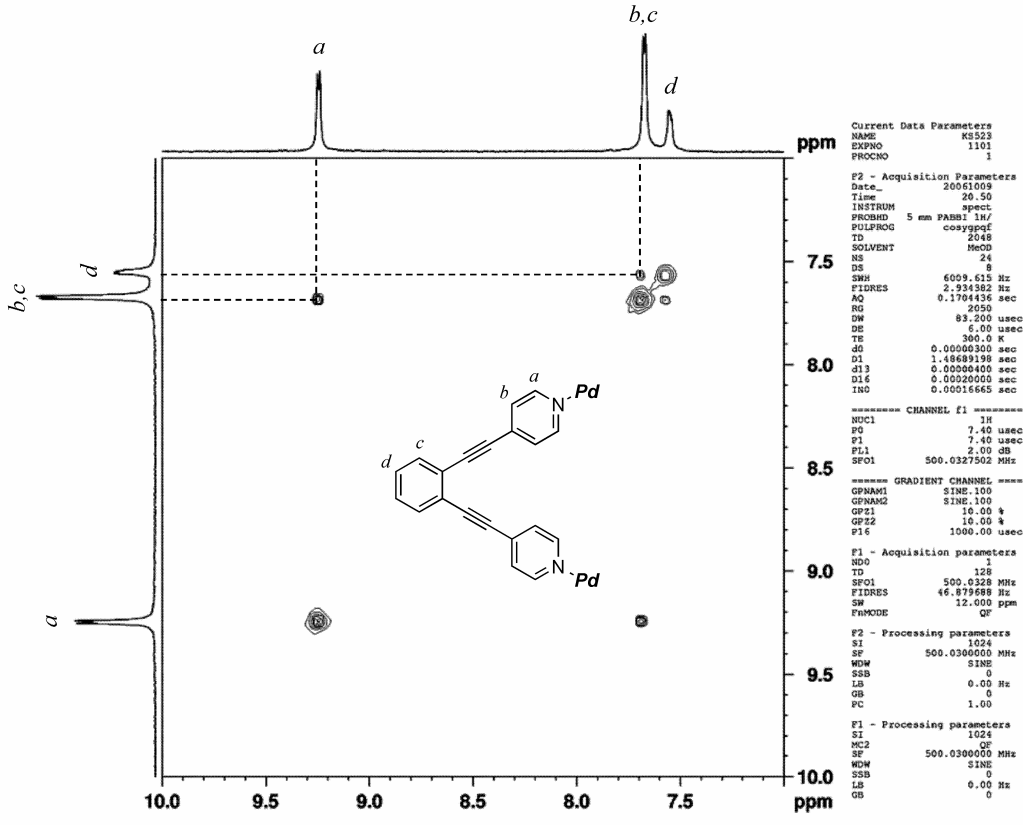
^{1}H NMR of complex **3**



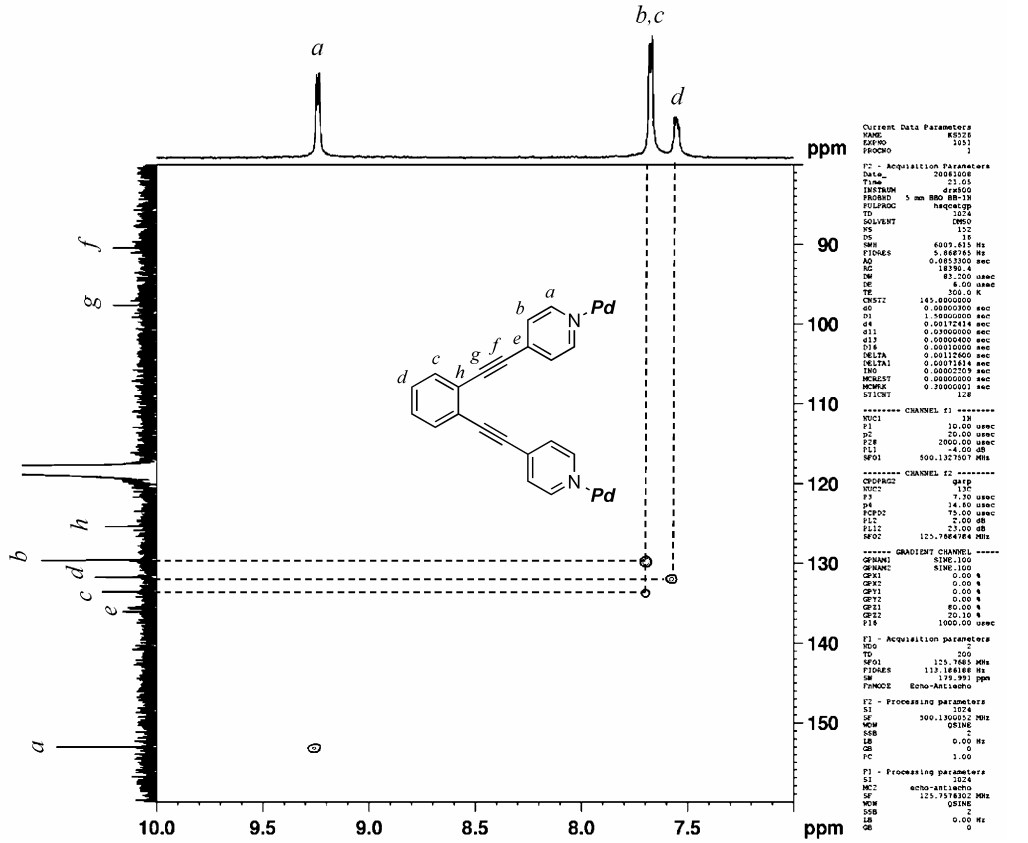
^{13}C NMR of complex **3**



H-H COSY of complex **3**



HSQC of complex **3**



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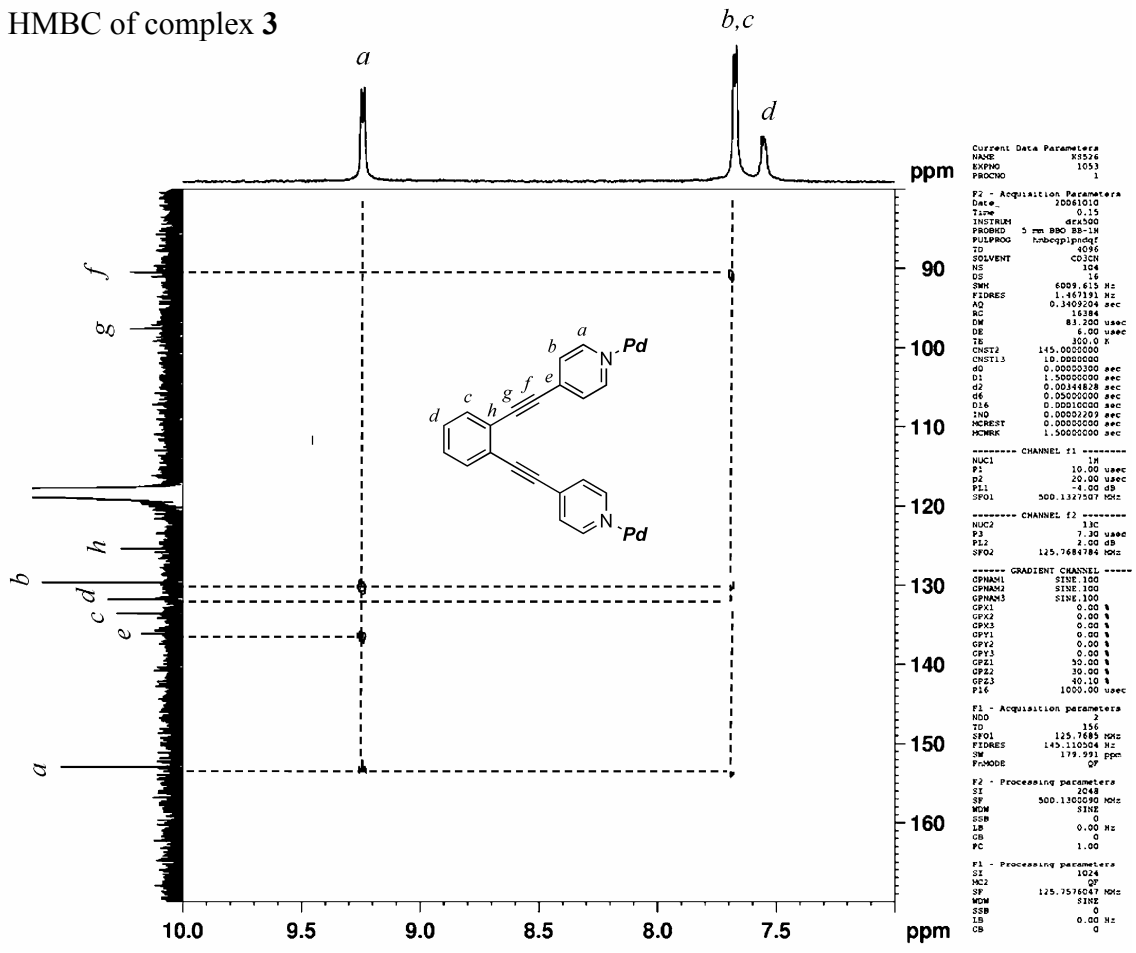
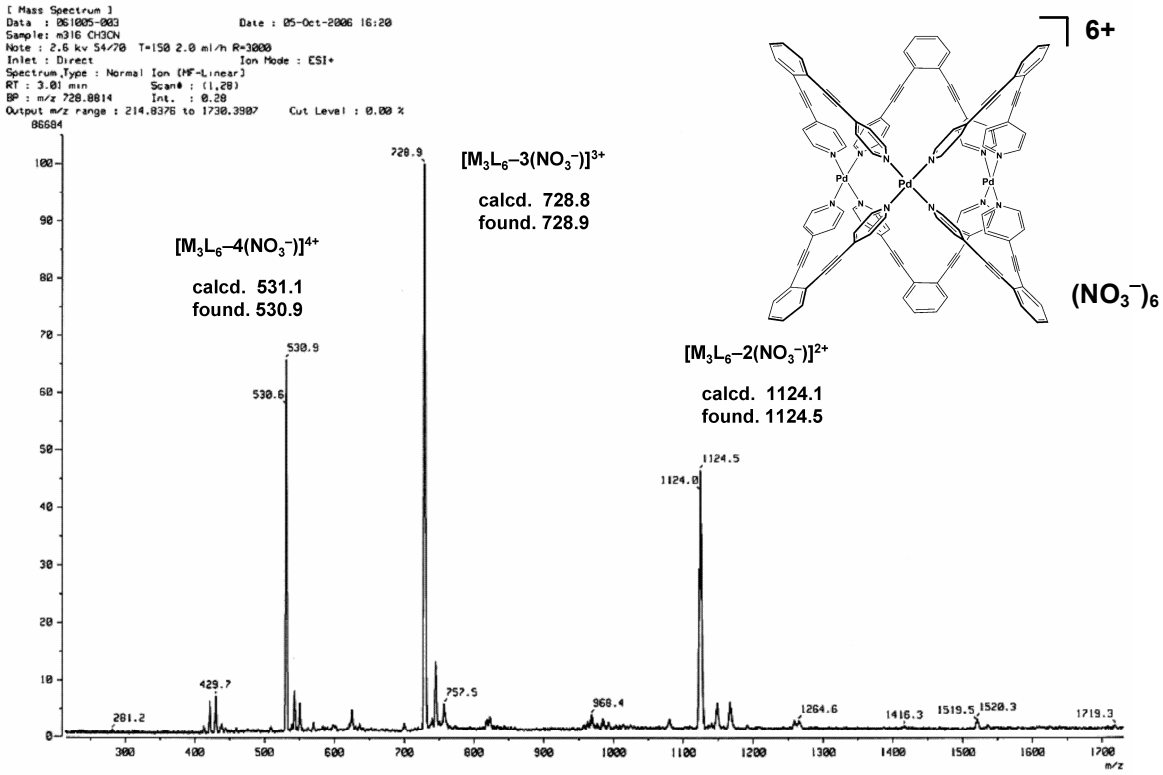
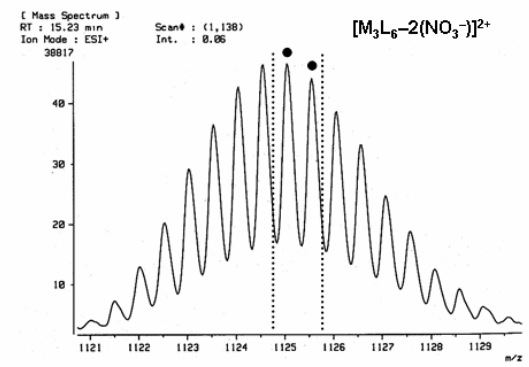
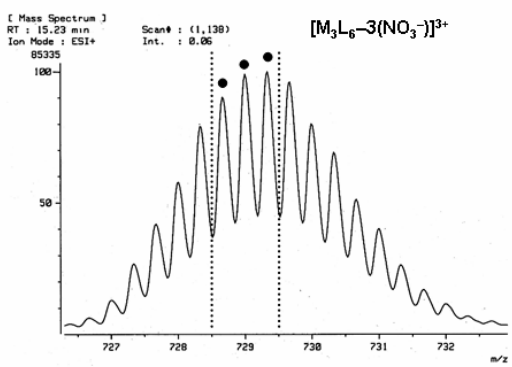
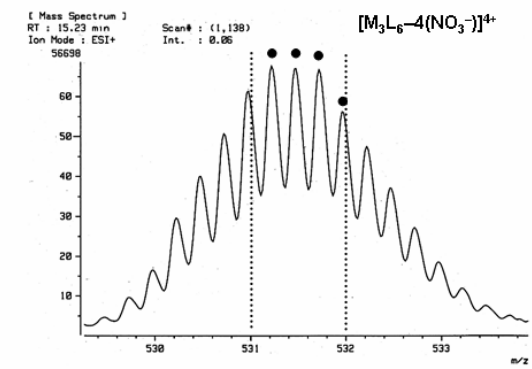


CSI-MS of complex **3** (CH_3CN)







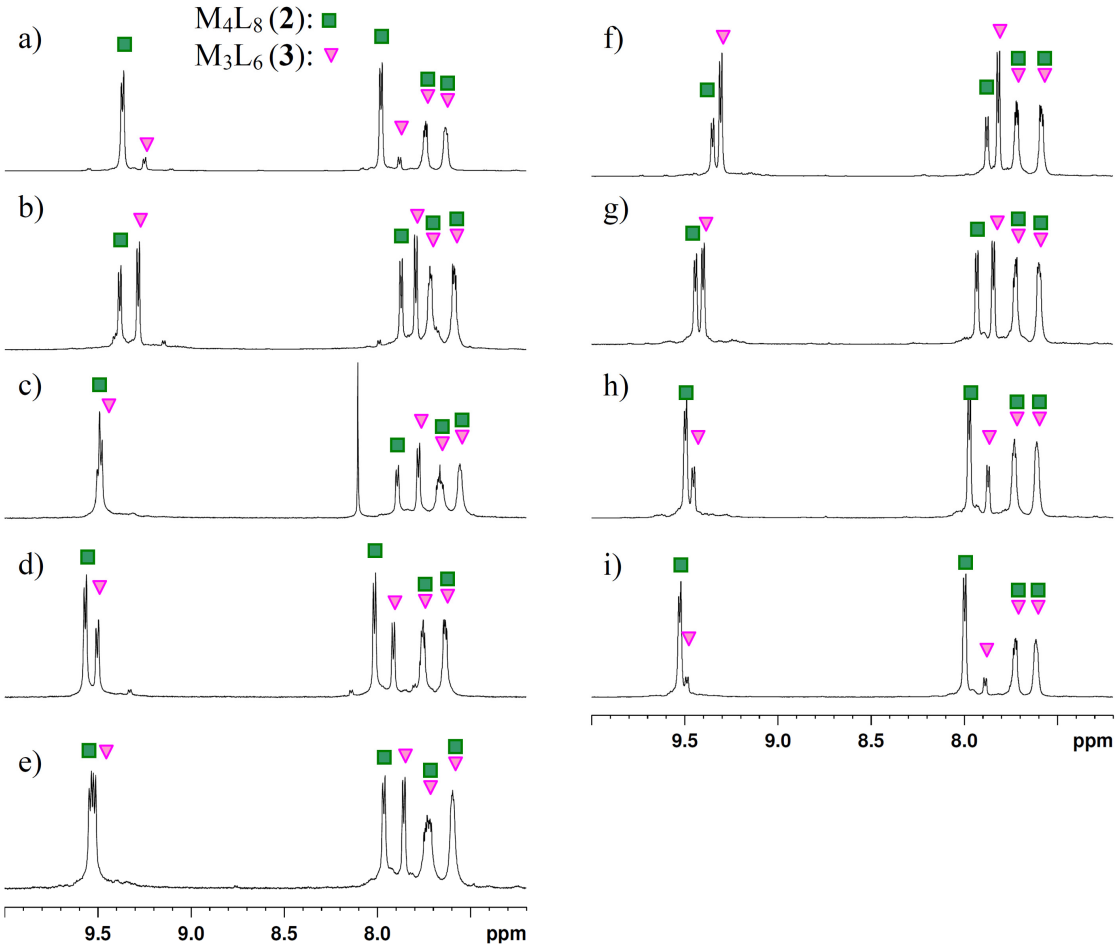


Structural conversion from M_4L_8 (2) to M_3L_6 (3) by adding various solvent

^{1}H NMR spectra (500 MHz, 300 K)

After addition of following solvents to the DMSO-d_6 solution of complex **2** ([**1**]=20 mM), and stirred at 60 °C for 3 h.

a) DMSO-d_6, b) CD_3CN, c) $CDCl_3$, d) acetone-d_6, e) 1,4-dioxane-d_8, f) MeOD-d_4, g) EtOD-d_6, h) *i*-PrOD-d_8, i) *t*-BuOD-d_{10}.



Structural interconversion between M_4L_8 (2) and M_3L_6 (3)

^{1}H NMR spectra (500 MHz, 300 K)

a) DMSO-d_6 solution of complex **2** ([**1**]=20 mM),

b) After addition of CD_3CN to the sample of (a) and stirred at 60 °C for 3 h,

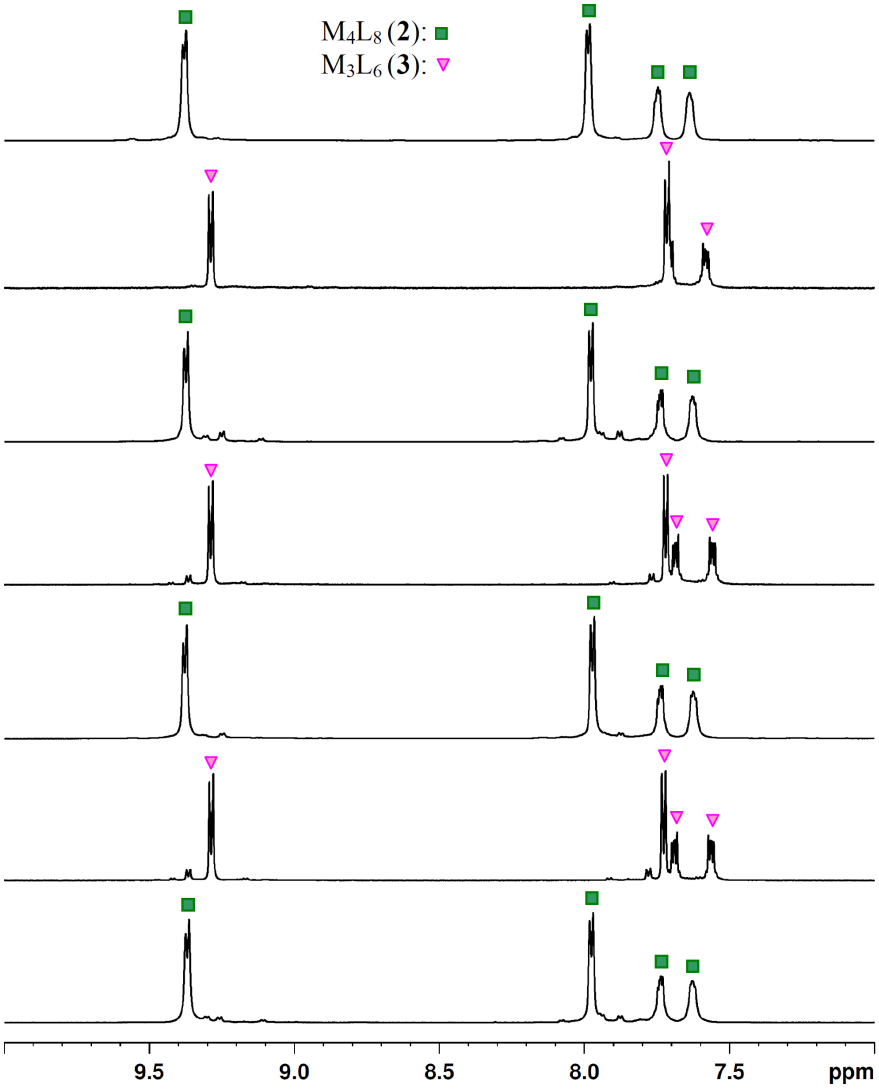
c) After removal of CD_3CN from the sample of (b) and stirred at r.t. for 3 h,

d) After addition of CD_3CN to the sample of (c) and stirred at 60 °C for 3 h,

e) After removal of CD_3CN from the sample of (d) and stirred at r.t. for 3 h,

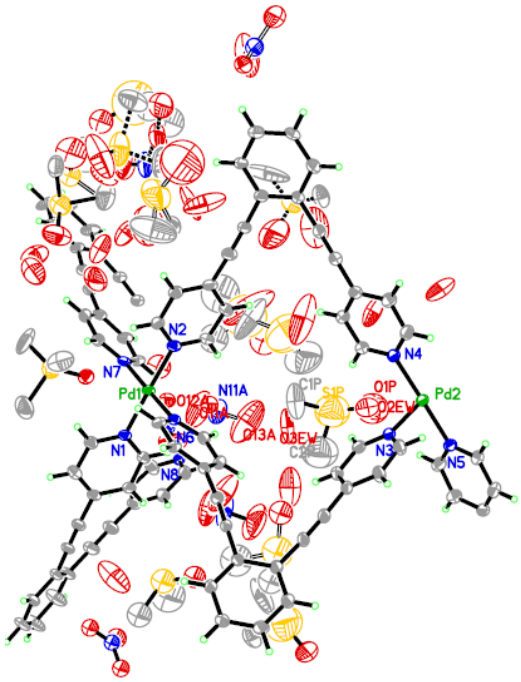
f) After addition of CD_3CN to the sample of (e) and stirred at 60 °C for 3 h,

g) After removal of CD_3CN from the sample of (f) and stirred at r.t. for 3 h,



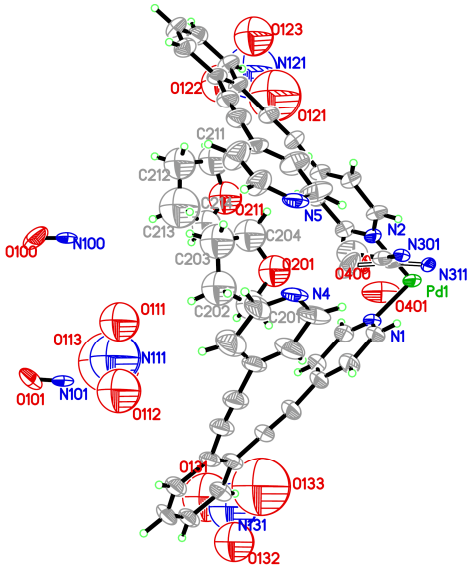
3. Crystal Structure

Crystal structure of complex 2 (M_4L_8)



Thermal ellipsoid plots (30 % probability level) of the molecular structure of complex **2**. All independent atoms including dimethyl sulfoxide, water and nitrate ions.

Crystal structure of complex 3 (M_3L_6)



Thermal ellipsoid plots (30 % probability level) of the molecular structure of complex **3**. All independent atoms including acetonitrile, tetrahydrofuran, water and nitrate ions.