SUPPORTING INFORMATION

Three-Metal-Center Spin Interactions through the Intercalation of Metal Azaporphines and Porphines into an Organic Pillared Coordination Box

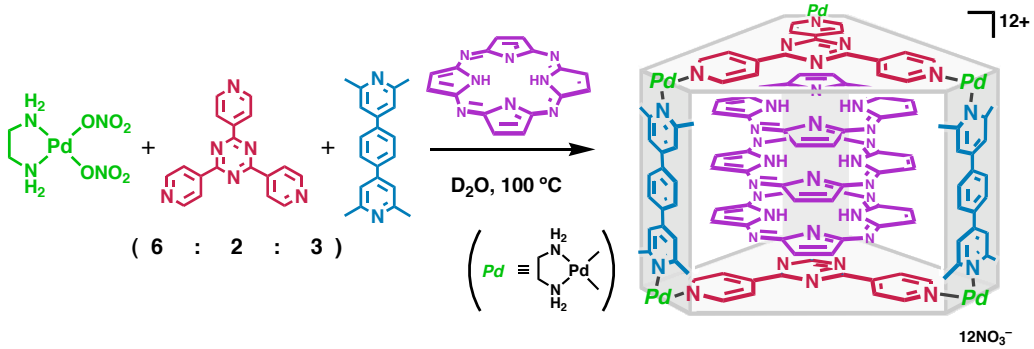
Kosuke Ono, Michito Yoshizawa, Tatsuhisa Kato, and Makoto Fujita

Contents

■ Materials and instrumentations.

NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. TMS ($CDCl_3$ solution) in a capillary served as external standard (δ 0 ppm). CSI-MS (cold-spray ionization mass spectroscopy) data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with the CSI source. IR measurements (ATR) were carried out using a DIGILAB Scimitar FTS-2000 instrument. UV-visible and ESR spectral data were recorded on a SHIMADZU UV-3150 and JEOL JMS-RE1X, respectively. Melting points were determined on a Yanaco MF-500 V micro melting point apparatus. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. Deuteration H_2O was acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements. Tetrazaporphine (**6a**) was prepared from maleinitrile (ref. *J. Chem. Soc.*, **1952**, 4839–4846).

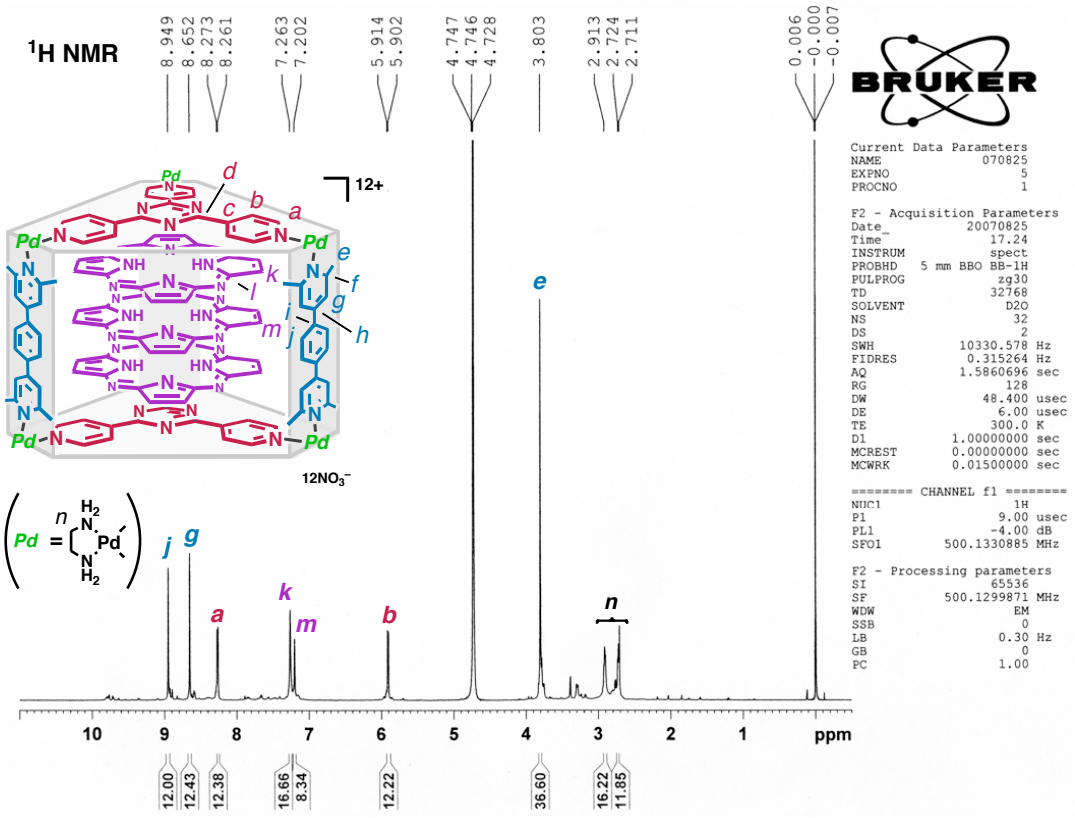
■ Synthesis of **1**⊃(**6a**)$_3$.

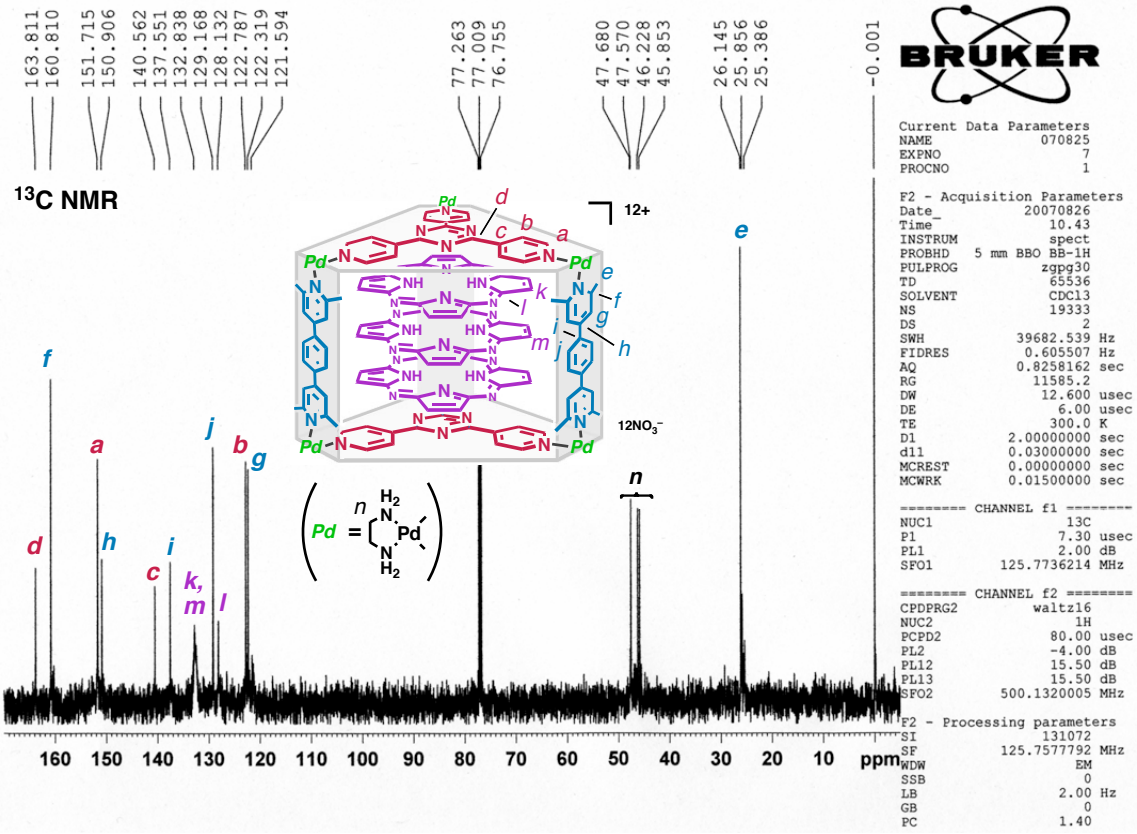


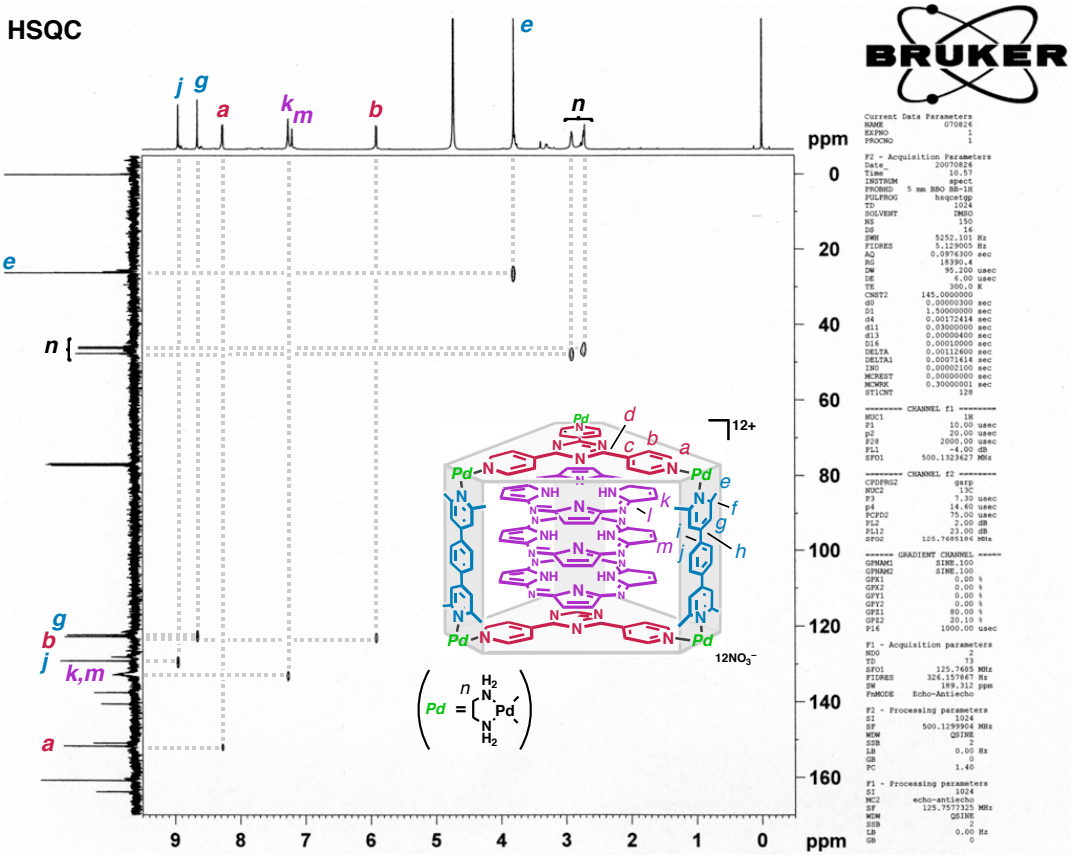
Typical procedure: (en)Pd(NO_3)$_2$ (**4**, 17.43 mg; 60.0 μmol), tris(4-pyridyl)triazine (**2**, 6.25 mg; 20.0 μmol), 1,4-bis(2,6-dimethyl-4-pyridyl)benzene (**3**, 8.65 mg; 15.0 μmol), and tetrazaporphine (**6a**, 12.56 mg; 40.0 μmol, 4 eq. per **1**) was suspended in a D_2O solution (1.0 mL) and the mixture was stirred at 100 °C for 2 h. After filtration of the dark purple solution, the ^{1}H NMR spectrum revealed the selective formation of **1**⊃(**6a**)$_3$ complex. The solution was evaporated and dried by vacuum freeze-drying equipment to give a purple solid of **1**⊃(**6a**)$_3$ complex (37.9 mg; 9.08 μmol) in 91% yield.

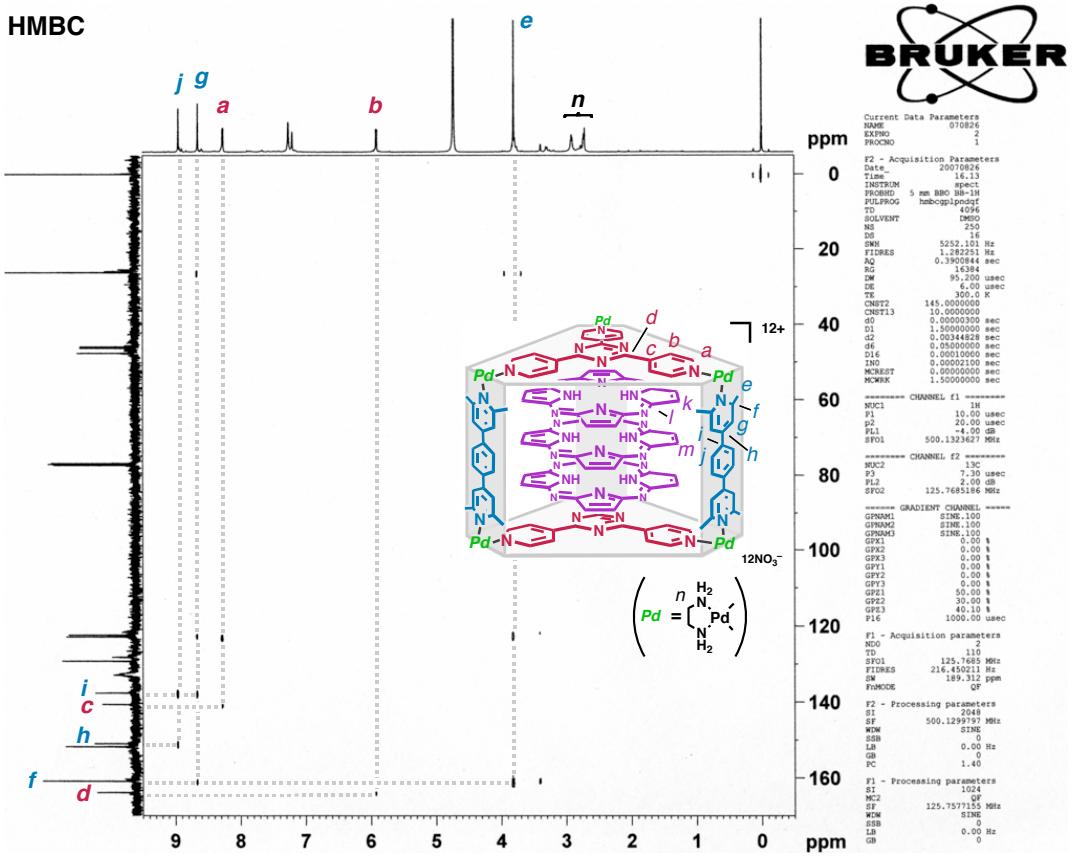
Physical data of **1**⊃(**6a**)$_3$: ^{1}H NMR (500 MHz, D_2O, 27 °C): δ 8.95 (s, 12H, **1**), 8.65 (s, 12H, **1**), 8.27 (d, J = 5.0 Hz, 12H, **1**), 7.26 (s, 16H, **6a**), 7.20 (s, 8H, **6a**), 5.91 (d, J = 5.0 Hz, 12H, **1**), 3.80 (s, 36H, **1**), 2.91 (br, 12H, **1**), 2.72 (br, 12H, **1**); ^{13}C NMR (125 MHz, D_2O, 27 °C): δ 163.8 (C_q, **1**), 160.8 (C_q, **1**), 151.7 (*C*H, **1**), 150.9 (C_q, **1**), 140.6 (C_q, **1**), 137.6 (C_q, **1**), 132.8

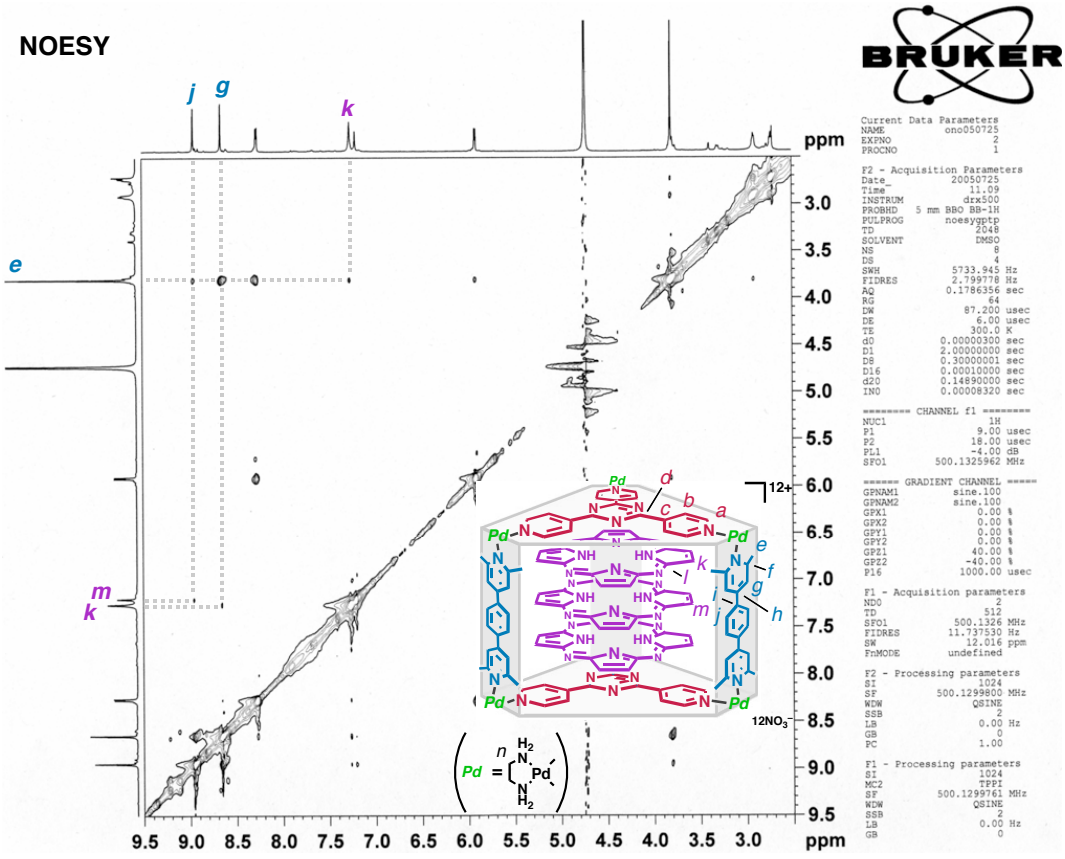
(C_q, **6a**), 129.2 (*C*H, **1**), 128.1 (*C*H, **6a**), 122.8 (*C*H, **1**), 122.3 (*C*H, **1**), 47.7 (CH_2, **1**), 46.2 (CH_2, **1**), 26.1 (CH_3, **1**); DOSY-NMR (cm^2/s): D = –9.85; IR (ATR, cm^{-1}): 3429 (br), 3213 (br), 3102 (br), 1615, 1519, 1329, 1157, 1053, 828; m.p.: ~200 ºC (decomposed); CSI-MS (H_2O:DMF = 20:1): *m/z* 4170.7 $[\mathbf{1}\supset(\mathbf{6a})_3–3•NO_3^-]^{3+}$, 1327.3 $[\mathbf{1}\supset(\mathbf{6a})_3–3•NO_3^-+DMF]^{3+}$, 1352.8 $[\mathbf{1}\supset(\mathbf{6a})_3–3•NO_3^-+2•DMF]^{3+}$, 1377.0 $[\mathbf{1}\supset(\mathbf{6a})_3–4•NO_3^-+DMF]^{4+}$, 998.2 $[\mathbf{1}\supset(\mathbf{6a})_3–4•NO_3^-+2•DMF]^{4+}$, 1017.5 $[\mathbf{1}\supset(\mathbf{6a})_3–4•NO_3^-+3•DMF]^{4+}$, 1035.0 $[\mathbf{1}\supset(\mathbf{6a})_3–4•NO_3^-+4•DMF]^{4+}$, 1053.3 $[\mathbf{1}\supset(\mathbf{6a})_3–4•NO_3^-+5•DMF]^{4+}$, 1071.7 $[\mathbf{1}\supset(\mathbf{6a})_3–5•NO_3^-+2•DMF]^{5+}$, 802.0 $[\mathbf{1}\supset(\mathbf{6a})_3–5•NO_3^-+3•DMF]^{5+}$, 816.9 $[\mathbf{1}\supset(\mathbf{6a})_3–5•NO_3^-+4•DMF]^{5+}$, 830.2 $[\mathbf{1}\supset(\mathbf{6a})_3–5•NO_3^-+5•DMF]^{5+}$, 845.0 $[\mathbf{1}\supset(\mathbf{6a})_3–5•NO_3^-+6•DMF]^{5+}$, 859.4 $[\mathbf{1}\supset(\mathbf{6a})_3–6•NO_3^-+2•DMF]^{6+}$, 657.8 $[\mathbf{1}\supset(\mathbf{6a})_3–6•NO_3^-+3•DMF]^{6+}$, 669.5 $[\mathbf{1}\supset(\mathbf{6a})_3–6•NO_3^-+8•DMF]^{6+}$, 730.6 $[\mathbf{1}\supset(\mathbf{6a})_3–6•NO_3^-+10•DMF]^{6+}$, 755.8 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+5•DMF]^{7+}$, 587.0 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+6•DMF]^{7+}$, 596.8 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+7•DMF]^{7+}$, 606.6 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+8•DMF]^{7+}$, 617.4 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+9•DMF]^{7+}$, 627.7 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+10•DMF]^{7+}$, 638.2 $[\mathbf{1}\supset(\mathbf{6a})_3–7•NO_3^-+11•DMF]^{7+}$, 648.5 $[\mathbf{1}\supset(\mathbf{6a})_3–8•NO_3^-+7•DMF]^{8+}$, 523.2 $[\mathbf{1}\supset(\mathbf{6a})_3–8•NO_3^-+8•DMF]^{8+}$, 533.3 $[\mathbf{1}\supset(\mathbf{6a})_3–8•NO_3^-+11•DMF]^{8+}$, 560.1 $[\mathbf{1}\supset(\mathbf{6a})_3–8•NO_3^-+12•DMF]^{8+}$, 568.5; UV-vis ($H_2O$, nm): λ_{max} 621 ($\varepsilon = 1.5 \times 10^4$), 544 ($\varepsilon = 2.0 \times 10^4$).

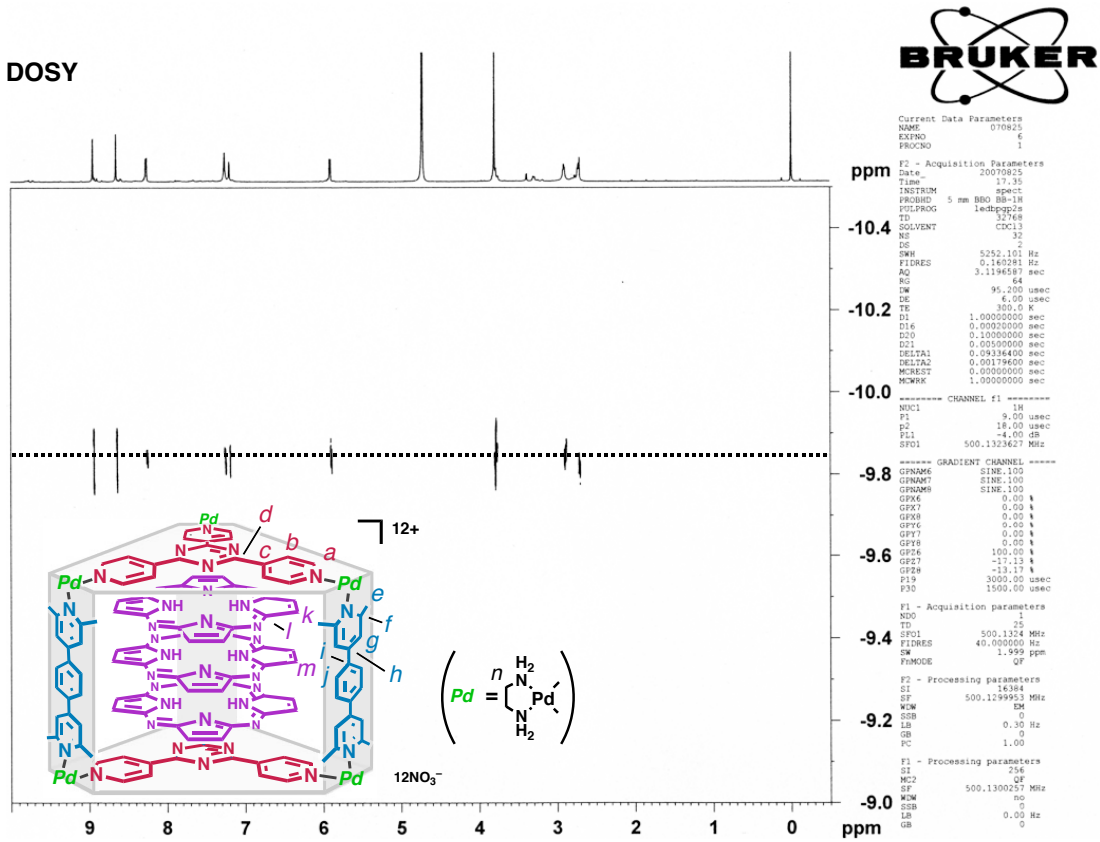

^{1}H NMR
8.949
8.652
8.273
8.261
7.263
7.202
5.914
5.902
4.747
4.746
4.728
3.803
2.913
2.724
2.711
0.006
-0.000
-0.007
12+
12NO$_3^-$
Pd = n H$_2$N Pd N H$_2$
a b c d e f g h i j k l m n
12.00
12.43
12.38
16.66
8.34
12.22
36.60
16.22
11.85
10 9 8 7 6 5 4 3 2 1 ppm
BRUKER
Current Data Parameters
NAME 070825
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070825
Time 17.24
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT D2O
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 128
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1299871 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


^{13}C NMR
163.811
160.810
151.715
150.906
140.562
137.551
132.838
129.168
128.132
122.787
122.319
121.594
77.263
77.009
76.755
47.680
47.570
46.228
45.853
26.145
25.856
25.386
-0.001
12+
12NO$_3^-$
Pd = n H$_2$N Pd N H$_2$
a b c d e f g h i j k, m l n
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
BRUKER
Current Data Parameters
NAME 070825
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070826
Time 10.43
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 19333
DS 2
SWH 39682.539 Hz
FIDRES 0.605507 Hz
AQ 0.8258162 sec
RG 11585.2
DW 12.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.30 usec
PL1 2.00 dB
SFO1 125.7736214 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.50 dB
PL13 15.50 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 131072
SF 125.7577792 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

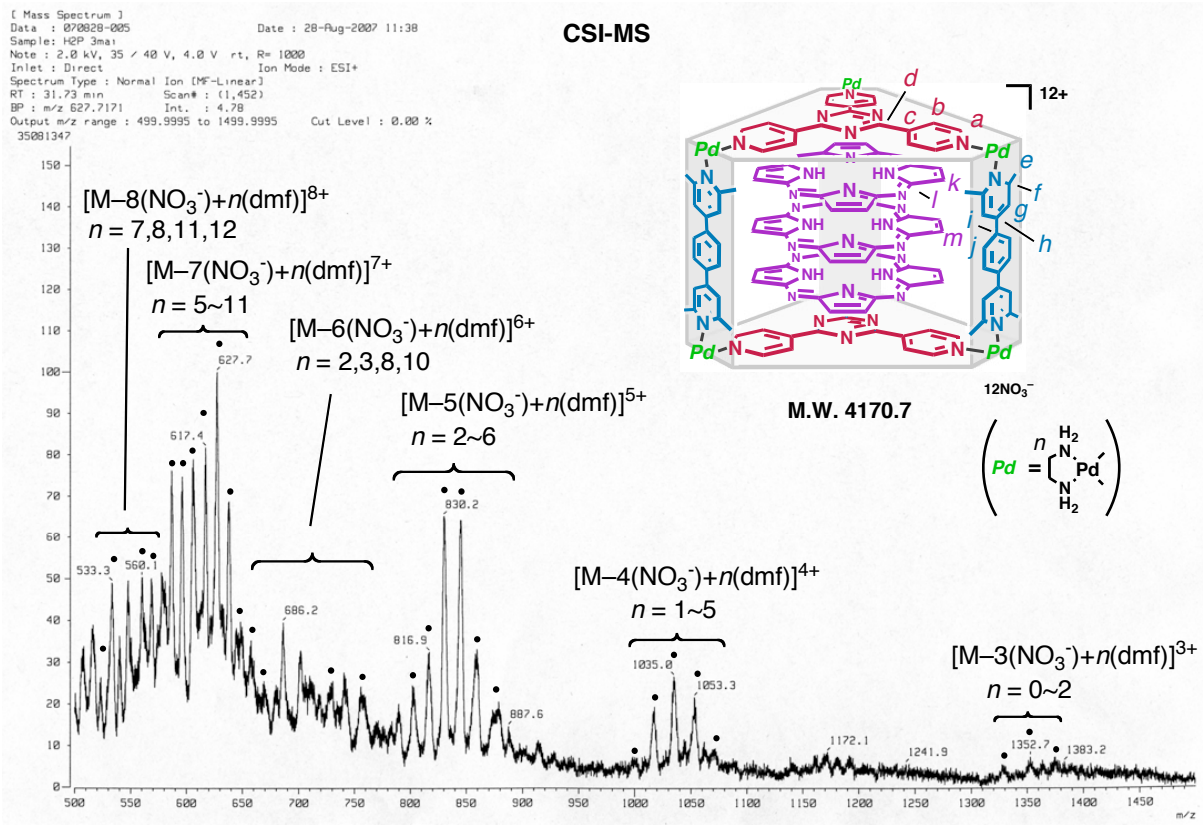

HSQC
BRUKER
ppm
12NO3−
Pd = n H2 N Pd N H2


HMBC
BRUKER
ppm
12NO3−
Pd = n H2 N Pd N H2


NOESY
BRUKER
j
g
k
e
m
k
ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
12+
12NO3−
Pd = n H2 N Pd N H2


DOSY
BRUKER
ppm
-10.4
-10.2
-10.0
-9.8
-9.6
-9.4
-9.2
-9.0
9 8 7 6 5 4 3 2 1 0 ppm
12+
12NO3−
Pd = n H2 N Pd N H2

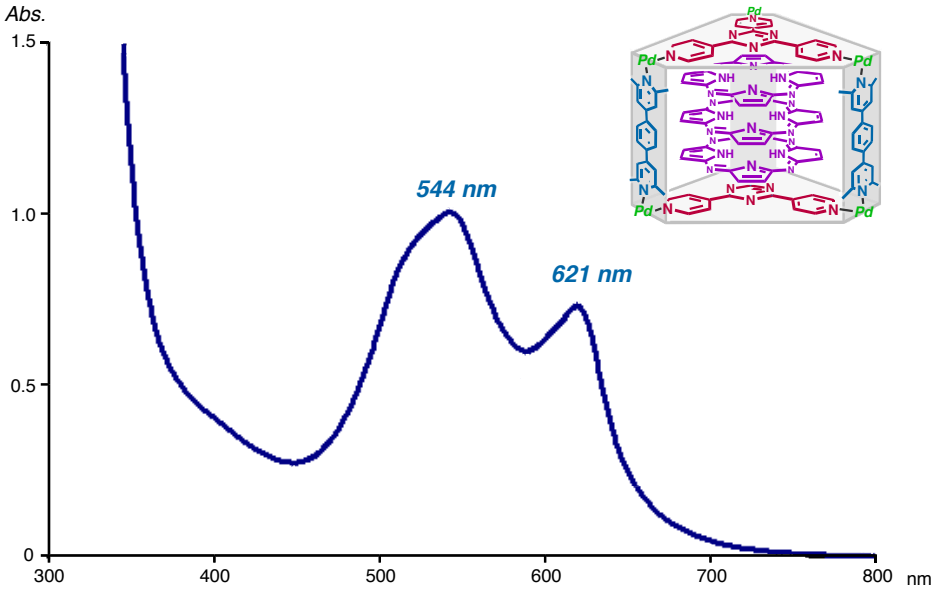
CSI-MS



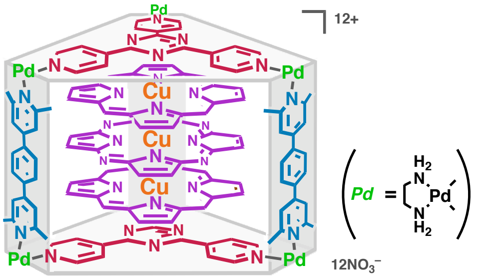
M.W. 4170.7

$12NO_3^-$

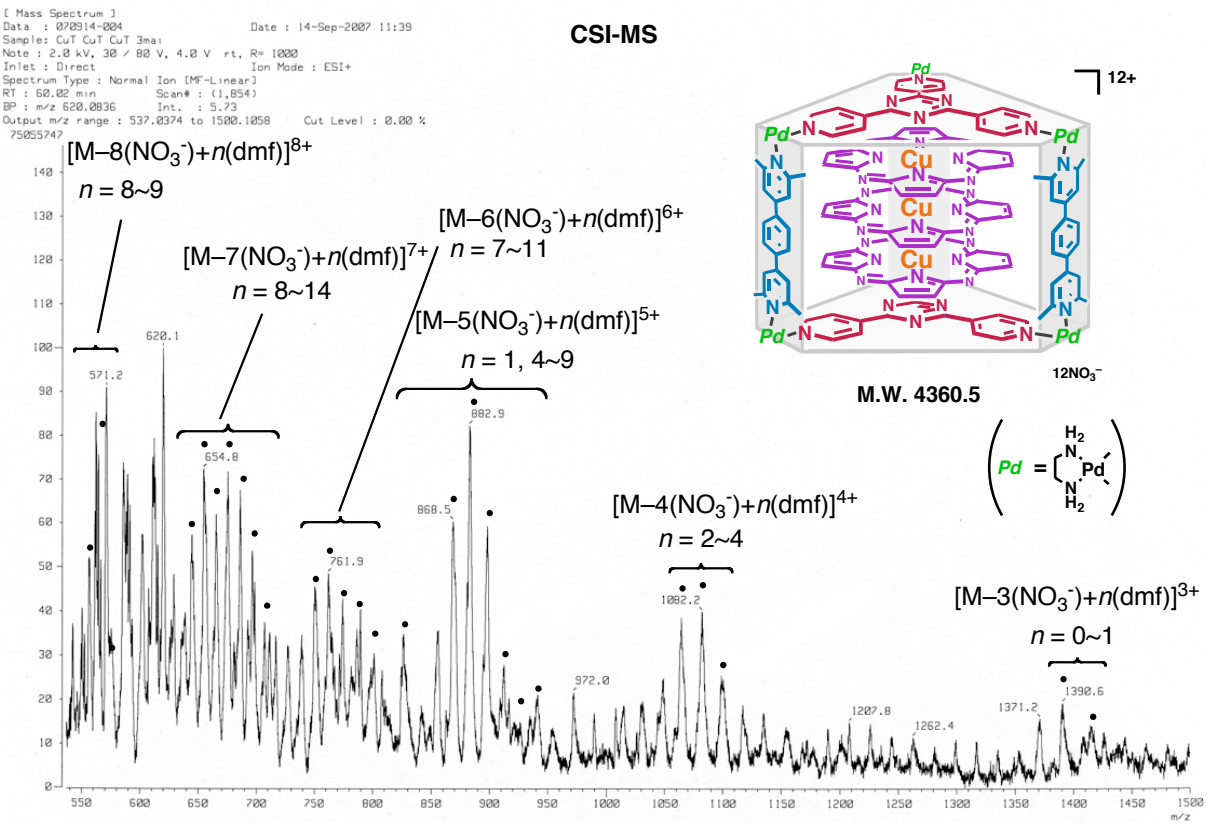
UV-vis (H_2O, r.t., 0.5 mM, l = 1 mm)

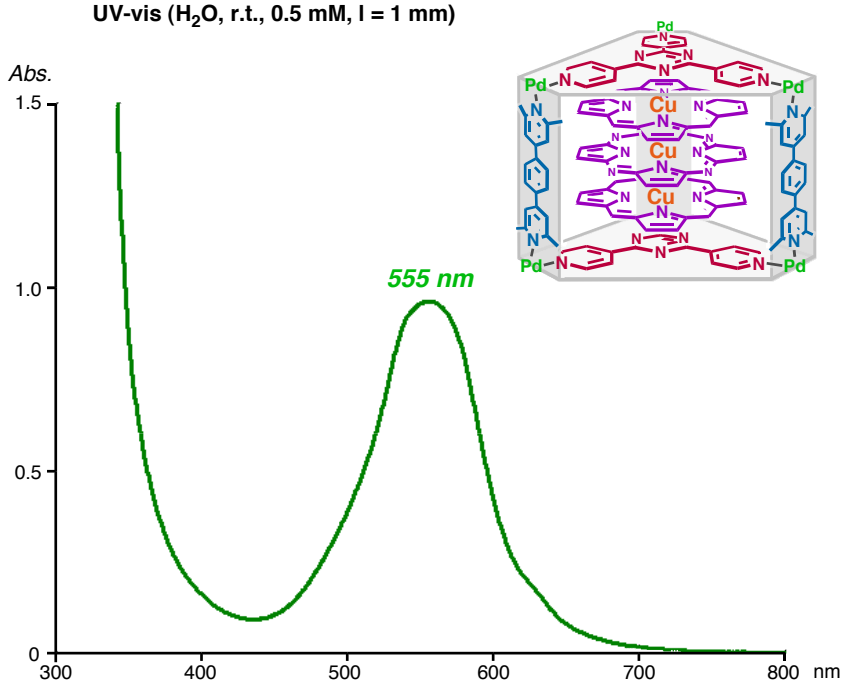


■ Physical data of **1**⊃(**6b**)$_3$:

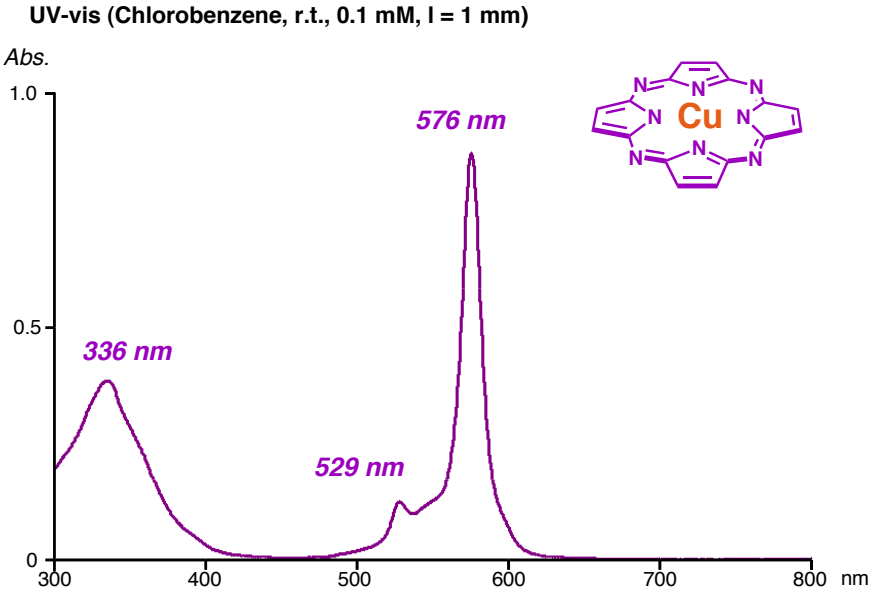


CSI-MS (H_2O:DMF = 20:1): *m/z* 4360.5 [**1**⊃(**6b**)$_3$–3•NO_3^-]$^{3+}$, 1390.5 [**1**⊃(**6b**)$_3$–3•NO_3^-+DMF]$^{3+}$, 1415.7 [**1**⊃(**6b**)$_3$–4•NO_3^-+2•DMF]$^{4+}$, 1064.5 [**1**⊃(**6b**)$_3$–4•NO_3^-+3•DMF]$^{4+}$, 1082.3 [**1**⊃(**6b**)$_3$–4•NO_3^-+4•DMF]$^{4+}$, 1100.5 [**1**⊃(**6b**)$_3$–5•NO_3^-+DMF]$^{5+}$, 825.6 [**1**⊃(**6b**)$_3$–5•NO_3^-+4•DMF]$^{5+}$, 869.2 [**1**⊃(**6b**)$_3$–5•NO_3^-+5•DMF]$^{5+}$, 882.9 [**1**⊃(**6b**)$_3$–5•NO_3^-+6•DMF]$^{5+}$, 898.1 [**1**⊃(**6b**)$_3$–5•NO_3^-+7•DMF]$^{5+}$, 912.3 [**1**⊃(**6b**)$_3$–5•NO_3^-+8•DMF]$^{5+}$, 926.1 [**1**⊃(**6b**)$_3$–5•NO_3^-+9•DMF]$^{5+}$, 941.4 [**1**⊃(**6b**)$_3$–6•NO_3^-+7•DMF]$^{6+}$, 750.4 [**1**⊃(**6b**)$_3$–6•NO_3^-+8•DMF]$^{6+}$, 761.9 [**1**⊃(**6b**)$_3$–6•NO_3^-+9•DMF]$^{6+}$, 774.3 [**1**⊃(**6b**)$_3$–6•NO_3^-+10•DMF]$^{6+}$, 786.5 [**1**⊃(**6b**)$_3$–6•NO_3^-+11•DMF]$^{6+}$, 798.5 [**1**⊃(**6b**)$_3$–7•NO_3^-+8•DMF]$^{7+}$, 644.6 [**1**⊃(**6b**)$_3$–7•NO_3^-+9•DMF]$^{7+}$, 654.9 [**1**⊃(**6b**)$_3$–7•NO_3^-+10•DMF]$^{7+}$, 665.5 [**1**⊃(**6b**)$_3$–7•NO_3^-+11•DMF]$^{7+}$, 675.6 [**1**⊃(**6b**)$_3$–7•NO_3^-+12•DMF]$^{7+}$, 686.1 [**1**⊃(**6b**)$_3$–6•NO_3^-+13•DMF]$^{7+}$, 696.5 [**1**⊃(**6b**)$_3$–7•NO_3^-+14•DMF]$^{7+}$, 707.1 [**1**⊃(**6b**)$_3$–8•NO_3^-+8•DMF]$^{8+}$, 556.7 [**1**⊃(**6b**)$_3$–8•NO_3^-+9•DMF]$^{8+}$, 564.3; IR (ATR, cm^{-1}): 3424 (br), 3206 (br), 3103 (br), 1679, 1615, 1524, 1331(br), 1196, 1057, 1130, 1057, 987; m.p.: ~200 ºC (decomposed); UV-vis (H_2O, nm): λ_{max} 555 ($\varepsilon = 1.9 \times 10^4$).


CSI-MS
[M–8(NO3-)+n(dmf)]8+
n = 8~9
[M–7(NO3-)+n(dmf)]7+
n = 8~14
[M–6(NO3-)+n(dmf)]6+
n = 7~11
[M–5(NO3-)+n(dmf)]5+
n = 1, 4~9
[M–4(NO3-)+n(dmf)]4+
n = 2~4
[M–3(NO3-)+n(dmf)]3+
n = 0~1
571.2
620.1
654.8
761.9
868.5
882.9
972.0
1082.2
1207.8
1262.4
1371.2
1390.6
12+
12NO3−
M.W. 4360.5
Pd = Pd
m/z

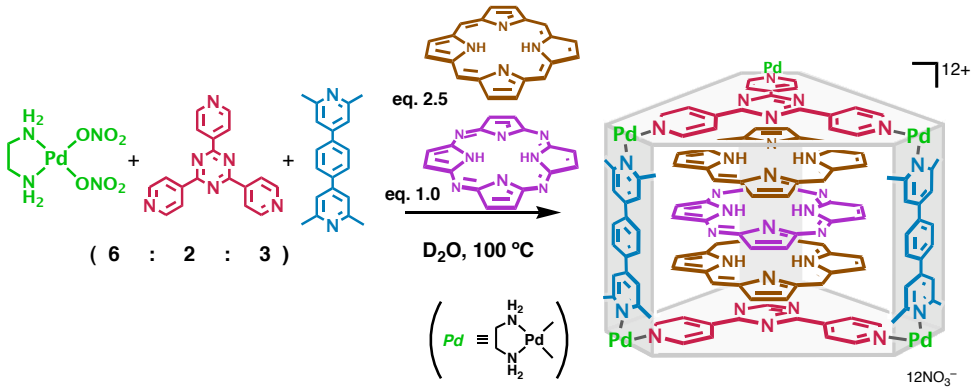

UV-vis (H2O, r.t., 0.5 mM, l = 1 mm)
Abs.
555 nm
nm

■ UV spectrum of **1**⊃(**6b**)$_3$:



UV-vis (H_2O, nm): λ_{max} 576 ($\varepsilon = 8.8 \times 10^4$), 529 ($\varepsilon = 1.2 \times 10^4$), 336 ($\varepsilon = 3.9 \times 10^4$).

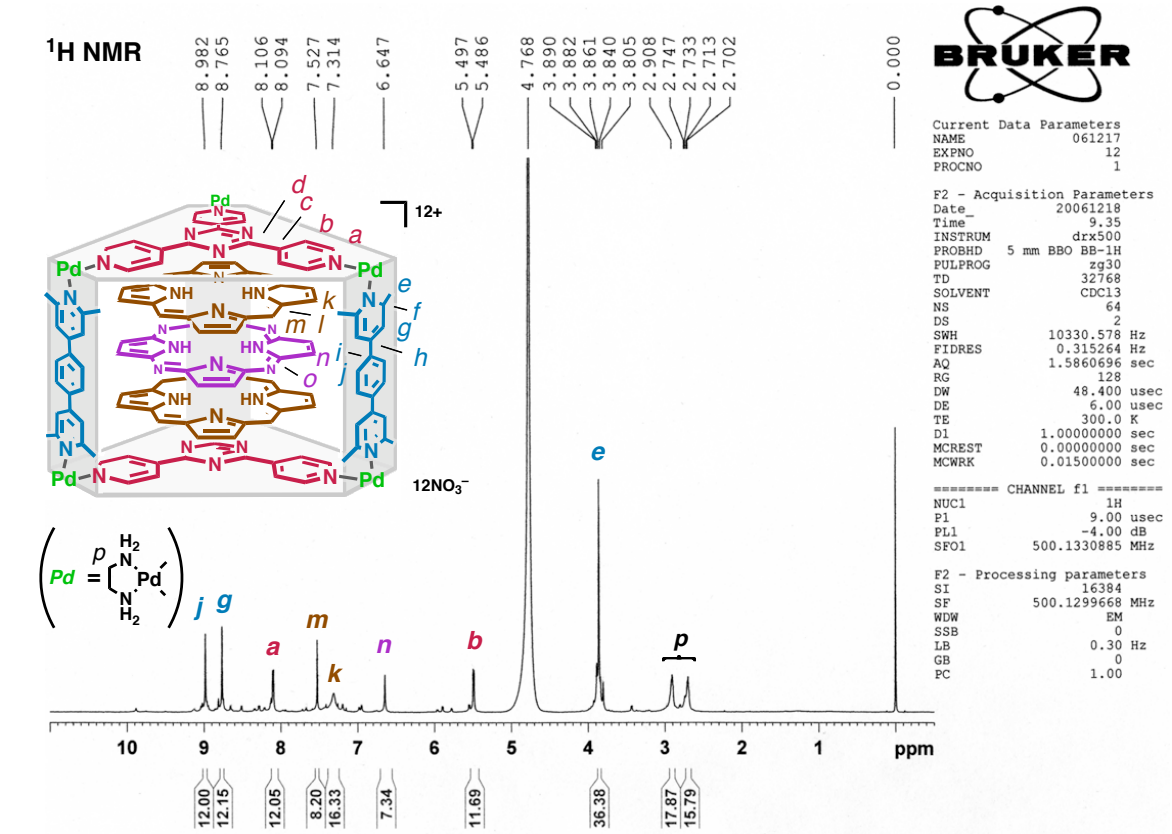
■ Synthesis of **1**⊃(**5a**•**6a**•**5a**).

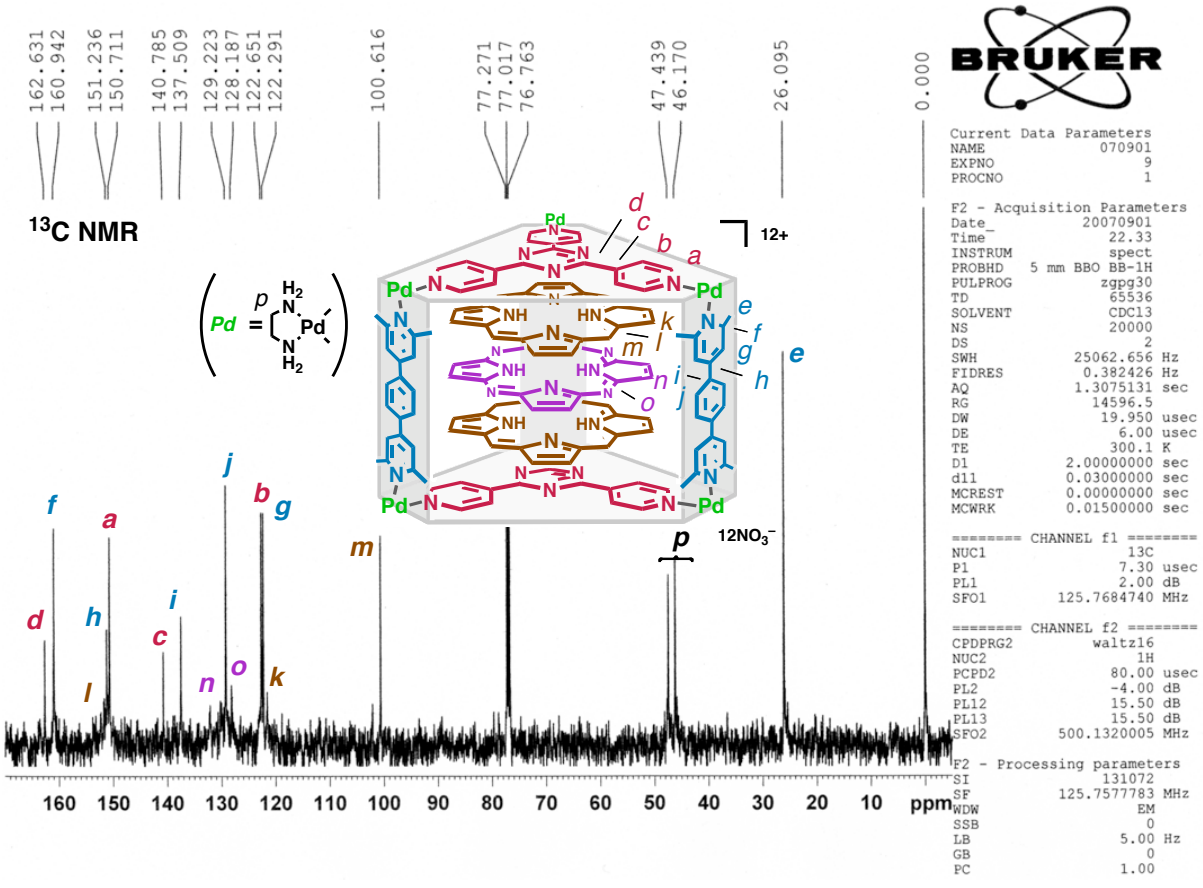


Typical procedure: (en)Pd(NO_3)$_2$ (**4**, 17.43 mg; 60.0 μmol), tris(4-pyridyl)triazine (**2**, 6.25 mg; 20.0 μmol), 1,4-bis(2,6-dimethyl-4-pyridyl)benzene (**3**, 8.65 mg; 15.0 μmol), tetrazaporphine (**6a**, 3.14 mg; 10.0 μmol, 1 eq. per **1**), and porphine (**5a**, 7.75 mg; 25 μmol, 2.5 eq. per **1**) was suspended in a D_2O solution (1.0 mL) and the mixture was stirred at 100 ºC for 2 h. After decantation of the solution, ^{1}H NMR spectrum of the resolved dark red-purple precipitation revealed the selective formation of **1**⊃(**5a**•**6a**•**5a**) complex. The solution was evaporated and dried by vacuum freeze-drying equipment to give a red-purple solid of **1**⊃(**5a**•**6a**•**5a**) complex (13.2 mg; 3.17 μmol) in 31% yield.

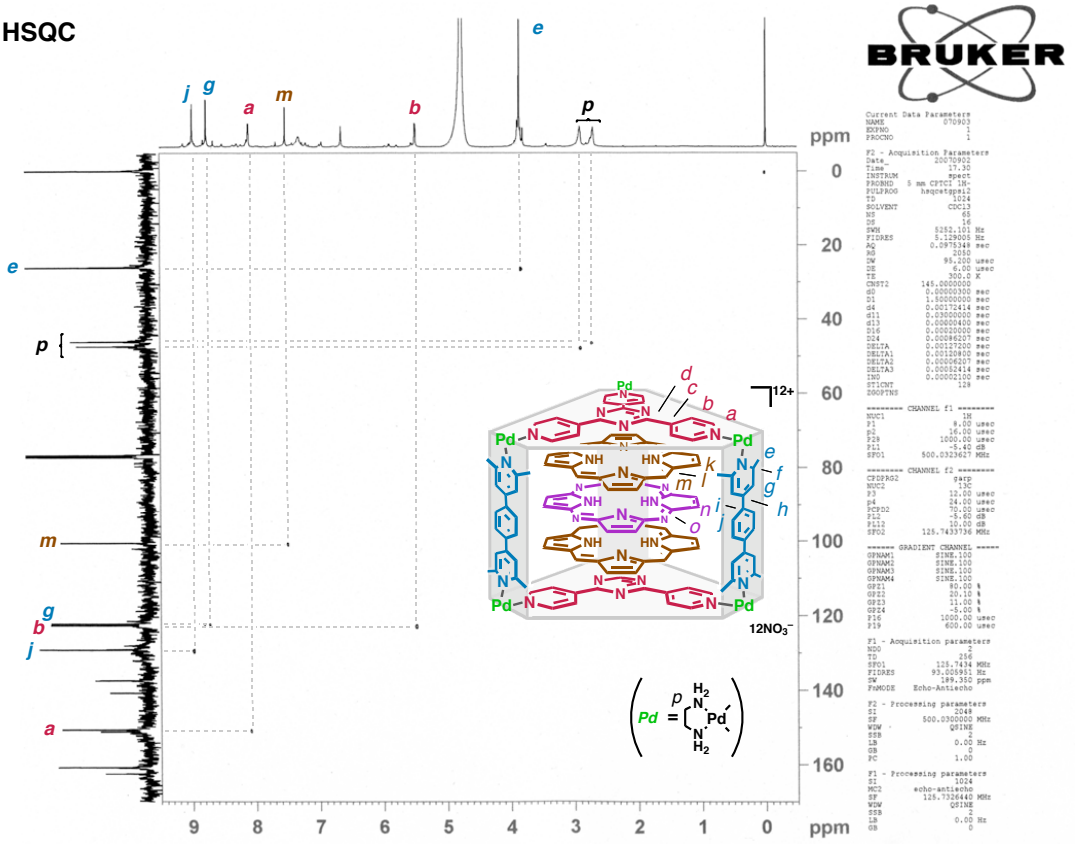
Physical data of **1**⊃(**5a**•**6a**•**5a**): ^{1}H NMR (500 MHz, D_2O, 27 ºC): δ 8.98 (s, 12H, **1**), 8.77 (s,

12H, **1**), 8.10 (d, J = 5.0Hz, 12H, **1**), 7.53 (s, 8H, **5a**), 7.31 (s, 16H, **5a**), 6.65 (s, 8H, **6a**), 5.49 (d, J = 5.0Hz, 12H, **1**), 3.86 (s, 36H, **1**), 2.91 (br, 12H, **1**), 2.71 (br, 12H, **1**); ^{13}C NMR (125 MHz, D_2O, 27 ºC): δ 162.6 (C_q, **1**), 160.9 (C_q, **1**), 151.7 (C_q, **3a**), 151.2 (C_q, **1**), 150.7 (*C*H, **1**), 140.8 (C_q, **1**), 137.5 (C_q, **1**), 132.1 (*C*H, **6a**), 129.2 (*C*H, **1**), 128.2 (C_q, **6a**), 122.7 (*C*H, **1**), 122.3 (*C*H, **1**), 121.7 (*C*H, **5a**), 100.6 (*C*H, **5a**), 47.4 (CH_2, **1**), 46.2 (CH_2, **1**), 26.1 (CH_3, **1**); DOSY-NMR (cm^2/s): D = –9.85; IR (ATR, cm^{-1}): 3452 (br), 3206 (br), 3107 (br), 1659, 1613, 1514, 1329, 1139, 1055, 949; m.p.: ~200 ºC (decomposed); CSI-MS (H_2O:DMF = 20:1): m/z 4168.0 [**1**⊃(**5a**•**6a**•**5a**)–3•NO_3^-]$^{3+}$, 1327.4 [**1**⊃(**5a**•**6a**•**5a**)–4•NO_3^-+2•DMF]$^{4+}$, 1017.3 [**1**⊃(**3a**•**2a**•**3a**)–4•NO_3^-+3•DMF]$^{4+}$, 1035.2 [**1**⊃(**5a**•**6a**•**5a**)–4•NO_3^-+4•DMF]$^{4+}$, 1053.7 [**1**⊃(**3a**•**2a**•**3a**)–4•NO_3^-+5•DMF]$^{4+}$, 1071.9 [**1**⊃(**5a**•**6a**•**5a**)–4•NO_3^-+6•DMF]$^{4+}$, 1089.4 [**1**⊃(**3a**•**2a**•**3a**)–5•NO_3^-+3•DMF]$^{5+}$, 816.2 [**1**⊃(**5a**•**6a**•**5a**)–5•NO_3^-+4•DMF]$^{5+}$, 830.6 [**1**⊃(**3a**•**2a**•**3a**)–5•NO_3^-+5•DMF]$^{5+}$, 845.0 [**1**⊃(**5a**•**6a**•**5a**)–5•NO_3^-+6•DMF]$^{5+}$, 860.1 [**1**⊃(**3a**•**2a**•**3a**)–5•NO_3^-+7•DMF]$^{5+}$, 874.1 [**1**⊃(**5a**•**6a**•**5a**)–5•NO_3^-+8•DMF]$^{5+}$, 889.1 [**1**⊃(**3a**•**2a**•**3a**)–5•NO_3^-+9•DMF]$^{5+}$, 904.1 [**1**⊃(**5a**•**6a**•**5a**)–5•NO_3^-+10•DMF]$^{5+}$, 917.1 [**1**⊃(**3a**•**2a**•**3a**)–5•NO_3^-+11•DMF]$^{5+}$, 933.2 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-]$^{6+}$, 633.2 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+DMF]$^{6+}$, 644.5 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+2•DMF]$^{6+}$, 656.2 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+3•DMF]$^{6+}$, 669.5 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+4•DMF]$^{6+}$, 680.8 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+5•DMF]$^{6+}$, 694.0 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+6•DMF]$^{6+}$, 706.2 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+7•DMF]$^{6+}$, 718.2 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+8•DMF]$^{6+}$, 730.7 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+9•DMF]$^{6+}$, 742.9 [**1**⊃(**5a**•**6a**•**5a**)–6•NO_3^-+10•DMF]$^{6+}$, 755.1 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+3•DMF]$^{7+}$, 564.5 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+6•DMF]$^{7+}$, 596.5 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+7•DMF]$^{7+}$, 605.9 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+8•DMF]$^{7+}$, 617.5 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+9•DMF]$^{7+}$, 628.1 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+10•DMF]$^{7+}$, 638.5 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+11•DMF]$^{7+}$, 649.0 [**1**⊃(**5a**•**6a**•**5a**)–7•NO_3^-+12•DMF]$^{7+}$, 659.3; UV-vis (H_2O, nm): λ_{max} 619 ($\varepsilon = 6.8 \times 10^3$), 554 ($\varepsilon = 9.1 \times 10^3$), 491 ($\varepsilon = 1.1 \times 10^4$), 398 ($\varepsilon = 8.4 \times 10^4$).

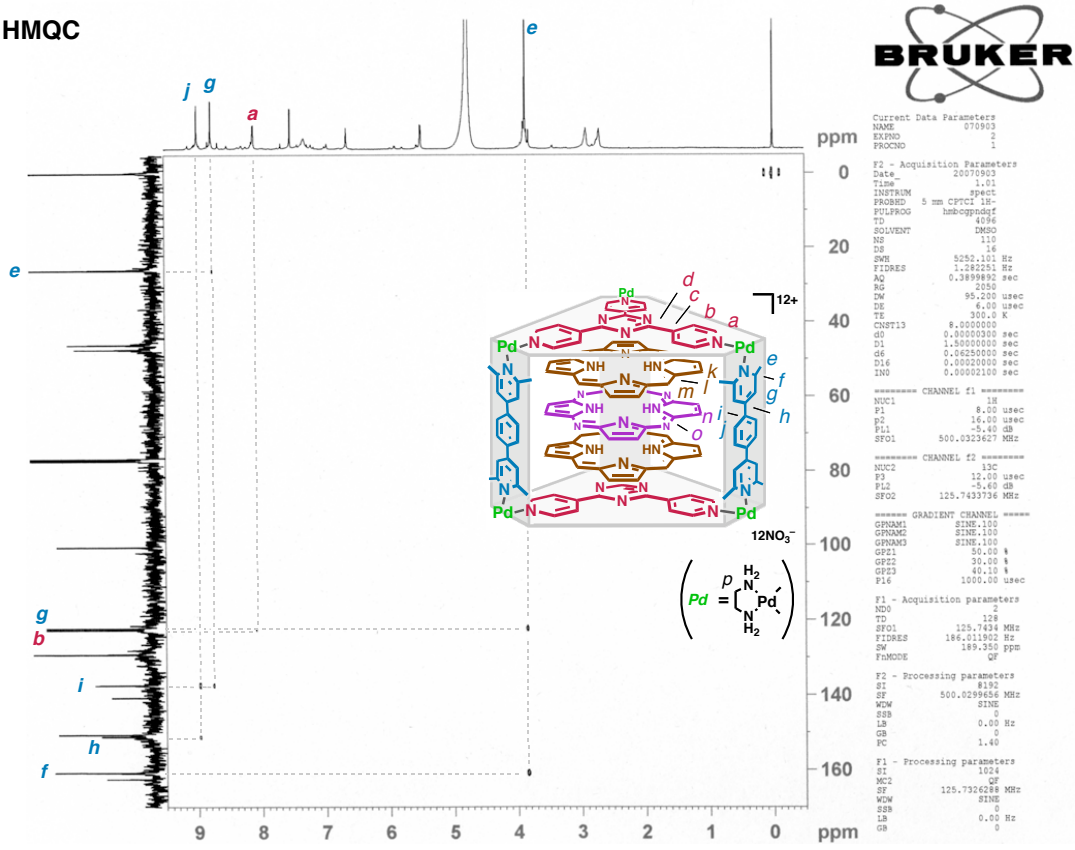

1H NMR
8.982
8.765
8.106
8.094
7.527
7.314
6.647
5.497
5.486
4.768
3.890
3.882
3.861
3.840
3.805
2.908
2.747
2.733
2.713
2.702
0.000
12+
12NO3−
Pd = p H2 N Pd N H2
j g a m k n b e p
10 9 8 7 6 5 4 3 2 1 ppm
12.00 12.15 12.05 8.20 16.33 7.34 11.69 36.38 17.87 15.79
BRUKER
Current Data Parameters
NAME 061217
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061218
Time 9.35
INSTRUM drx500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 128
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 16384
SF 500.1299668 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


13C NMR
162.631
160.942
151.236
150.711
140.785
137.509
129.223
128.187
122.651
122.291
100.616
77.271
77.017
76.763
47.439
46.170
26.095
0.000
12+
12NO3−
Pd = p H2 N Pd N H2
f a d h l i c j b g n o k m p e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
BRUKER
Current Data Parameters
NAME 070901
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070901
Time 22.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 20000
DS 2
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3075131 sec
RG 14596.5
DW 19.950 usec
DE 6.00 usec
TE 300.1 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.30 usec
PL1 2.00 dB
SFO1 125.7684740 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.50 dB
PL13 15.50 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 131072
SF 125.7577783 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.00

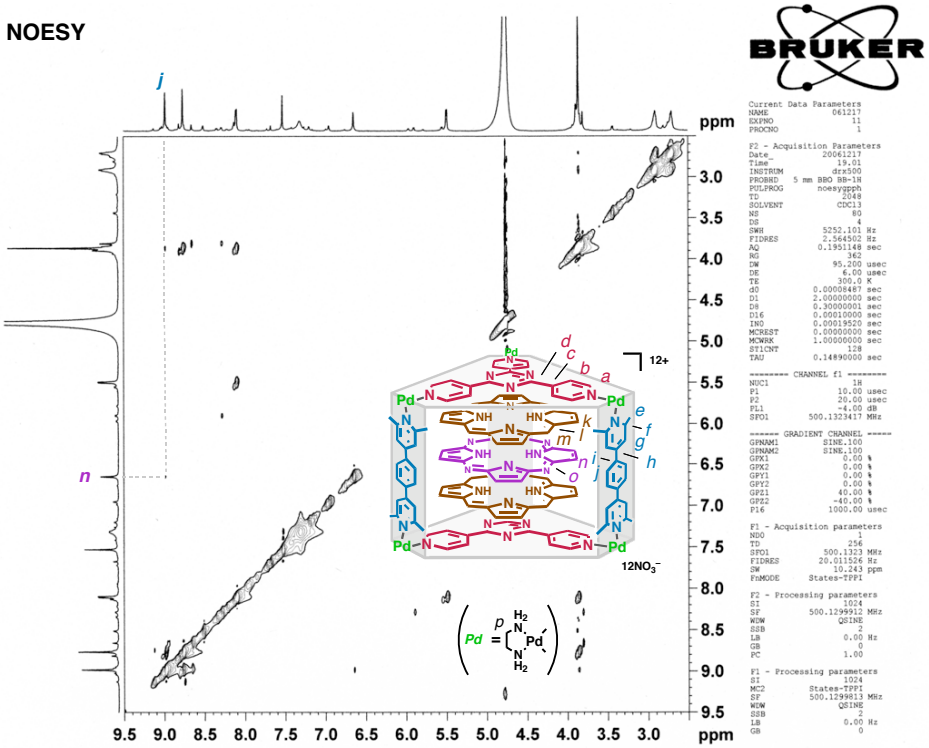
HSQC


BRUKER
e
j g a m b p
ppm
0 20 40 60 80 100 120 140 160
9 8 7 6 5 4 3 2 1 0 ppm
e
p
m
g
b
j
a
d c b a
12+
Pd
e f g h
k l m n i j o
12NO3−
Pd = p H2 N Pd N H2

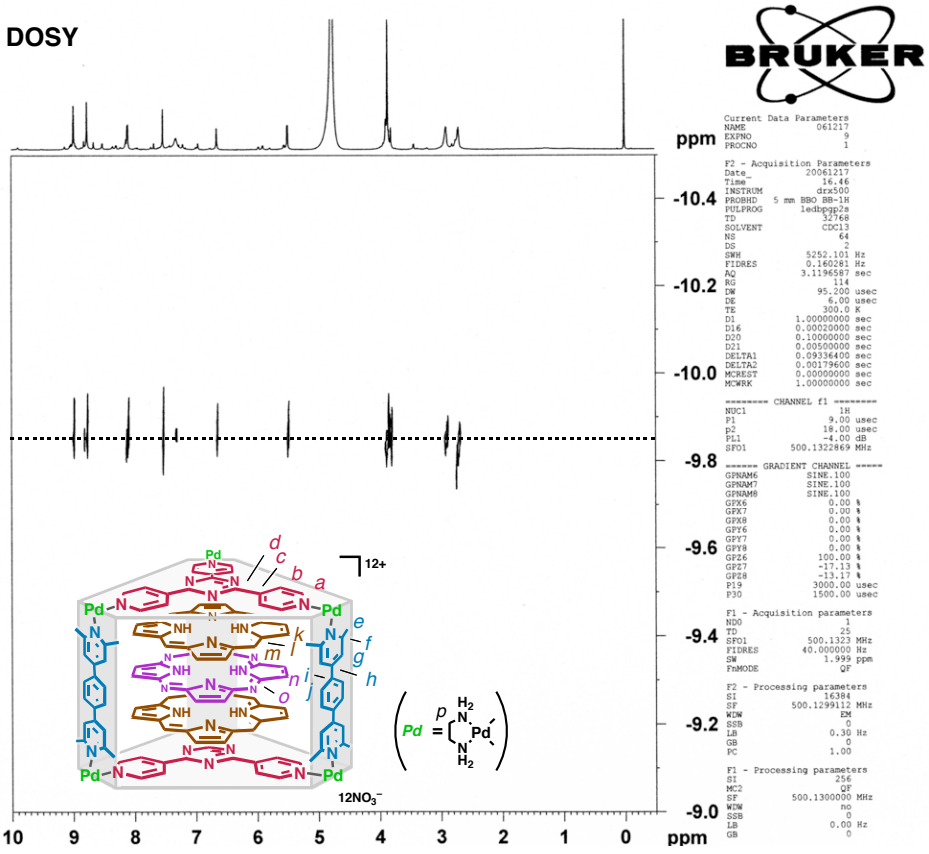
HMQC


BRUKER
e
j g a
ppm
0 20 40 60 80 100 120 140 160
9 8 7 6 5 4 3 2 1 0 ppm
e
g
b
i
h
f
d c b a
12+
Pd
e f g h
k l m n i j o
12NO3−
Pd = p H2 N Pd N H2

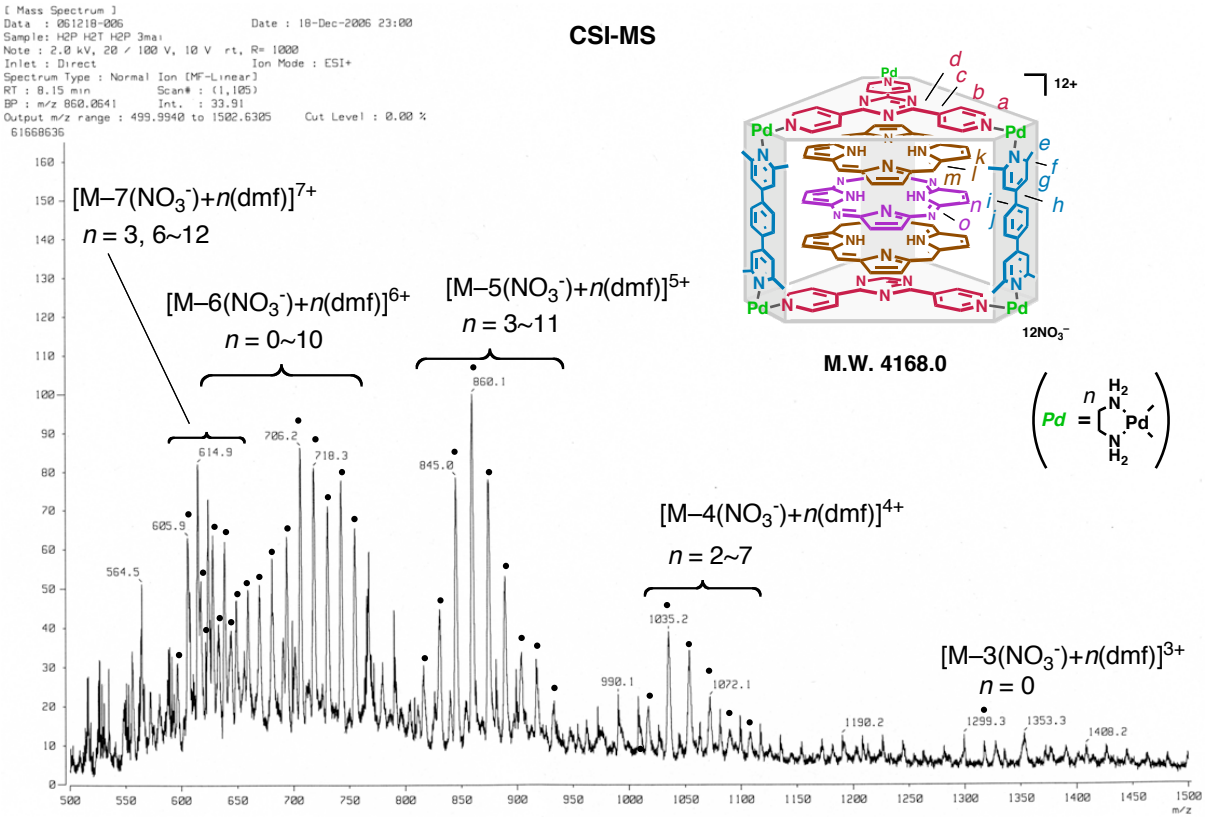
NOESY


BRUKER
ppm
12+
12NO3−
Pd = p H2 N Pd N H2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm

DOSY

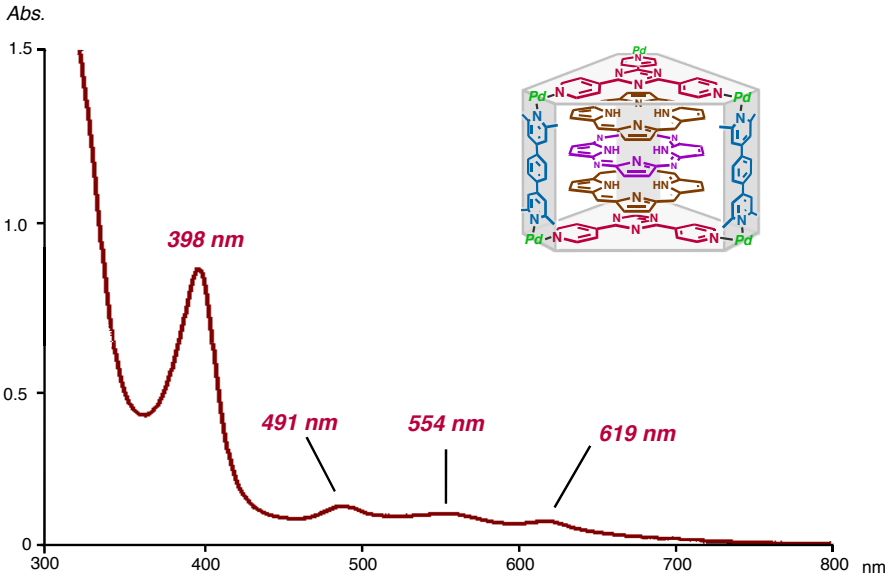

BRUKER
ppm
12+
12NO3−
Pd = p H2 N Pd N H2
10 9 8 7 6 5 4 3 2 1 0 ppm

CSI-MS

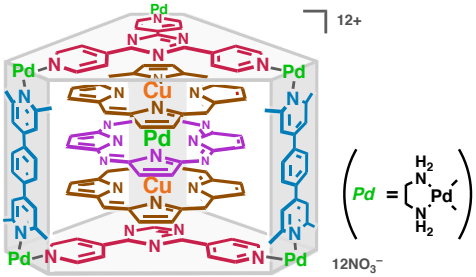


M.W. 4168.0

UV-vis (H_2O, r.t., 0.1 mM, l = 1 mm)

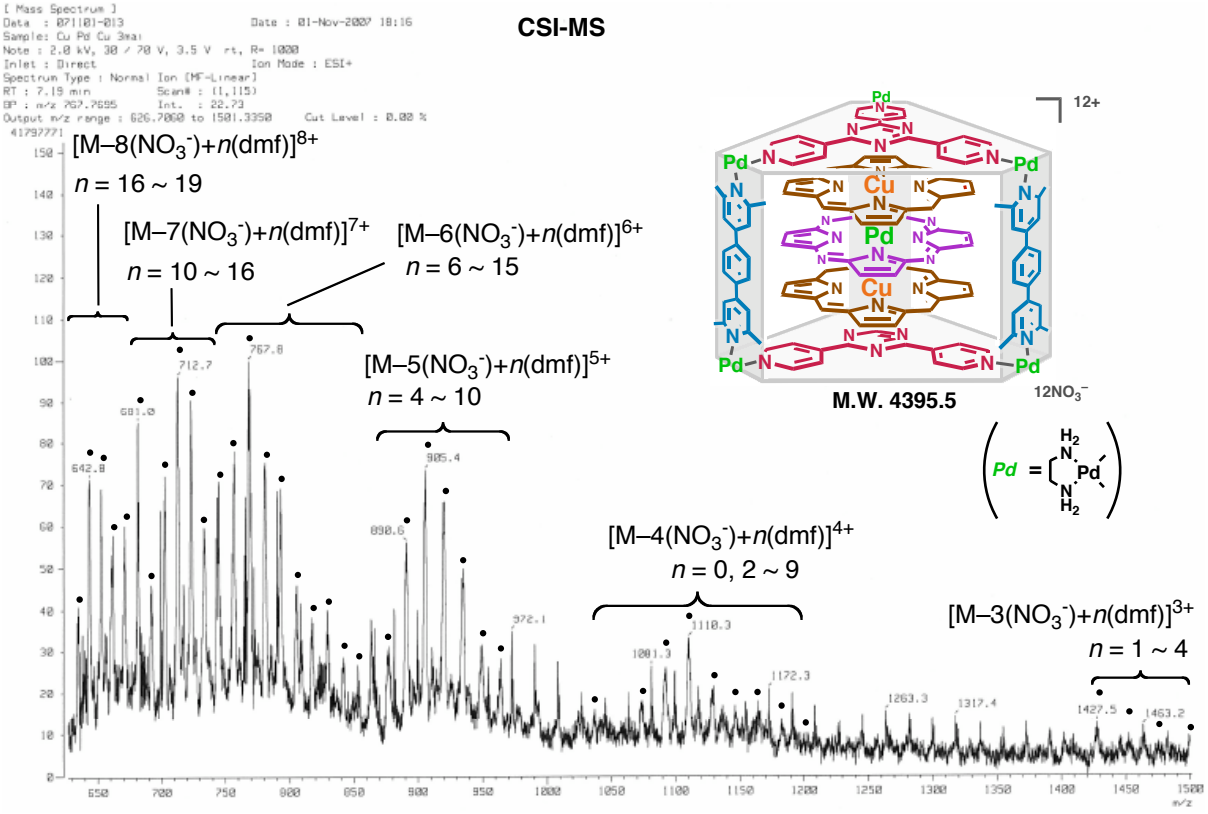


■ Physical data of **1**⊃(**5b•6c•5b**):

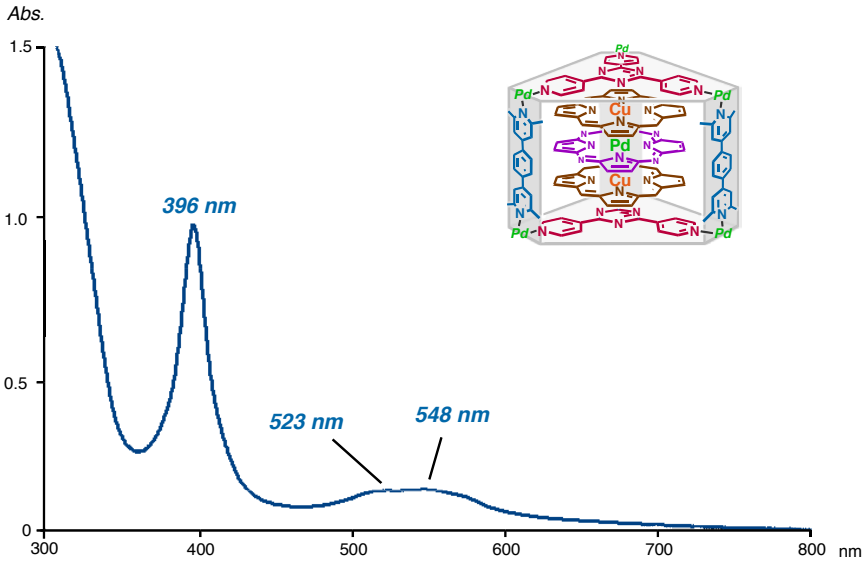


CSI-MS (H_2O:DMF = 20:1): *m/z* 4395.5 [**1**⊃(**5b•6c•5b**)–3•NO_3^-+DMF]$^{3+}$, 1427.5 [**1**⊃(**5b•6c•5b**)–3•NO_3^-+2•DMF]$^{3+}$, 1452.4 [**1**⊃(**5b•6c•5b**)–3•NO_3^-+3•DMF]$^{3+}$, 1475.6 [**1**⊃(**5b•6c•5b**)–3•NO_3^-+4•DMF]$^{3+}$, 1499.8 [**1**⊃(**5b•6c•5b**)–4•NO_3^-]$^{4+}$, 1036.9 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+2•DMF]$^{4+}$, 1073.9 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+3•DMF]$^{4+}$, 1092.2 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+4•DMF]$^{4+}$, 1110.3 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+5•DMF]$^{4+}$, 1129.2 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+6•DMF]$^{4+}$, 1146.2 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+7•DMF]$^{4+}$, 1163.5 [**1**⊃(**5b•6c•5b**)–4•NO_3^-+8•DMF]$^{4+}$, 1182.4 [**1**⊃(**5b•6d•5b**)–4•NO_3^-+9•DMF]$^{4+}$, 1202.1 [**1**⊃(**5b•6c•5b**)–5•NO_3^-]$^{5+}$, 816.9 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+4•DMF]$^{5+}$, 876.4 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+5•DMF]$^{5+}$, 890.6 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+6•DMF]$^{5+}$, 905.4 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+7•DMF]$^{5+}$, 919.8 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+8•DMF]$^{5+}$, 934.7 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+9•DMF]$^{5+}$, 949.2 [**1**⊃(**5b•6c•5b**)–5•NO_3^-+10•DMF]$^{5+}$, 963.6 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+6•DMF]$^{6+}$, 744.6 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+7•DMF]$^{6+}$, 756.8 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+8•DMF]$^{6+}$, 767.8 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+9•DMF]$^{6+}$, 780.7 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+10•DMF]$^{6+}$, 792.6 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+11•DMF]$^{6+}$, 805.3 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+12•DMF]$^{6+}$, 816.8 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+13•DMF]$^{6+}$, 828.8 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+14•DMF]$^{6+}$, 841.5 [**1**⊃(**5b•6c•5b**)–6•NO_3^-+15•DMF]$^{6+}$, 852.7 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+10•DMF]$^{7+}$, 670.7 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+11•DMF]$^{7+}$, 681.0 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+12•DMF]$^{7+}$, 691.1 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+13•DMF]$^{7+}$, 702.1 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+14•DMF]$^{7+}$, 712.7 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+15•DMF]$^{7+}$, 722.3 [**1**⊃(**5b•6c•5b**)–7•NO_3^-+16•DMF]$^{7+}$, 733.0 [**1**⊃(**5b•6c•5b**)–8•NO_3^-+16•DMF]$^{8+}$, 634.7 [**1**⊃(**5b•6c•5b**)–8•NO_3^-+17•DMF]$^{8+}$, 642.9 [**1**⊃(**5b•6c•5b**)–8•NO_3^-+18•DMF]$^{8+}$, 652.3 [**1**⊃(**5b•6c•5b**)–8•NO_3^-+19•DMF]$^{8+}$, 661.6; IR (ATR, cm^{-1}): 3412 (br), 3206 (br), 3104 (br), 1614, 1519, 1331(br), 1152, 1057, 996, 827, 804; m.p.: ~200 ºC (decomposed); UV-vis (H_2O, nm): λ_{max} 548 ($\varepsilon = 1.3 \times 10^4$), 523 ($\varepsilon = 1.2 \times 10^4$), 396 ($\varepsilon = 9.5 \times 10^4$).

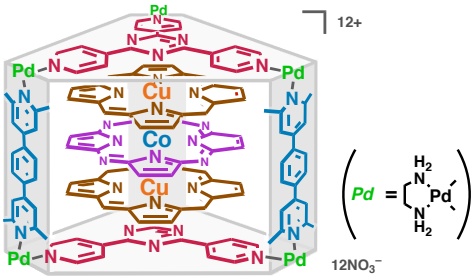
CSI-MS



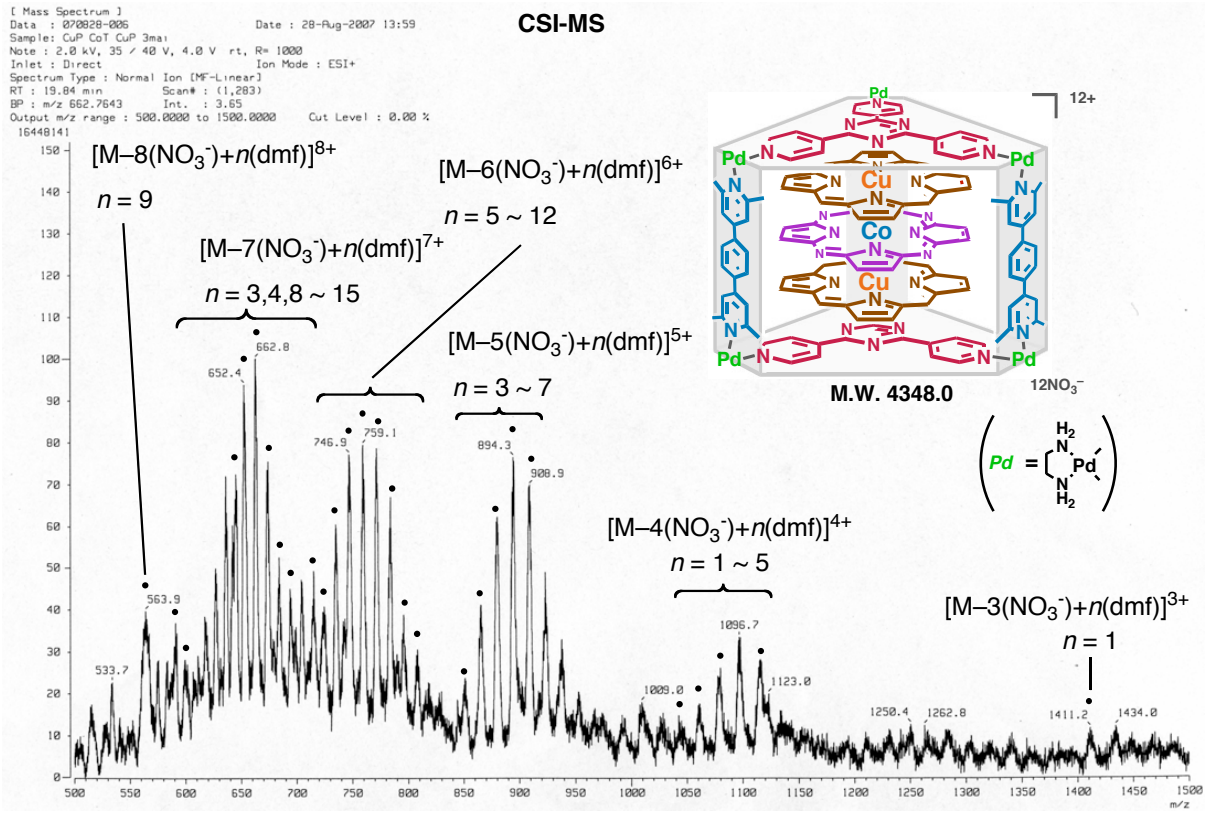
UV-vis (H_2O, r.t., 0.1 mM, l = 1 mm)

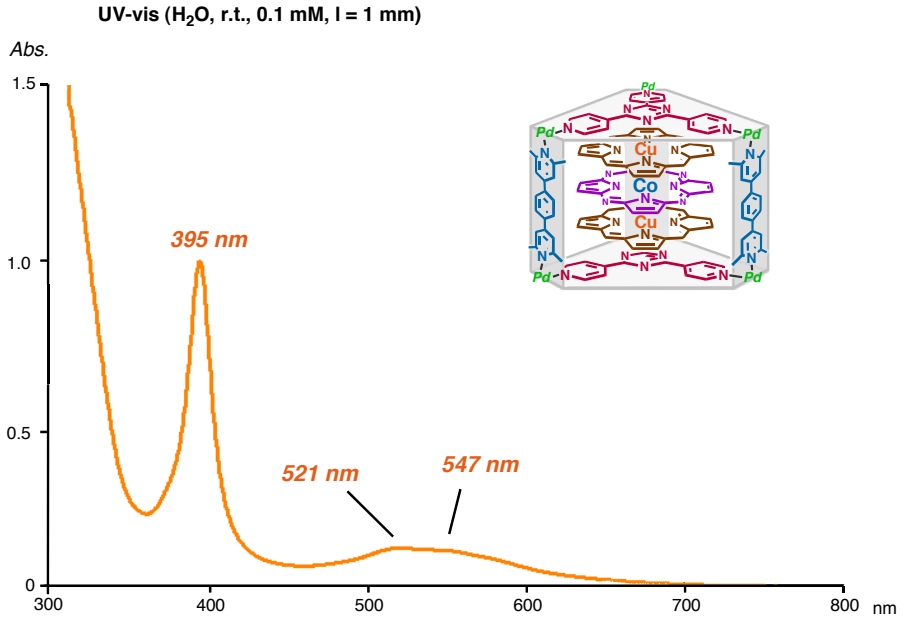


■ Physical data of **1**⊃(**5b•6d•5b**):

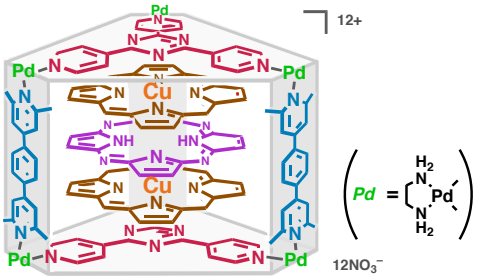


CSI-MS (H_2O:DMF = 20:1): *m/z* 4348.0 [**1**⊃(**5b•6d•5b**)–3•NO_3^-+DMF]$^{3+}$, 1411.2 [**1**⊃(**5b•6d•5b**)–4•NO_3^-+DMF]$^{4+}$, 1042.4 [**1**⊃(**5b•6d•5b**)–4•NO_3^-+2•DMF]$^{4+}$, 1060.8 [**1**⊃(**5b•6d•5b**)–4•NO_3^-+3•DMF]$^{4+}$, 1079.8 [**1**⊃(**5b•6d•5b**)–4•NO_3^-+5•DMF]$^{4+}$, 1115.6 [**1**⊃(**5b•6d•5b**)–5•NO_3^-+3•DMF]$^{5+}$, 850.8 [**1**⊃(**5b•6d•5b**)–5•NO_3^-+4•DMF]$^{5+}$, 865.1 [**1**⊃(**5b•6b•5b**)–5•NO_3^-+5•DMF]$^{5+}$, 879.9 [**1**⊃(**5b•6b•5b**)–5•NO_3^-+6•DMF]$^{5+}$, 894.3 [**1**⊃(**5b•6b•5b**)–5•NO_3^-+7•DMF]$^{5+}$, 908.9 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+5•DMF]$^{6+}$, 724.6 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+6•DMF]$^{6+}$, 735.1 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+7•DMF]$^{6+}$, 746.9 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+8•DMF]$^{6+}$, 759.1 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+9•DMF]$^{6+}$, 771.5 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+10•DMF]$^{6+}$, 783.9 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+11•DMF]$^{6+}$, 795.6 [**1**⊃(**5b•6b•5b**)–6•NO_3^-+12•DMF]$^{6+}$, 808.0 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+3•DMF]$^{7+}$, 590.8 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+4•DMF]$^{7+}$, 599.4 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+8•DMF]$^{7+}$, 642.1 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+9•DMF]$^{7+}$, 652.4 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+10•DMF]$^{7+}$, 662.8 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+11•DMF]$^{7+}$, 674.2 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+12•DMF]$^{7+}$, 683.9 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+13•DMF]$^{7+}$, 693.8 [**1**⊃(**5b•6b•5b**)–7•NO_3^-+15•DMF]$^{7+}$, 715.1 [**1**⊃(**5b•6b•5b**)–8•NO_3^-+9•DMF]$^{8+}$, 563.9; IR (ATR, cm^{-1}): 3425 (br), 3211 (br), 3108 (br), 1613, 1524, 1519, 1331(br), 1153, 1059, 994; m.p.: ~200 ºC (decomposed); UV-vis (H_2O, nm): λ_{max} 547 ($\varepsilon = 1.1 \times 10^4$), 521 ($\varepsilon = 1.2 \times 10^4$), 395 ($\varepsilon = 9.8 \times 10^4$).


CSI-MS
[M–8(NO3-)+n(dmf)]8+
n = 9
[M–7(NO3-)+n(dmf)]7+
n = 3,4,8 ~ 15
[M–6(NO3-)+n(dmf)]6+
n = 5 ~ 12
[M–5(NO3-)+n(dmf)]5+
n = 3 ~ 7
[M–4(NO3-)+n(dmf)]4+
n = 1 ~ 5
[M–3(NO3-)+n(dmf)]3+
n = 1
12+
M.W. 4348.0
12NO3−
Pd = [H2N, Pd, NH2]
m/z

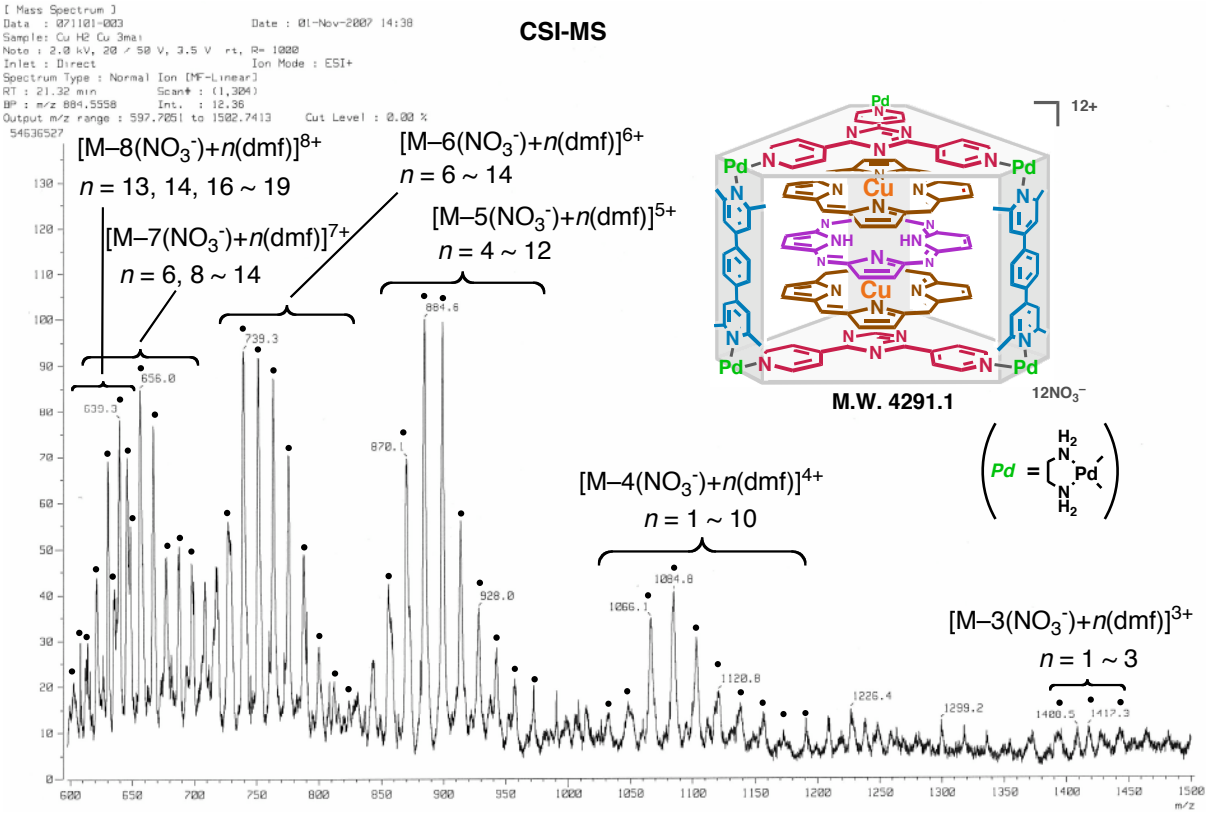

UV-vis (H2O, r.t., 0.1 mM, l = 1 mm)
Abs.
395 nm
521 nm
547 nm
nm

■ Physical data of **1**⊃(**5b•6a•5b**):

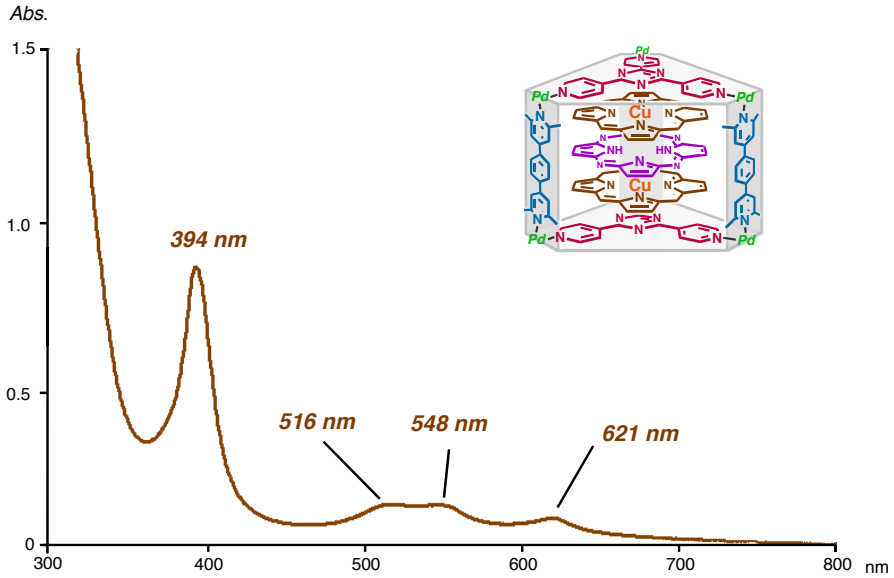


CSI-MS (H_2O:DMF = 20:1): *m/z* 4291.1 [**1**⊃(**5b•6a•5b**)–3•NO_3^-+DMF]$^{3+}$, 1392.5 [**1**⊃(**5b•6a•5b**)–3•NO_3^-+2•DMF]$^{3+}$, 1417.3 [**1**⊃(**5b•6a•5b**)–3•NO_3^-+3•DMF]$^{3+}$, 1442.5 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+DMF]$^{4+}$, 1030.0 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+2•DMF]$^{4+}$, 1047.8 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+3•DMF]$^{4+}$, 1066.1 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+4•DMF]$^{4+}$, 1084.8 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+5•DMF]$^{4+}$, 1102.9 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+6•DMF]$^{4+}$, 1120.8 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+7•DMF]$^{4+}$, 1138.2 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+8•DMF]$^{4+}$, 1156.3 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+9•DMF]$^{4+}$, 1172.3 [**1**⊃(**5b•6a•5b**)–4•NO_3^-+10•DMF]$^{4+}$, 1193.1 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+4•DMF]$^{5+}$, 855.6 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+5•DMF]$^{5+}$, 870.1 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+6•DMF]$^{5+}$, 884.6 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+7•DMF]$^{5+}$, 899.0 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+8•DMF]$^{5+}$, 913.5 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+9•DMF]$^{5+}$, 928.0 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+10•DMF]$^{5+}$, 942.3 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+11•DMF]$^{5+}$, 957.2 [**1**⊃(**5b•6a•5b**)–5•NO_3^-+12•DMF]$^{5+}$, 972.2 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+6•DMF]$^{6+}$, 726.9 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+7•DMF]$^{6+}$, 739.3 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+8•DMF]$^{6+}$, 751.0 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+9•DMF]$^{6+}$, 763.3 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+10•DMF]$^{6+}$, 775.2 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+11•DMF]$^{6+}$, 787.7 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+12•DMF]$^{6+}$, 799.9 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+13•DMF]$^{6+}$, 812.1 [**1**⊃(**5b•6a•5b**)–6•NO_3^-+14•DMF]$^{6+}$, 823.2 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+8•DMF]$^{7+}$, 634.8 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+9•DMF]$^{7+}$, 645.6 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+10•DMF]$^{7+}$, 656.0 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+11•DMF]$^{7+}$, 666.5 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+12•DMF]$^{7+}$, 676.9 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+13•DMF]$^{7+}$, 687.3 [**1**⊃(**5b•6a•5b**)–7•NO_3^-+14•DMF]$^{7+}$, 697.5 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+13•DMF]$^{8+}$, 593.8 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+14•DMF]$^{8+}$, 602.8 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+16•DMF]$^{8+}$, 621.0 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+17•DMF]$^{8+}$, 630.0 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+18•DMF]$^{8+}$, 639.3 [**1**⊃(**5b•6a•5b**)–8•NO_3^-+18•DMF]$^{8+}$, 647.8; IR (ATR, cm^{-1}): 3406 (br), 3204 (br), 3102 (br), 1614, 1519, 1454, 1327(br), 1152, 1057, 995, 937, 827, 805; m.p.: ~200 ºC (decomposed); UV-vis (H_2O, nm): λ_{max} 621 ($\varepsilon = 7.8 \times 10^3$), 548 ($\varepsilon = 1.2 \times 10^4$), 516 ($\varepsilon = 1.2 \times 10^4$), 394 ($\varepsilon = 8.4 \times 10^4$).

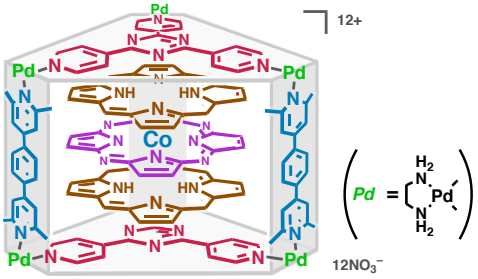
CSI-MS



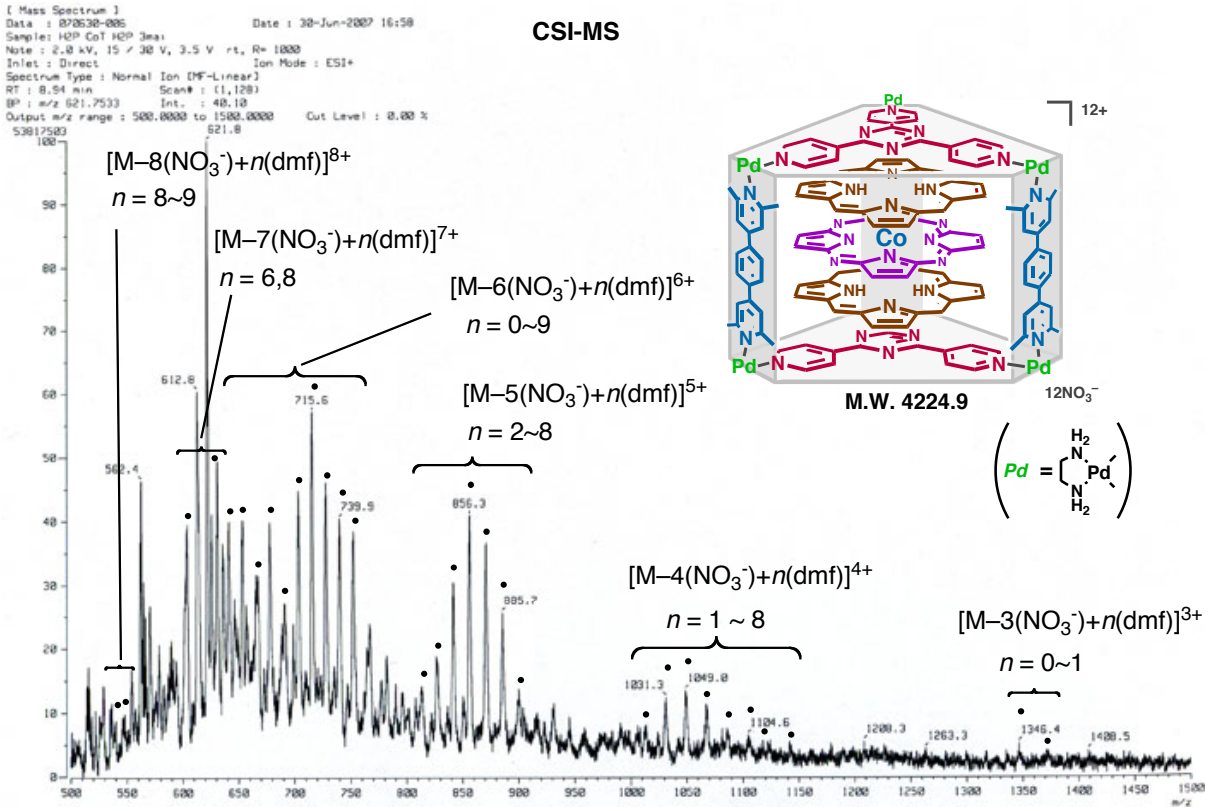
UV-vis (H_2O, r.t., 0.1mM, l = 1 mm)

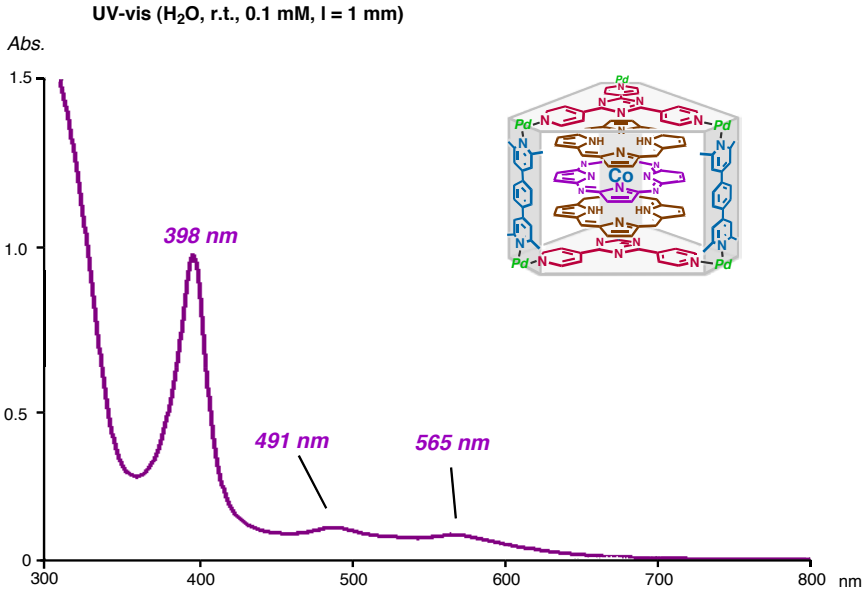


■ Physical data of **1**⊃(**5a•6d•5a**):

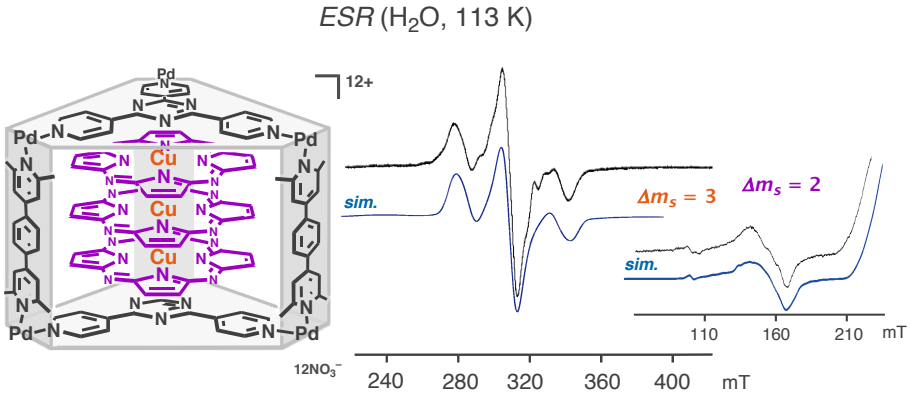


CSI-MS (H_2O:DMF = 20:1): *m/z* 4224.9 [**1**⊃(**5a•6d•5a**)–3•NO_3^-]$^{3+}$, 1346.4 [**1**⊃(**5a•6d•5a**)–3•NO_3^-+DMF]$^{3+}$, 1371.5 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+DMF]$^{4+}$, 1013.2 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+2•DMF]$^{4+}$, 1031.3 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+3•DMF]$^{4+}$, 1049.0 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+4•DMF]$^{4+}$, 1067.2 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+5•DMF]$^{4+}$, 1085.9 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+6•DMF]$^{4+}$, 1104.6 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+7•DMF]$^{4+}$, 1122.1 [**1**⊃(**5a•6d•5a**)–4•NO_3^-+8•DMF]$^{4+}$, 1141.2 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+2•DMF]$^{5+}$, 813.1 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+3•DMF]$^{5+}$, 826.4 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+4•DMF]$^{5+}$, 841.7 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+5•DMF]$^{5+}$, 856.3 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+6•DMF]$^{5+}$, 871.2 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+7•DMF]$^{5+}$, 885.7 [**1**⊃(**5a•6d•5a**)–5•NO_3^-+8•DMF]$^{5+}$, 900.0 [**1**⊃(**5a•6d•5a**)–6•NO_3^-]$^{6+}$, 641.3 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+DMF]$^{6+}$, 653.6 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+2•DMF]$^{6+}$, 665.5 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+3•DMF]$^{6+}$, 677.7 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+4•DMF]$^{6+}$, 691.1 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+5•DMF]$^{6+}$, 703.3 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+6•DMF]$^{6+}$, 715.6 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+7•DMF]$^{6+}$, 727.5 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+8•DMF]$^{6+}$, 739.9 [**1**⊃(**5a•6d•5a**)–6•NO_3^-+9•DMF]$^{6+}$, 752.4 [**1**⊃(**5a•6d•5a**)–7•NO_3^-+6•DMF]$^{7+}$, 603.8 [**1**⊃(**5a•6d•5a**)–7•NO_3^-+8•DMF]$^{7+}$, 625.7 [**1**⊃(**5a•6d•5a**)–8•NO_3^-+8•DMF]$^{8+}$, 539.8 [**1**⊃(**5a•6d•5a**)–8•NO_3^-+9•DMF]$^{8+}$, 547.6; IR (ATR, cm^{-1}): 3413 (br), 3201 (br), 3098 (br), 1659, 1613, 1514, 1329(br), 1137, 1055, 989, 951; m.p.: ~200 ºC (decomposed); UV-vis (H_2O, nm): λ_{max} 565 ($\varepsilon = 7.8 \times 10^3$), 491 ($\varepsilon = 9.9 \times 10^3$), 398 ($\varepsilon = 9.5 \times 10^4$).


CSI-MS
[M–8(NO3-)+n(dmf)]8+
n = 8~9
[M–7(NO3-)+n(dmf)]7+
n = 6,8
[M–6(NO3-)+n(dmf)]6+
n = 0~9
[M–5(NO3-)+n(dmf)]5+
n = 2~8
[M–4(NO3-)+n(dmf)]4+
n = 1 ~ 8
[M–3(NO3-)+n(dmf)]3+
n = 0~1
12+
M.W. 4224.9
12NO3−
Pd = H2 N Pd N H2
612.8
715.6
562.4
739.5
856.3
885.7
1031.3
1049.0
1124.6
1208.3
1263.3
1346.4
1408.5

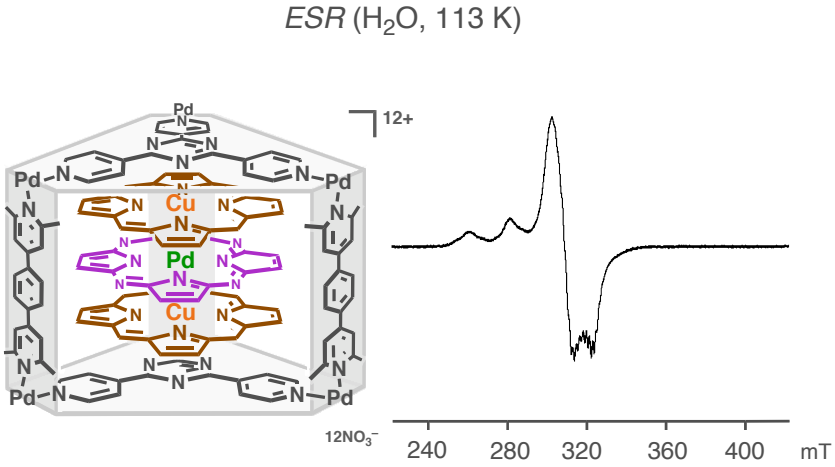

UV-vis (H2O, r.t., 0.1 mM, l = 1 mm)
Abs.
398 nm
491 nm
565 nm
nm

■ ESR data of **1**⊃(**6b**)$_3$ (113 K):

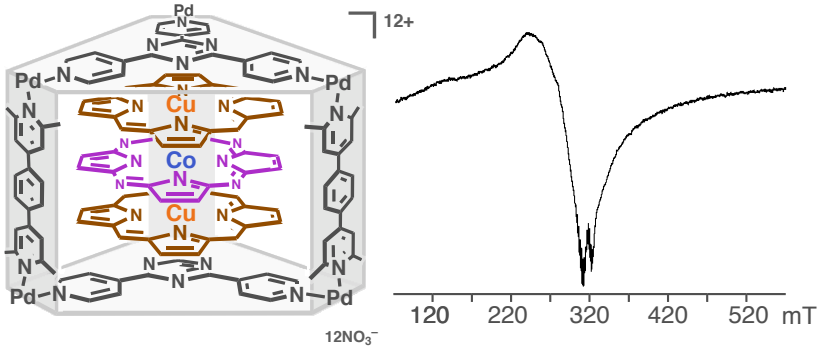


The observed spectrum is reproduced by the simulation using the following parameters. Spin quantum number: S = 3/2, g tensor: g = (2.01, 2.01, 2.147), hyperfine coupling tensor of Cu nuclear spin: A_{Cu} = (1.03, 1.03, 7.17) / mT, spin-spin dipole interaction parameters : D = 27.3 / mT, E = 1.5 / mT.

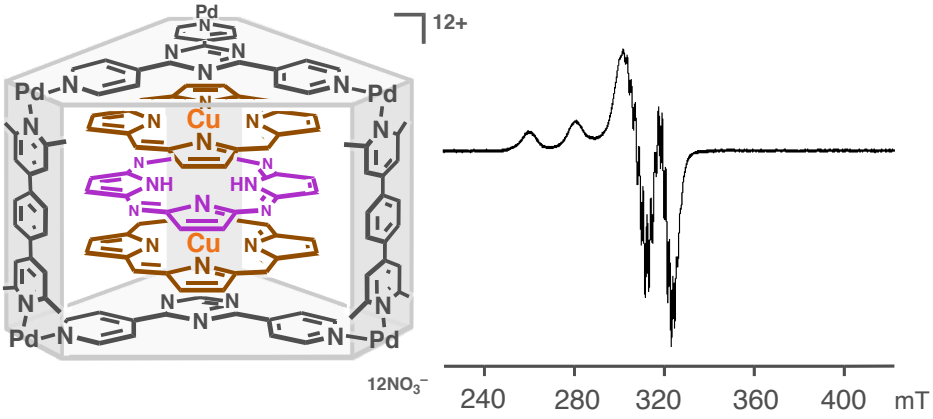
■ ESR spectrum of **1**⊃(**5b•6c•5b**) (113 K, SW = 100 mT):



■ ESR spectrum of **1**⊃(**5b•6d•5b**) (113 K, SW = 250 mT):



■ ESR spectrum of **1**⊃(**5b•6a•5b**) (113 K, SW = 100 mT)



■ ESR spectrum of **1**⊃(**5a•6d•5a**) (113 K, SW = 250 mT)

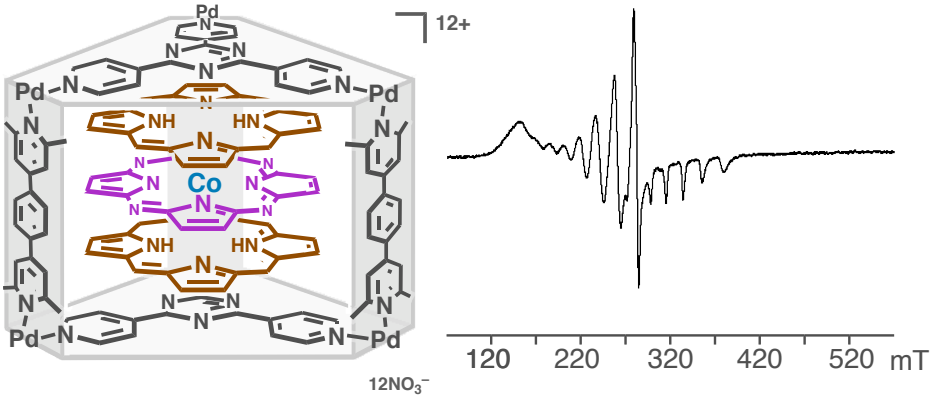


Table S1. Crystal data and structure refinement for **1'**⊃$(\mathbf{6a})_3$.

Identification code	3p-1	
Empirical formula	C168 H186 N64.75 O104.5 Pd6	
Formula weight	5404.12	
Temperature	80(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 20.025(3) Å	α = 107.593(2)°
	b = 26.094(4) Å	β = 102.779(2)°
	c = 26.215(4) Å	γ = 95.762(2)°
Volume	12526(3) Å^3	
Z	2	
Density (calculated)	1.438 Mg/m^3	
Absorption coefficient	0.525 mm^{-1}	
F(000)	5519	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.95 to 27.62°	
Index ranges	-26<=h<=25, -32<=k<=30, -31<=l<=32	
Reflections collected	99554	
Independent reflections	50850 [R(int) = 0.0302]	
Completeness to theta = 27.62°	87.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	50850 / 1141 / 3085	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.2028	
R indices (all data)	R1 = 0.1319, wR2 = 0.2556	
Largest diff. peak and hole	1.762 and -0.995 e.Å^{-3}	
CCDC No.	666139	

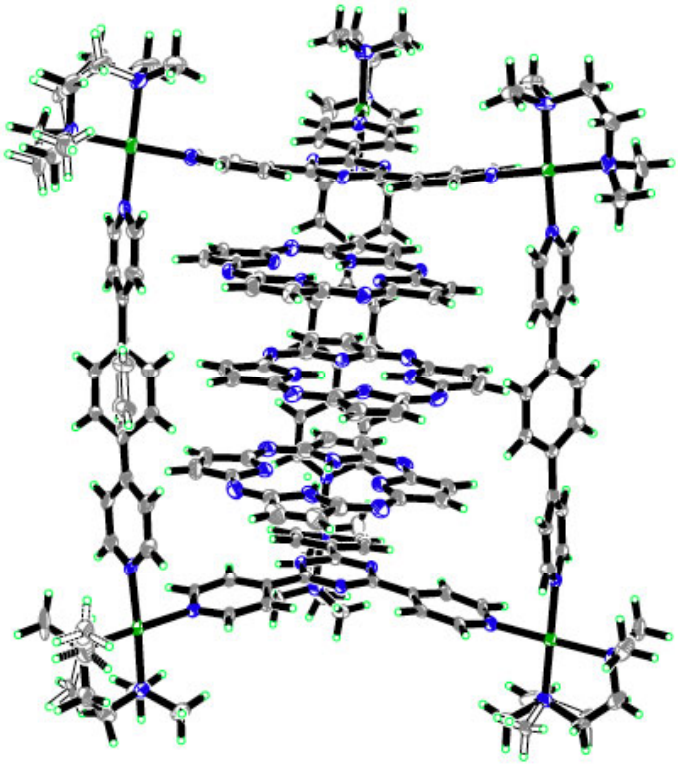


Figure S2. ORTEP drawing (30% probability ellipsoids) of **1'**⊃(**6a**)$_2$: crystal structure of **1'**⊃(**6a**)$_2$ without NO_3^- ions and oxygen atoms.