Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Discrete Stacking of Large Aromatic Molecules within Organic-Pillared Coordination Cages

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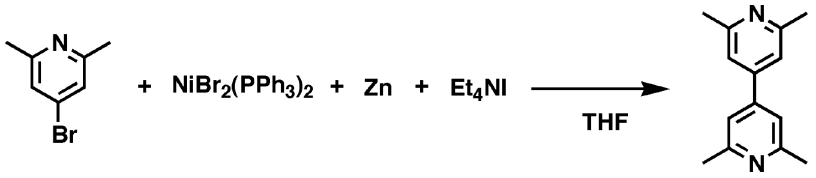
Contents

Materials and Instrumentations.

NMR spectral data 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 were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. UV-visible spectral data were recorded on a SHIMADZU UV-3150. Melting points were determined on a Yanaco MF-500 V melting point apparatus. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich chemical., Ltd. All the chemicals were of reagent grade and used without any further purification. Deuterated solvents were acquired from Cambridge Isotope Laboratories, Ins and used as supplied for the complexation reactions and NMR measurements.

Synthesis of 2,2',6,6'-Tetramethyl-4,4'-bipyridine Ligand (**3**).

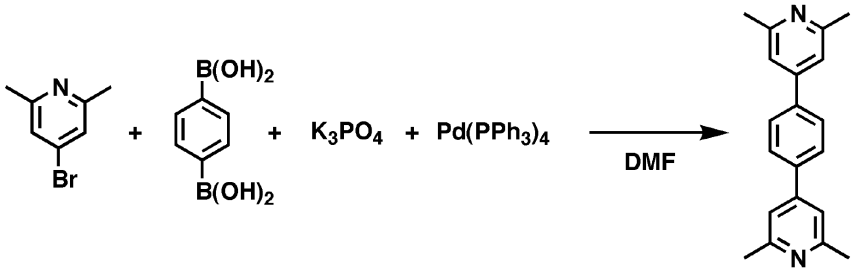


Typical procedure: A mixture of 4-bromo-2,6-lutidine 470 mg (2.50 mmol), $NiBr_2(PPh_3)_2$ 560 mg (0.750 mmol), Zn powder 245 mg (3.80 mmol), and Et_4NI 640 mg (2.50 mmol) was refluxed in dry-THF solution (15 mL) for 18 h under argon atmosphere. The mixture was filtrated, and then the solvent was evaporated to obtain a crude residue. The residue was treated with 10% aqueous solution of ethylenediamine, and then extracted with $CHCl_3$. An aqueous solution of HCl (1N) was added to the organic layer. After separation, the aqueous layer was treated with an aqueous solution of NaOH (1N). When the extraction ($CHCl_3$) was dried over $MgSO_4$ and evaporated, the residue was sublimated to obtain 2,2',6,6'-tetramethyl-4,4'-bipyridine (**3**) as a white solid (193 mg, 0.909 mmol) in 70.0% yield.

Physical data: ^1H NMR (500 MHz, D_2O, 27 ºC): δ 7.17 (s, 4H), 2.60 (s, 12H).

Ref. Berson, J. A.; Cohen, T. *J. Org. Chem.* **1955**, *20*, 1461.

Synthesis of 1,4-(2,2',6,6'-Tetramethyl-4,4'-bipyridyl)benzene Ligand (**7**).

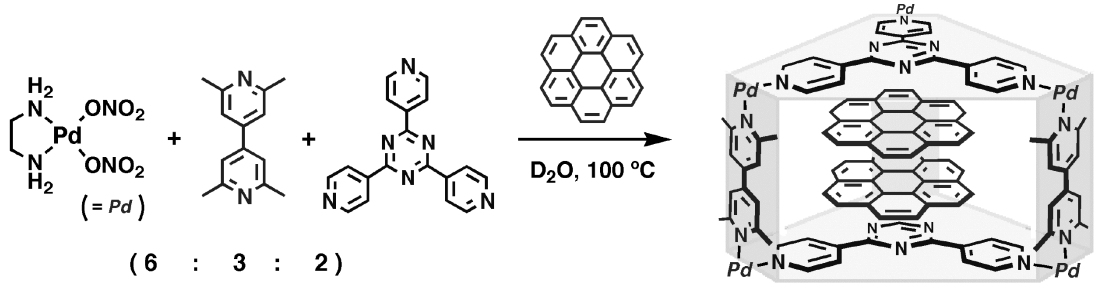


Typical procedure: A mixture of 4-bromo-2,6-lutidine 1.87 g (10.0 mmol), 1,4-phenylenebisboronic acid 0.480 g (2.90 mmol), K_3PO_4 5.49 g (25.8 mmol), and $Pd(PPh_3)_4$ 0.170 g (0.140 mmol) was stirred in a DMF (ca. 45 mL) solution under argon atmosphere at 100 ºC for 2 days. After filtration and evaporation, obtained brown solid was treated with HCl solution. The aqueous solution was washed by $CHCl_3$. After separation, an aqueous solution of NaOH was added to the aqueous layer to obtain white precipitate. After the purification by sublimation and column chromatography (silica gel, AcOEt),

1,4-(2,2',6,6'-tetramethyl-4,4'-bipyridyl)benzene (**7**) 0.460 g (1.60 mmol) was obtained as white powder in 55.6% yield.

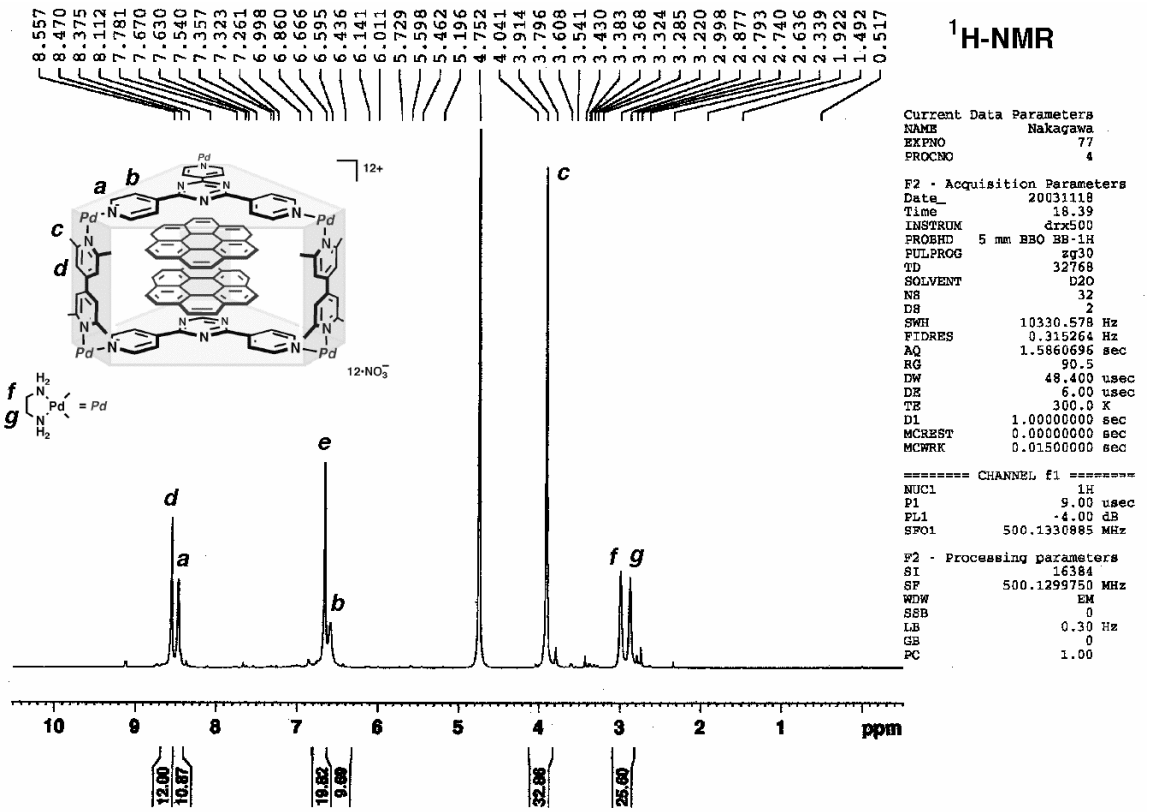
Physical data: ^{1}H NMR (500 MHz, D_2O, 27 ºC): δ 7.72 (s, 4H), 7.22 (s, 4H), 2.61(s, 12H). ^{13}C NMR (125 MHz, D_2O, 27 ºC): δ 158.4 (C_q), 148.2 (C_q), 139.1 (*C*H), 127.6 (C_q), 118.2 (*C*H), 24.6 (CH_3). IR (KBr, cm^{-1}): 3035, 2958, 2923, 2855, 1728, 1664, 1605, 1562, 1519, 1433, 1392, 832. E.A. Calcd. for $C_{20}H_{20}N_2 \cdot 1/3H_2O$: C, 81.69; H, 6.97; N, 9.53. Found: C, 81.82; H, 6.94; N, 9.25. m.p. ~188 ºC.

¦ Self-Assembly of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$.



Typical procedure: 2,2',6,6'-tetramethyl-4,4'-bipyridine (**3**) 6.4 mg (30.0 μmol), 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (**2**) 6.2 mg (20.0 μmol), and coronene (**5**) 18.0 mg (60.0 μmol) were added to an aqueous solution (1.0 mL) of (en)Pd$(NO_3)_2$ ($\mathbf{4}^{2+}$) 17.4 mg (60.0 μmol), and then, the suspended mixture was stirred at 100 ºC for 2 h. When obtained deep red solution was filtrated and the solution was evaporated and dried by vacuum freeze-drying equipment, $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ (30.0 mg (8.33 μmol)) was obtained as a deep red solid in 83.3% yield. For CSI-MS measurement, $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ was treated with an aqueous solution of KPF_6.

Physical data: ^{1}H NMR (500 MHz, D_2O, 27 ºC): δ 8.56 (s, 12H), 8.47 (s, 12H), 6.67 (s, 24H), 6.60 (br, 12H), 3.91 (s, 36H), 3.00 (s, 12H), 2.88 (s, 12H). ^{13}C NMR (125 MHz, D_2O, 27 ºC): δ 165.0 (C_q), 161.9 (C_q), 151.4 (*C*H), 147.8 (C_q), 142.3 (C_q), 125.7 (C_q), 124.2 (*C*H × 2), 122.9 (*C*H), 118.1 (C_q), 47.6 (CH_2), 46.5 (CH_2), 26.2 (CH_3). DOSY-NMR (cm^2/s): D = –9.80. IR (KBr, cm^{-1}): 3429, 3211, 3058, 2924, 2854, 1605, 1519, 1381, 1137, 1057, 857, 806; m.p.: ~255 ºC (decomposed); CSI-MS (PF_6^- counter, 7.0 mg, CH_3CN:DMF = 20:1): *m/z* 767.7 $[M+6\bullet PF_6^-+12\bullet DMF]^{6+}$, 906.2 $[M+7\bullet PF_6^-+9\bullet DMF]^{5+}$, 1023.3 $[M+8\bullet PF_6^-+DMF]^{4+}$; ($NO_3^-$ counter, H_2O:DMF = 20:1): *m/z* 636.3 $[M+6\bullet NO_3^-+8\bullet DMF]^{6+}$, 732.1 $[M+7\bullet NO_3^-+5\bullet DMF]^{5+}$, 857.4 $[M+8\bullet NO_3^-+DMF]^{4+}$, 1140.2 $[M+9\bullet NO_3^-]^{3+}$. E.A. Calcd. For $C_{138}H_{144}N_{42}O_{36}Pd_6 \cdot (CH_3COCH_3)_3 \cdot (H_2O)_{28}$: C, 41.21; H, 5.13; N, 13.73. Found: C, 41.32; H, 5.23; N, 13.65.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PL1 -4.00 dB
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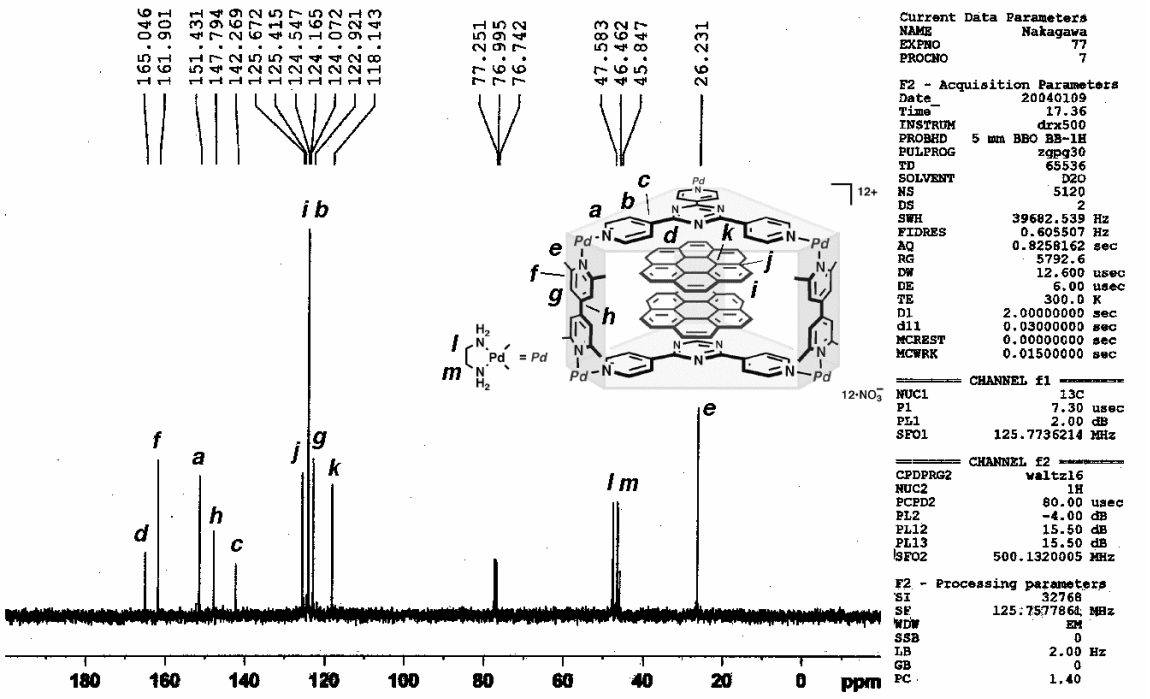
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77.251 76.995 76.742
47.583 46.462 45.847
26.231
12+
12·NO3−
= Pd
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TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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PL1 2.00 dB
SFO1 125.7736214 MHz
======== CHANNEL f2 ========
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PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.50 dB
PL13 15.50 dB
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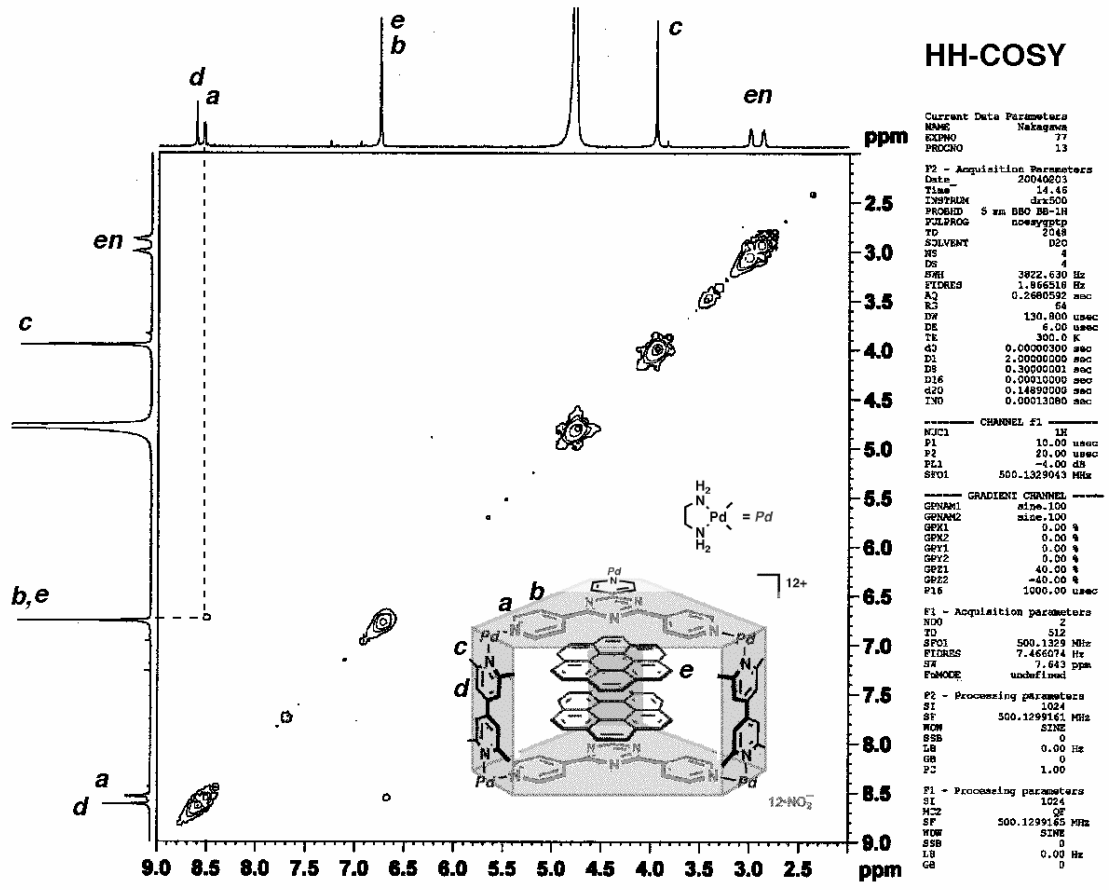
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b
d
a
c
en
ppm
en
c
b,e
d
a
= Pd
12+
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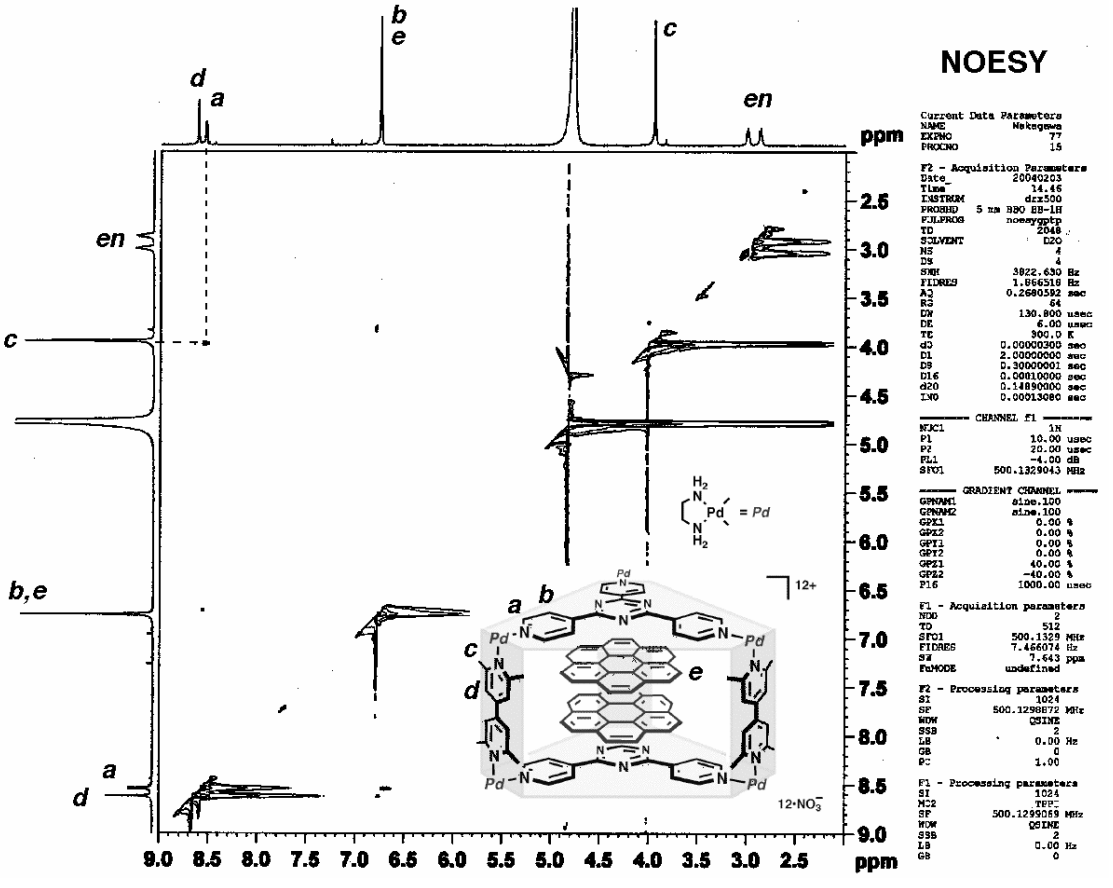
NOESY
b
e
d
a
c
en
ppm
en
c
b,e
d
a
= Pd
12+
12·NO3−
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
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D16 0.00010000 sec
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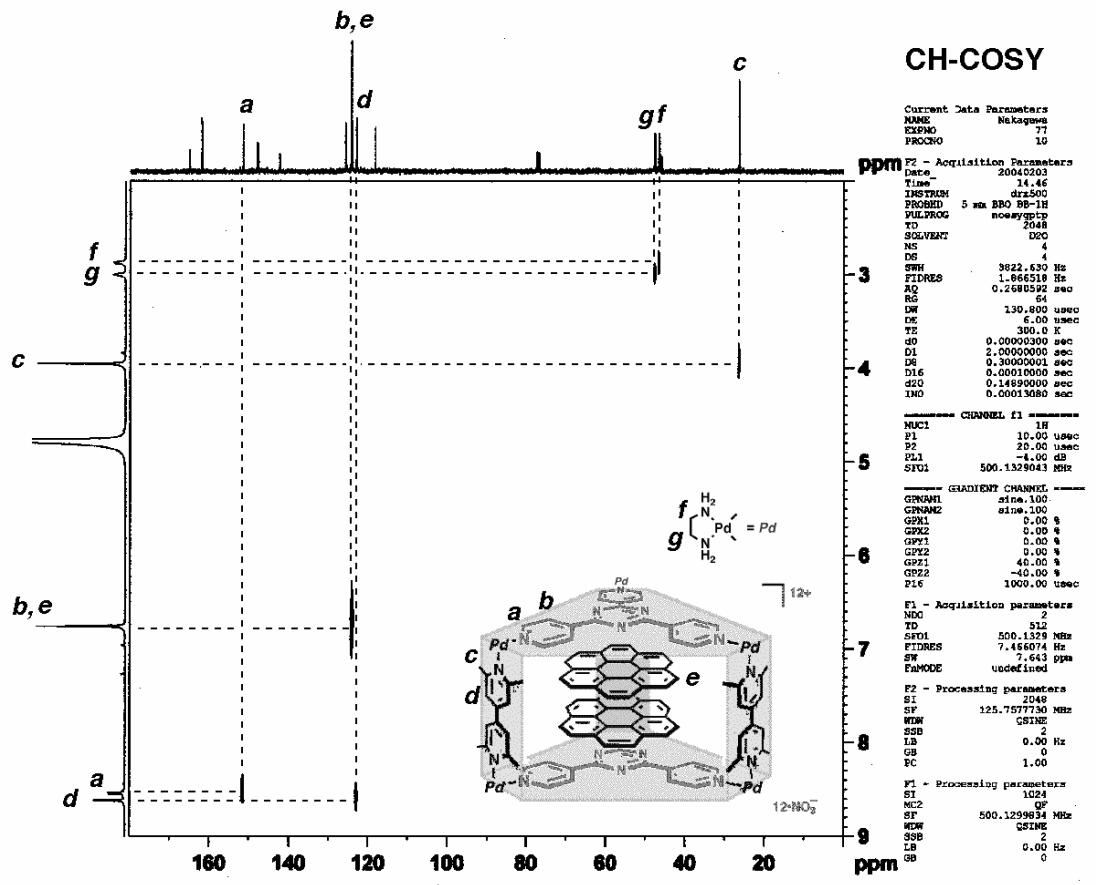
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d
c
g f
f
g
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a
d
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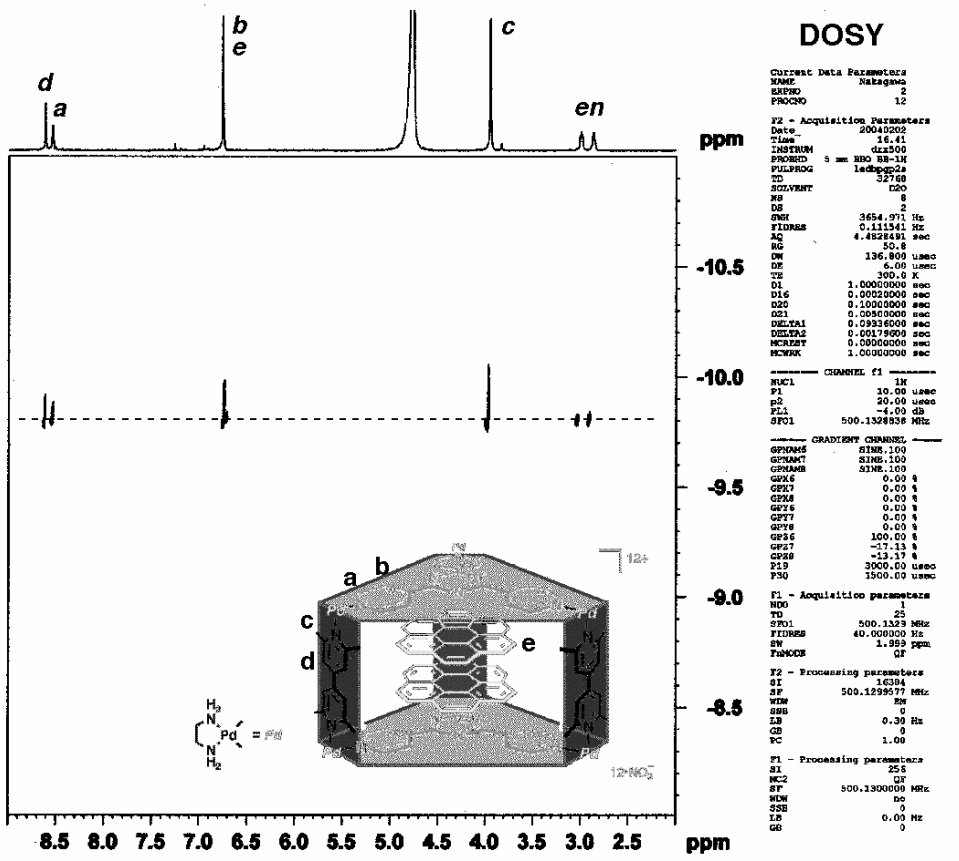
12+
12+NO3-
Pd
= Pd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d
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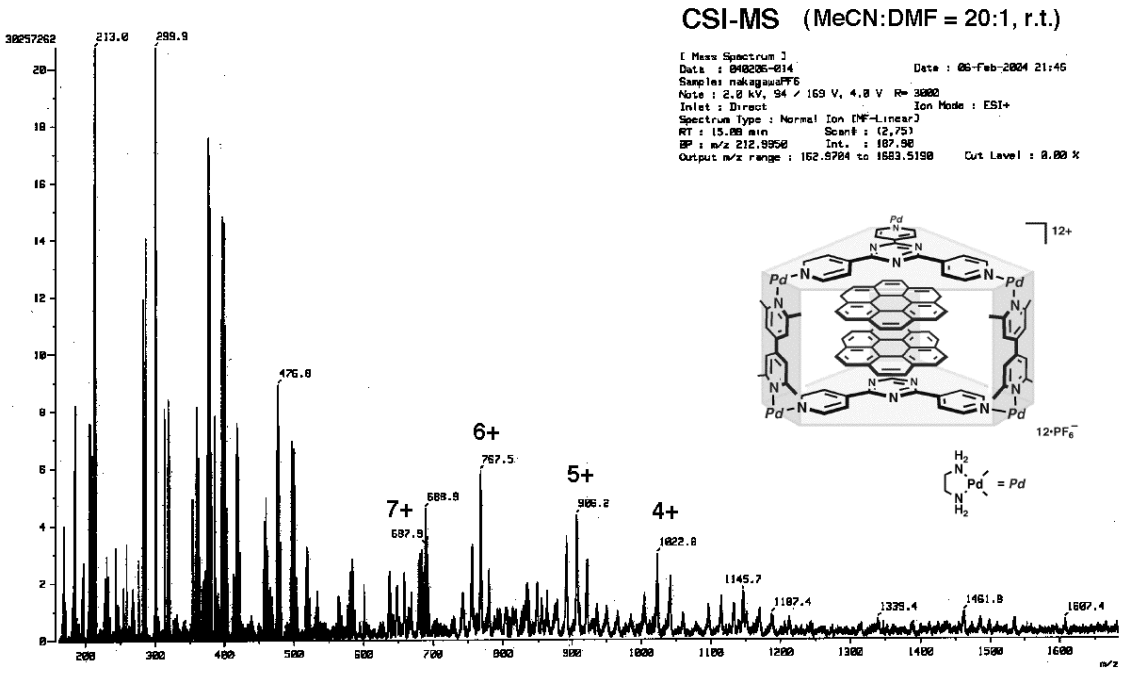
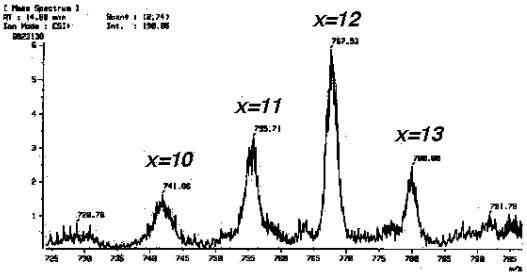
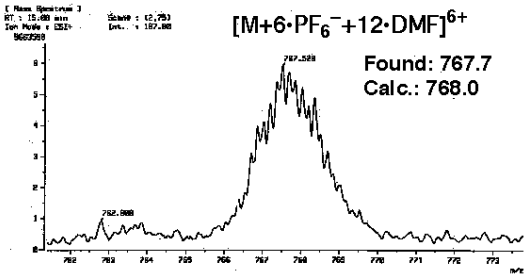
12+NO3-
Pd
= Pd



$[M+6\cdot PF_6^-+x\cdot DMF]^{6+}$





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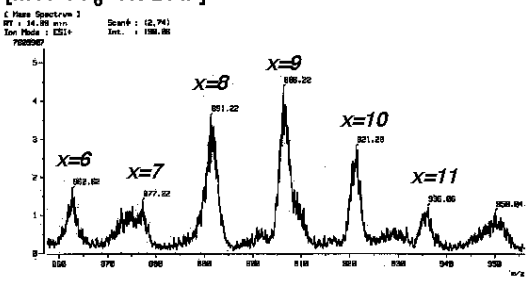

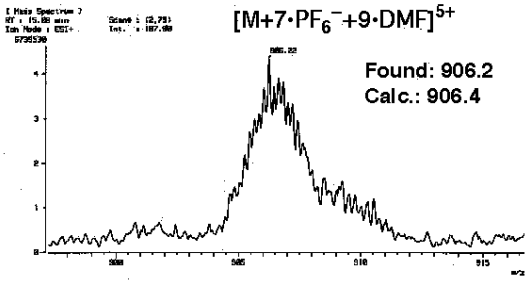

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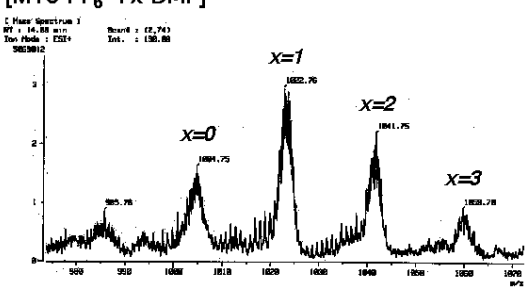

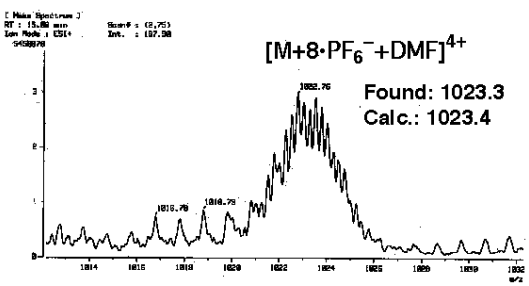

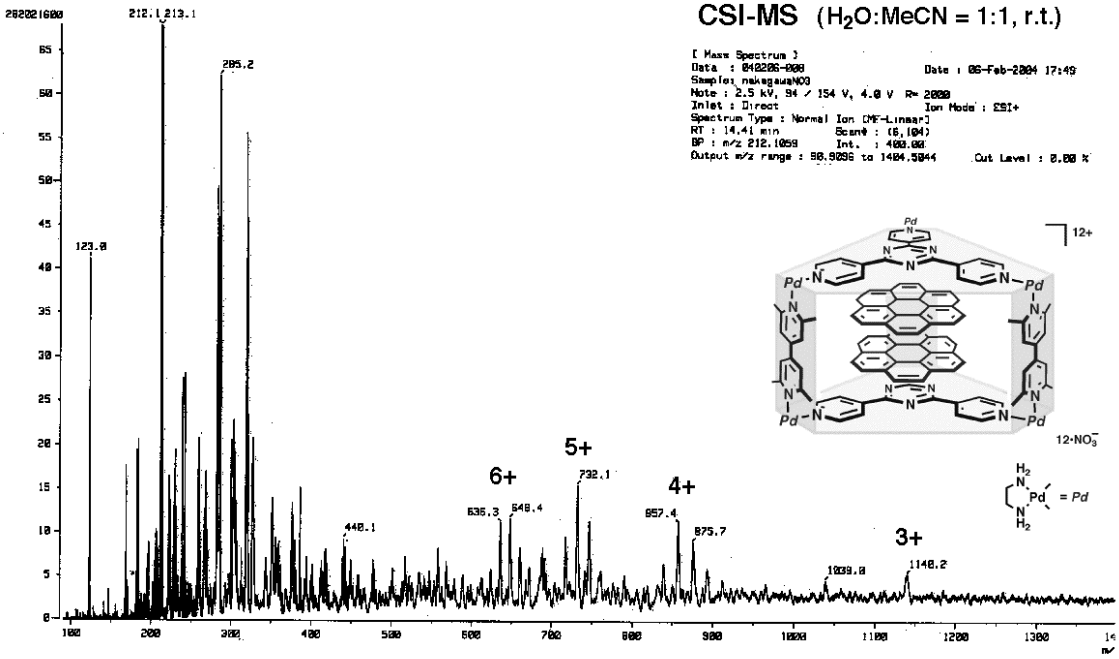
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213.1
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123.0
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5+
4+
3+
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875.7
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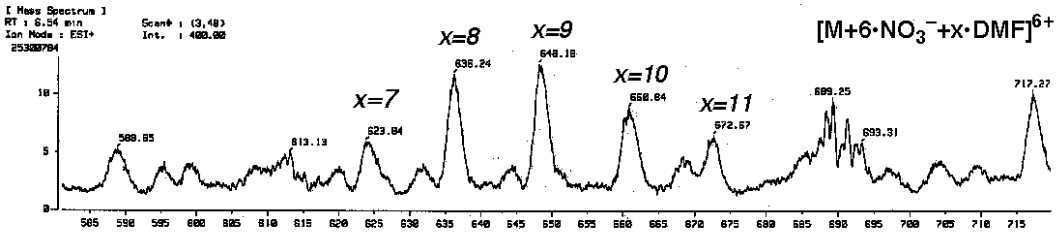
1148.2
12+
12·NO3−
= Pd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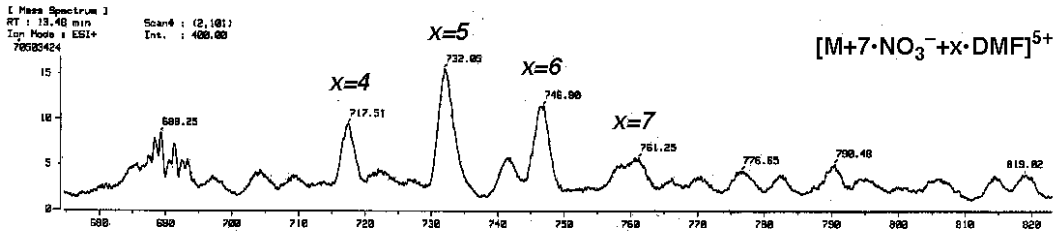
613.13
693.31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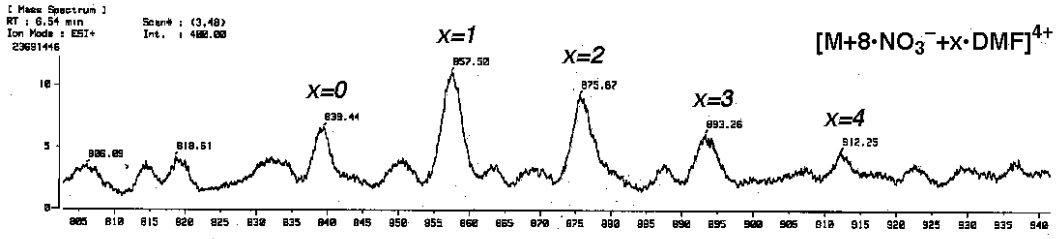
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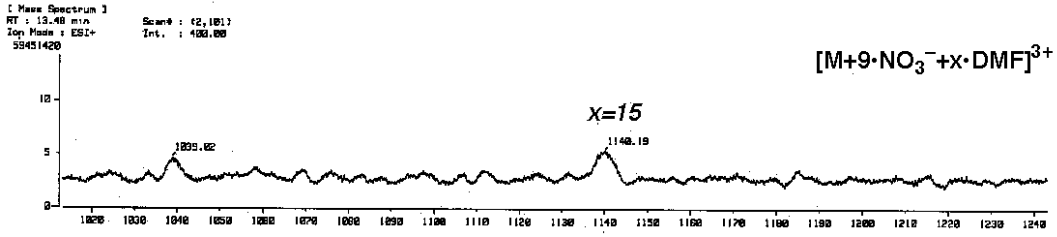
893.26
912.25
818.61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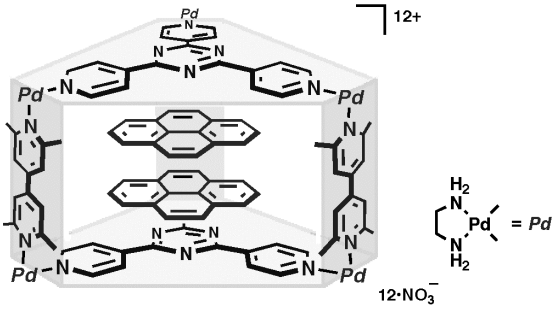
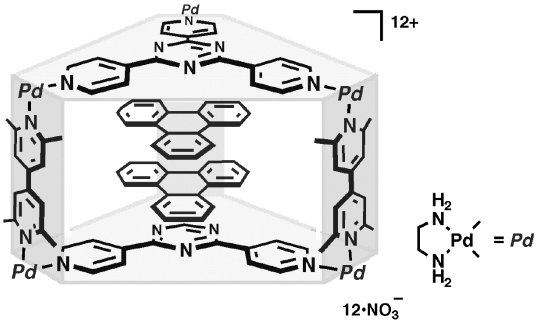
¦ Self-Assembly of [**1**⊃(**6**)$_2$]$^{12+}$.



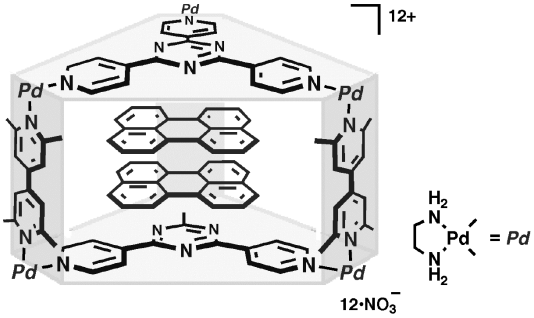
Physical data: ^{1}H NMR (500.13 MHz, D_2O, 27 ºC): δ 8.57 (s, 12H), 8.01 (s, 12H), 7.26 (s, 12H), 6.47 (s, 12H), 4.81 (s, 12H), 3.67 (s, 36H), 3.00-2.98 (m, 24H); ^{13}C NMR (125.77 MHz, D_2O, 27 ºC): δ 166.9 (C_q), 1601.3 (C_q), 151.7 (*C*H), 147.5 (C_q), 143.2 (C_q), 126.9 (C_q), 126.9 (C_q), 122.6 (*C*H), 121.5 (*C*H), 47.6 (*C*H$_2$), 46.6 (*C*H$_2$), 26.0 (*C*H$_3$); IR (KBr, cm^{-1}): 3407, 3067, 1520, 1375, 1059, 951, 804, 674; m.p.: ~250 ºC (decomposed); Elemental Analysis Calcd for $C_{126}H_{144}N_{42}O_{36}Pd_6\cdot(H_2O)_{17.3}$: C, 40.11; H, 4.77; N, 15.59. Found: C, 39.71; H, 5.01; N, 15.99.

¦ Self-Assembly of [**1**⊃(triphenylene)$_2$]$^{12+}$.



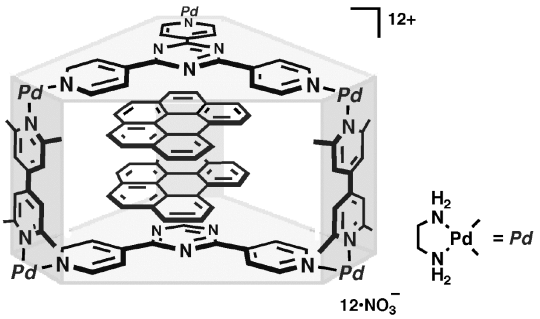
Physical data: ^{1}H NMR (500.13 MHz, D_2O, 27 ºC, TMS as external standard): δ 8.57 (s, 12H), 8.01 (s, 12H), 7.26 (s, 12H), 6.47 (s, 12H), 4.81 (s, 12H), 3.67 (s, 36H), 3.00-2.98 (m, 24H); ^{13}C NMR (125.77 MHz, D_2O, 27 °C, TMS as external standard): δ 166.9 (C_q), 1601.3 (C_q), 151.7 (*C*H), 147.5 (C_q), 143.2 (C_q), 126.9 (C_q), 126.9 (C_q), 122.6 (*C*H), 121.5 (*C*H), 47.6 (*C*H$_2$), 46.6 (*C*H$_2$), 26.0 (*C*H$_3$); IR (KBr, cm^{-1}): 3407, 3067, 1520, 1375, 1059, 951, 804, 674; m.p.: ~244 ºC (decomposed); Elemental Analysis Calcd. for $C_{126}H_{144}N_{42}O_{36}Pd_6\cdot(H_2O)_{12}$: C, 41.15; H, 4.60; N, 16.00. Found: C, 41.20; H, 4.70; N, 16.24.

¦ Self-Assembly of [**1**⊃(perylene)$_2$]$^{12+}$.



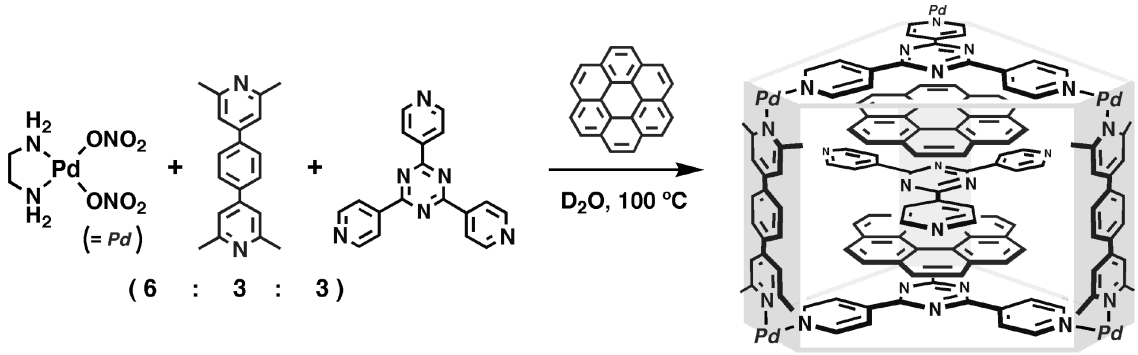
Physical data: ^{1}H NMR (500.13 MHz, D_2O, 27 ºC, TMS as external standard): δ 8.69 (d, *J* = 5.5 Hz, 12H), 8.03 (s, 12H), 7.73 (s, 12H), 5.95 (d, *J* = 8.0 Hz, 8H), 5.71 (d, *J* = 7.5 Hz, 8H), 5.53 (dd, *J* = 8.0, 7.5 Hz, 8H), 3.72 (s, 36H), 2.99 (s, 12H), 2.94 (s, 12H). ^{13}C NMR (125.77 MHz, D_2O, 27 ºC, TMS as external standard): δ 167.5 (C_q), 161.4 (C_q), 151.8 (*C*H), 148.4 (C_q), 144.1 (C_q), 132.7, 128.2, 126.4, 126.2, 124.7, 122.9, 118.5, 47.6 (CH_2), 46.5 (CH_2), 26.0 (CH_3). IR (KBr, cm^{-1}): 3431, 3183, 3071, 2944, 2887, 1605, 1519, 1383, 1129, 1057, 857, 807, 772.

¦ Self-Assembly of [**1**⊃(benzo[g,h,i]perylene)$_2$]$^{12+}$.



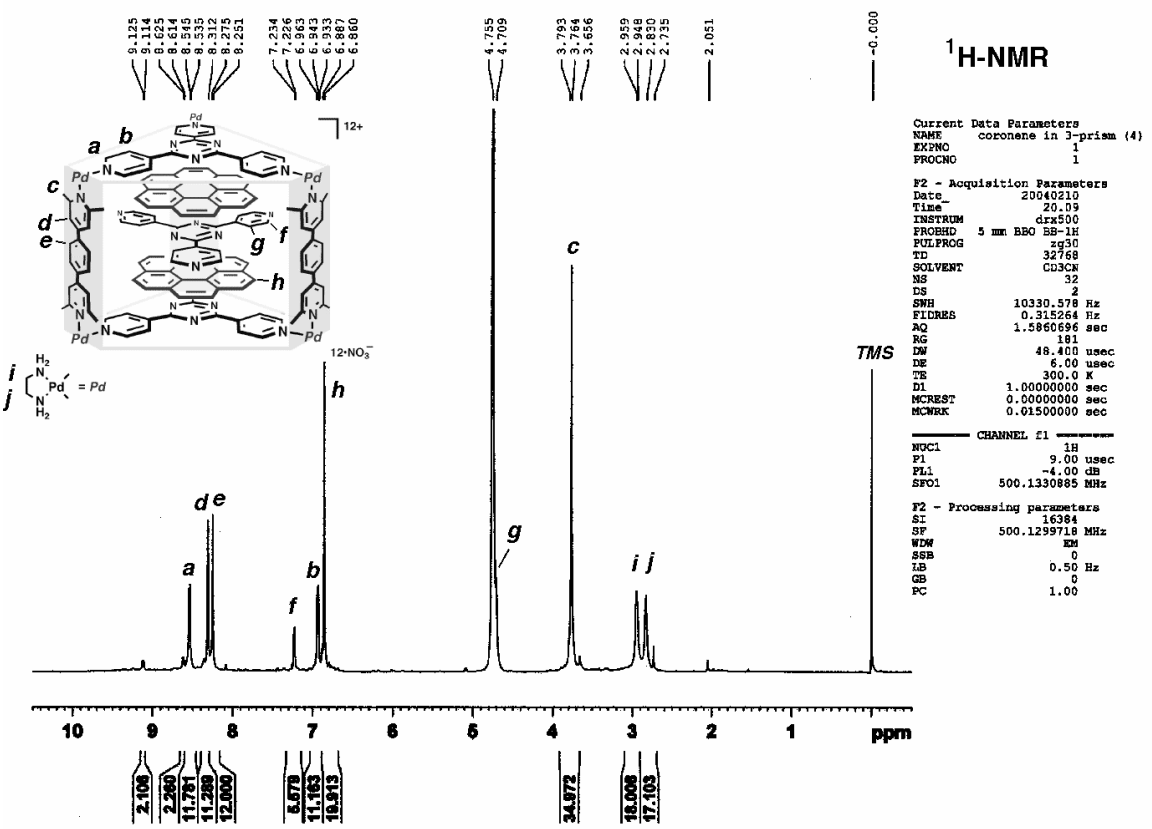
Physical data: ^{1}H NMR (500.13 MHz, D_2O, 27 ºC, TMS as external standard): δ 8.58 (d, *J* = 4.5 Hz, 12H), 8.27 (s, 12H), 7.22 (br, 12H), 6.58 (d, *J* = 6.5 Hz, 4H), 6.38 (d, *J* = 8.2 Hz, 4H), 6.29 (d, *J* = 8.2 Hz, 4H), 5.92 (d, *J* = 6.5 Hz, 4H), 5.85 (s, 4H), 5.74 (dd, *J* = 6.5 Hz, 4H), 3.80 (s, 36H), 2.98 (s, 12H), 2.83 (s, 12H). ^{13}C NMR (125.77 MHz, D_2O, 27 ºC, TMS as external standard): δ 166.1 (C_q), 161.6 (C_q), 151.6 (*C*H), 148.0 (C_q), 143.0 (C_q), 129.6, 126.9, 126.5, 125.8, 125.6, 124.5 (*C*H), 124.3, 123.7, 122.9 (*C*H), 122.2, 129.2, 118.7, 47.6 (CH_2), 46.5 (CH_2), 26.1(CH_3). IR (KBr, cm^{-1}): 3433, 3206, 3075, 2952, 2883, 1605, 1519, 1381, 1131, 1057, 854, 806, 769, 521.

¦ Self-Assembly of [**8**⊃(**5**•**2**•**5**)]$^{12+}$.



Typical procedure: A suspended mixture of (en)Pd(NO_3)$_2$ (**4**$^{2+}$) 17.4mg (60.0 μmol), 1,4-bis(2',2'',6',6''-tetramethyl-4,4'-bipyridyl)benzene (**7**) 8.6mg (30.0 μmol), 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (**2**) 9.1 mg (20.0 μmol), and coronene (**5**) 18.0 mg (60.0 μmol) was stirred in an aqueous solution (1.0 mL) at 100 ºC for 2 h to give orange solution. After filtration, the solution was evaporated and dried by vacuum freeze-drying equipment to obtain [**8**⊃(**5**•**2**•**5**)]$^{12+}$ (11.3 mg, 2.75 μmol) as an orange solid in 27.5% yield. For CSI-MS measurement, [**8**⊃(**5**•**2**•**5**)]$^{12+}$ was treated with an aqueous solution of KPF_6 to obtain the orange solid.

Physical data: ^{1}H NMR (500.13 MHz, D_2O, 27 ºC, TMS as external standard): δ 8.54 (d, *J* = 5.0 Hz, 12H), 8.31 (s, 12H), 8.25 (s, 12H), 7.23 (d, *J* = 4.0 Hz, 6H), 6.94 (d, *J* = 5.0 Hz, 12H), 6.87 (s, 24H), 4.71 (d, *J* = 4.0 Hz, 6H), 3.76 (s, 36H), 2.95 (s, 12H), 2.83 (s, 12H). ^{13}C NMR (125.77 MHz, D_2O, 27 ºC, TMS as external standard): δ 165.5 (C_q), 162.9 (C_q), 160.9 (C_q), 151.6 (*C*H), 151.5 (C_q), 147.6 (*C*H), 142.8 (C_q), 138.5 (C_q), 137.9 (*C*H), 128.7 (*C*H), 126.6 (*C*q), 124.9 (*C*H), 124.0 (*C*H), 122.4 (*C*H), 119.6 (C_q), 119.4 (*C*H), 47.5 (CH_2), 45.8 (CH_2), 26.0 (CH_3). IR (KBr, cm^{-1}): 2954, 2922, 2851, 1618 1519, 1383, 1356, 1057, 863, 833, 805, 644. m.p.: ~240 ºC (decomposed). CSI-MS (8.0 mg, CH_3CN:DMF = 20:1): 807.5 [M+6•(PF_6^-)+9•DMF]$^{6+}$, 998.2 [M+7•(PF_6^-)+9•DMF]$^{5+}$, 1247.5 [M+8•(PF_6^-)+7•DMF]$^{4+}$.



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PROCNO 1

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Date_ 20040210
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INSTRUM drx500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CD3CN
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 181
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
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F2 - Processing parameters
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SF 500.1299718 MHz
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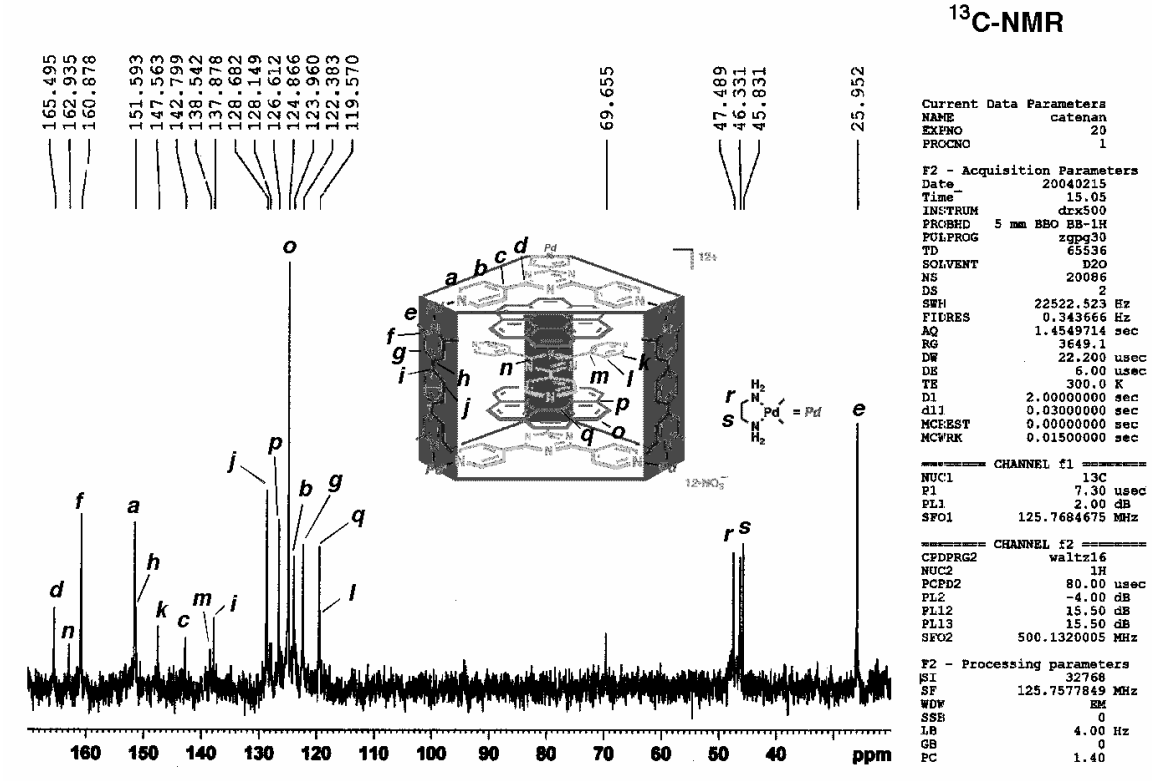
SSB 0
LB 0.50 Hz
GB 0
PC 1.00



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PROCNO 1

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Time_ 15.05
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PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 20086
DS 2
SWH 22522.523 Hz
FIDRES 0.343666 Hz
AQ 1.4549714 sec
RG 3649.1
DW 22.200 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 125.7684675 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
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SF 125.7577849 MHz
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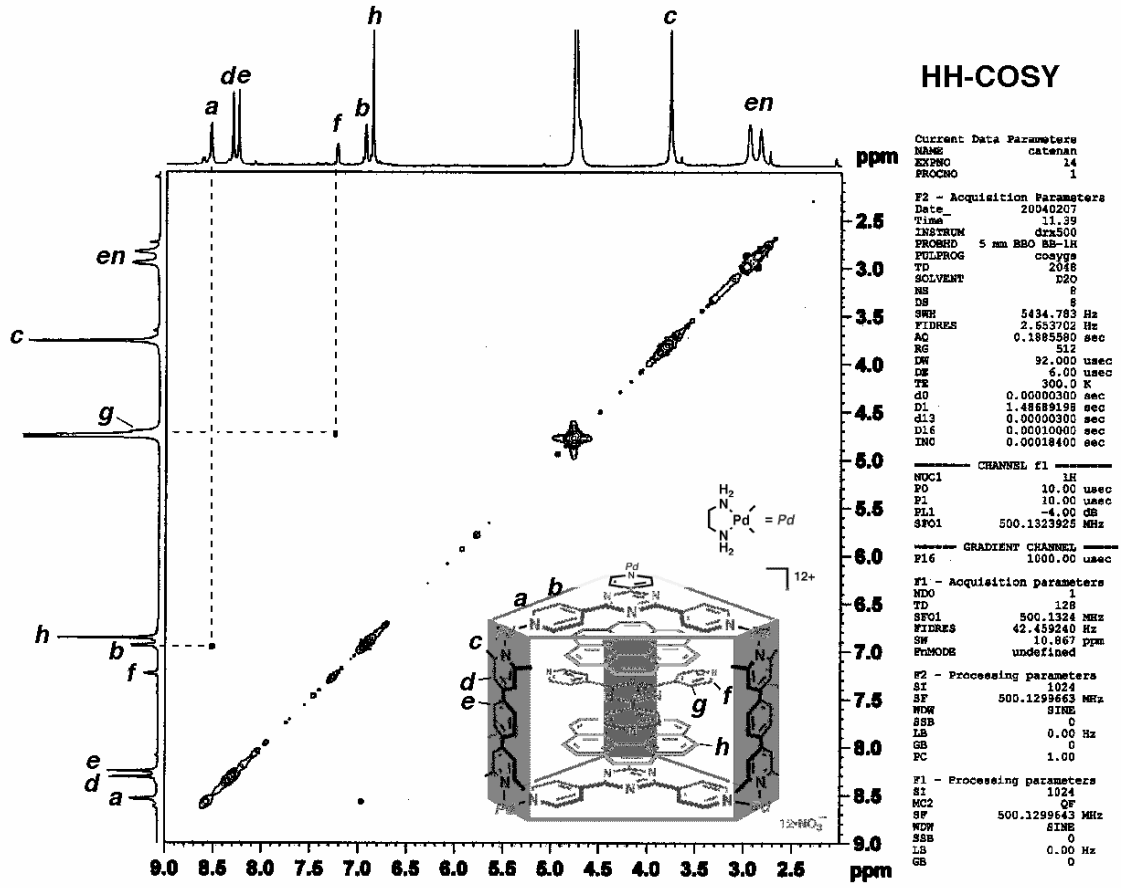
SSB 0
LB 4.00 Hz
GB 0
PC 1.40


HH-COSY
h
c
de
a
f
b
en
ppm
en
c
g
h
b
f
e
d
a
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12+
12·NO3−
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 2.5
ppm
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NAME catenan
EXPNO 14
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040207
Time 11.39
INSTRUM drx500
PROBHD 5 mm BBO BB-1H
PULPROG cosygs
TD 2048
SOLVENT D2O
NS 8
DS 8
SWH 5434.783 Hz
FIDRES 2.653702 Hz
AQ 0.1885580 sec
RG 512
DW 92.000 usec
DE 6.00 usec
TE 300.0 K
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D1 1.48689198 sec
d13 0.00000300 sec
D16 0.00010000 sec
INC 0.00018400 sec
CHANNEL f1
NUC1 1H
P0 10.00 usec
P1 10.00 usec
PL1 -4.00 dB
SFO1 500.1323925 MHz
GRADIENT CHANNEL
P16 1000.00 usec
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SFO1 500.1324 MHz
FIDRES 42.459240 Hz
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F2 - Processing parameters
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SF 500.1299663 MHz
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SSB 0
LB 0.00 Hz
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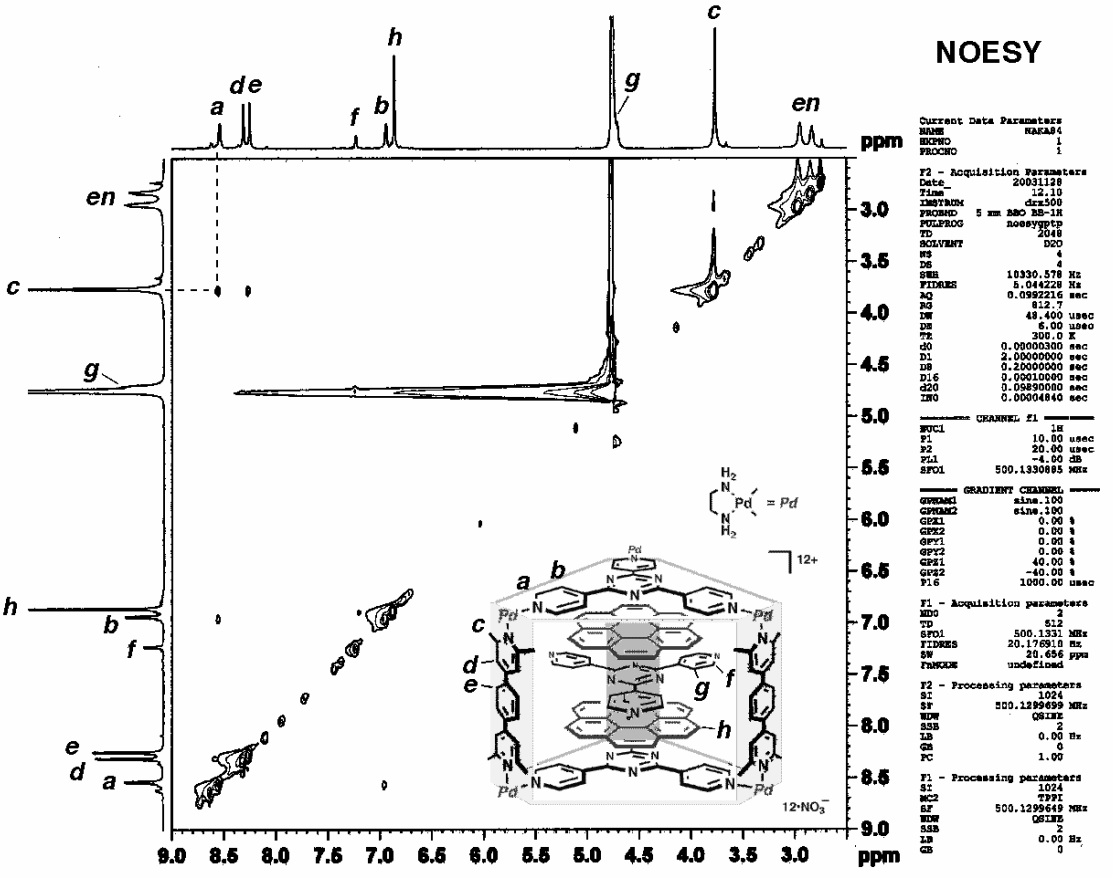
LB 0.00 Hz
GB 0


NOESY
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de
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f
b
g
en
ppm
en
c
g
h
b
f
e
d
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= Pd
12+
12·NO3−
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
Current Data Parameters
NAME NAKA84
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20031128
Time 12.10
INSTRUM drx500
PROBHD 5 mm BBO BB-1H
PULPROG noesygpph
TD 2048
SOLVENT D2O
NS 4
DS 4
SWH 10330.578 Hz
FIDRES 5.044228 Hz
AQ 0.0992216 sec
RG 812.7
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
d0 0.00000300 sec
D1 2.00000000 sec
D8 0.20000000 sec
D16 0.00010000 sec
d20 0.05890000 sec
IN0 0.00004840 sec
CHANNEL f1
NUC1 1H
P1 10.00 usec
P2 20.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
GRADIENT CHANNEL
GPNAM1 sine.100
GPNAM2 sine.100
GPZ1 0.00 %
GPZ2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
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TD 512
SFO1 500.1331 MHz
FIDRES 20.176918 Hz
SW 20.656 ppm
FnMODE undefined
F2 - Processing parameters
SI 1024
SF 500.1299699 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing parameters
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MC2 TPPI
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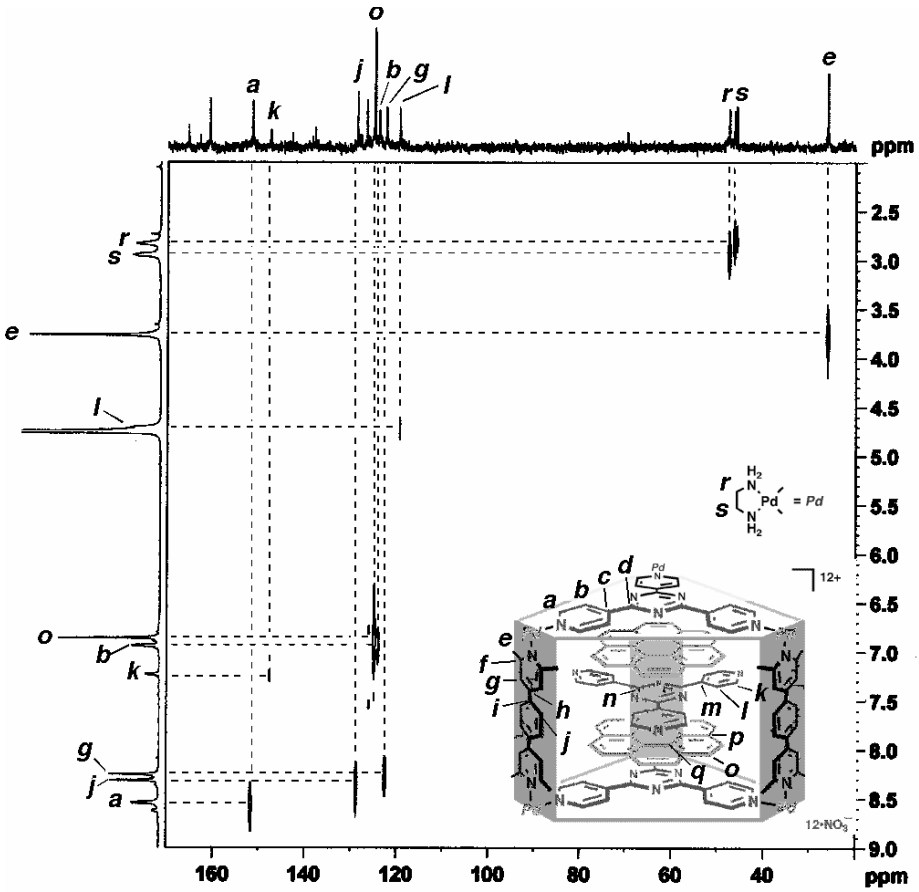
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0



CH-COSY

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NAME                  catenan
EXPNO                      17
PROCNO                      1

F2 - Acquisition Parameters
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Time               20.23
INSTRUM            drx500
PROBHD     5 mm BBO BB-1H
PULPROG            hxco
TD                 4096
SOLVENT            D2O
NS                 104
DS                 4
SWH                39682.539 Hz
FIDRES             9.688120 Hz
AQ                 0.0516722 sec
RG                 8192
DW                 12.600 usec
DE                 6.00 usec
TE                 300.0 K
CNST2              145.0000000
CNST11             3.0000000
d0                 0.00000030 sec
D1                 2.00000000 sec
d2                 0.00344828 sec
d3                 0.00229885 sec
d11                0.03000000 sec
d12                0.00002000 sec
IN0                0.00004840 sec

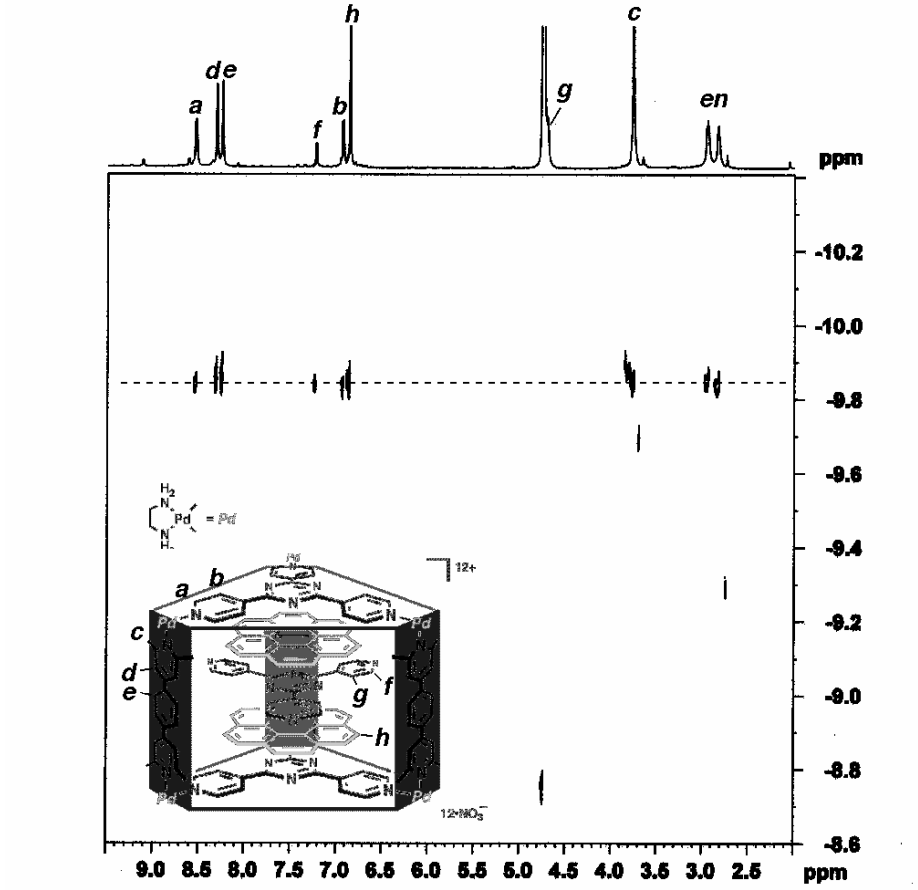
======== CHANNEL f1 ========
NUC1                    13C
P1                     6.70 usec
p2                    13.40 usec
PL1                    2.00 dB
SFO1           125.7736214 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                   -4.00 dB
PL12                  15.50 dB
SFO2           500.1330885 MHz

F1 - Acquisition parameters
NDO                        2
TD                       128
SFO1           500.1331 MHz
FIDRES         80.707642 Hz
SW             20.656 ppm
FnMODE         undefined

F2 - Processing parameters
SI                      2048
SF             125.7577833 MHz
WDW                   QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
PC                      1.00

F1 - Processing parameters
SI                      1024
MC2                       QF
SF             500.1300000 MHz
WDW                   QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
```



DOSY

```
Current Data Parameters
NAME                  catenan
EXPNO                      15
PROCNO                      1

F2 - Acquisition Parameters
Date_              20040207
Time               12.30
INSTRUM            drx500
PROBHD     5 mm BBO BB-1H
PULPROG            ledbpgp2s
TD                 32768
SOLVENT            D2O
NS                 8
DS                 2
SWH                5434.783 Hz
FIDRES             0.165856 Hz
AQ                 3.0147979 sec
RG                 71.5
DW                 92.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                 1.00000000 sec
D16                0.00020000 sec
D20                0.10000000 sec
D21                0.00500000 sec
DELTA1             0.09336000 sec
DELTA2             0.00179600 sec
MCREST             0.00000000 sec
MCWRK              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    10.00 usec
p2                    20.00 usec
PL1                   -4.00 dB
SFO1           500.1323925 MHz

======== GRADIENT CHANNEL ========
GPNAM6             SINE.100
GPNAM7             SINE.100
GPNAM8             SINE.100
GPZ6                   0.00 %
GPZ7                   0.00 %
GPZ8                   0.00 %
GPY6                   0.00 %
GPY7                   0.00 %
GPY8                   0.00 %
GPZ6                 100.00 %
GPZ7                 -17.13 %
GPZ8                 -13.17 %
P19                 3000.00 usec
P30                 1500.00 usec

F1 - Acquisition parameters
NDO                        1
TD                        25
SFO1           500.1324 MHz
FIDRES         40.000000 Hz
SW             1.999 ppm
FnMODE                    QF

F2 - Processing parameters
SI                     16384
SF             500.1299783 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                         0
PC                      1.00

F1 - Processing parameters
SI                       256
MC2                       QF
SF             500.1300000 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                         0
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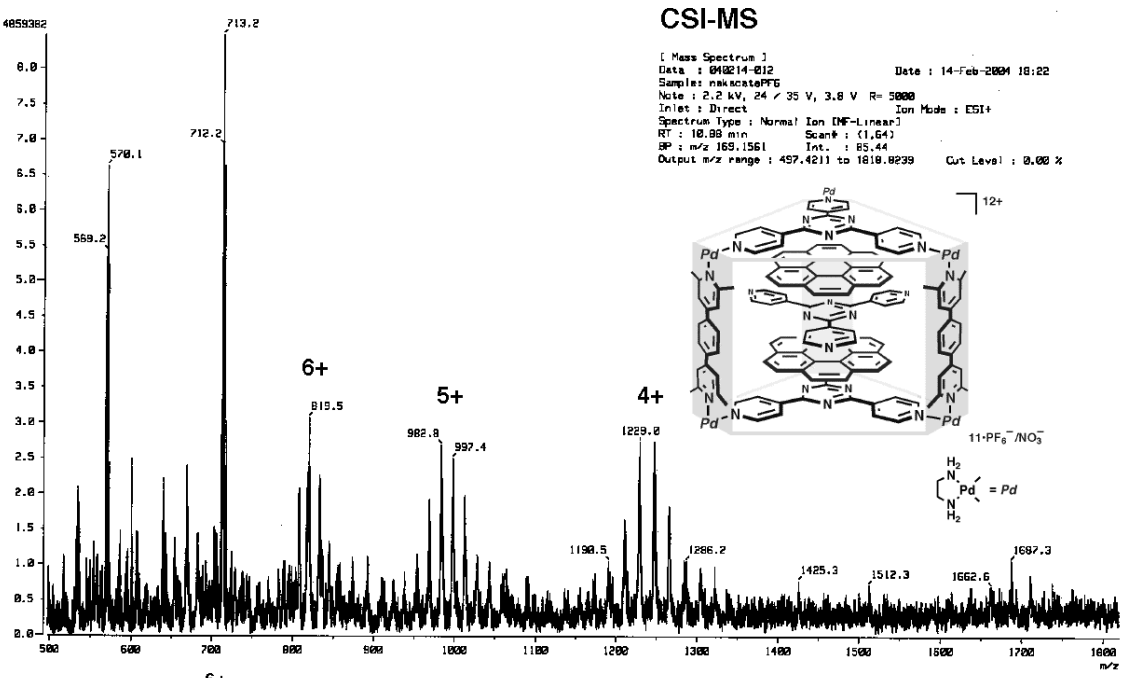
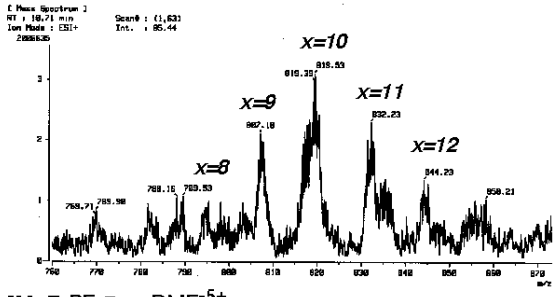
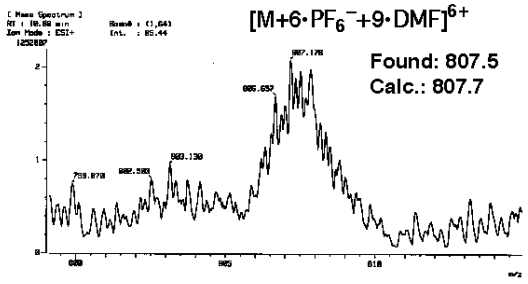


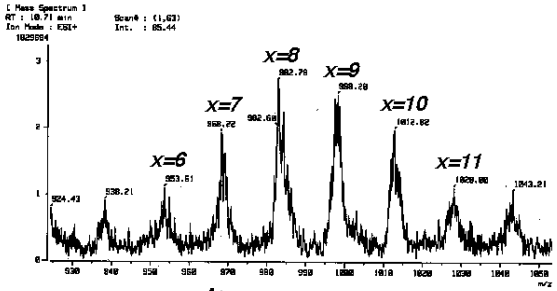
$[M+6\cdot PF_6^-+x\cdot DMF]^{6+}$



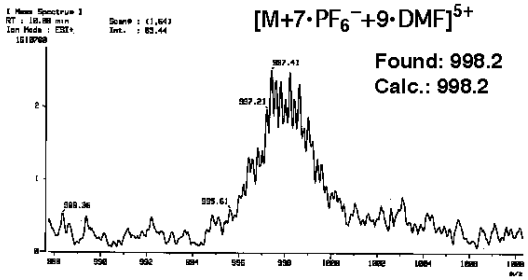
$[M+6\cdot PF_6^-+9\cdot DMF]^{6+}$



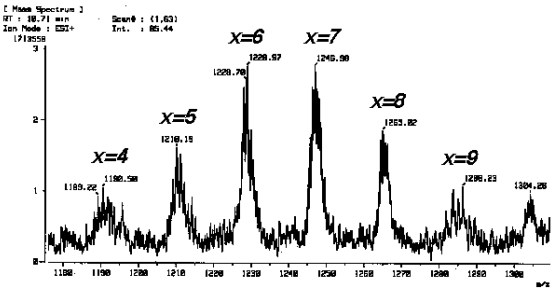
$[M+7\cdot PF_6^-+x\cdot DMF]^{5+}$



$[M+7\cdot PF_6^-+9\cdot DMF]^{5+}$



$[M+8\cdot PF_6^-+x\cdot DMF]^{4+}$



$[M+8\cdot PF_6^-+7\cdot DMF]^{4+}$

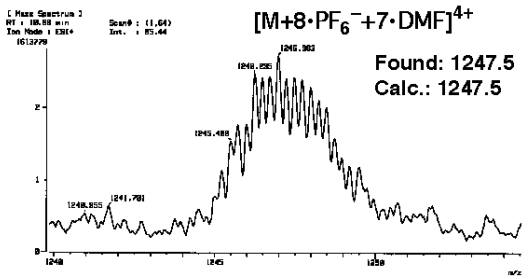


Table S1. Crystal data and structure refinement for $[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$.

Identification code	$[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$	
Empirical formula	C244 H272 N60 O80 Pd12	
Formula weight	6602.02	
Temperature	89(2) K	
Wavelength	0.68900 Å	
Crystal system	Orthorhombic	
Space group	C222(1)	
Unit cell dimensions	a = 20.4596(14) Å	a = 90°
	b = 35.453(3) Å	b = 90°
	c = 53.544(6) Å	g = 90°
Volume	38839(6) Å^3	
Z	4	
Density (calculated)	1.129 Mg/m^3	
Absorption coefficient	0.557 mm^{-1}	
F(000)	13392	
Crystal size	0.48 x 0.04 x 0.04 mm^3	
Theta range for data collection	2.48 to 25.51°	
Index ranges	-25<=h<=24, -43<=k<=43, -47<=l<=50	
Reflections collected	56652	
Independent reflections	25550 [R(int) = 0.1703]	
Completeness to theta = 25.51°	70.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9781 and 0.7758	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25550 / 1167 / 1376	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.1579, wR2 = 0.3822	
R indices (all data)	R1 = 0.2260, wR2 = 0.4168	
Absolute structure parameter	0.13(8)	
Largest diff. peak and hole	0.621 and -0.549 e.Å^{-3}	

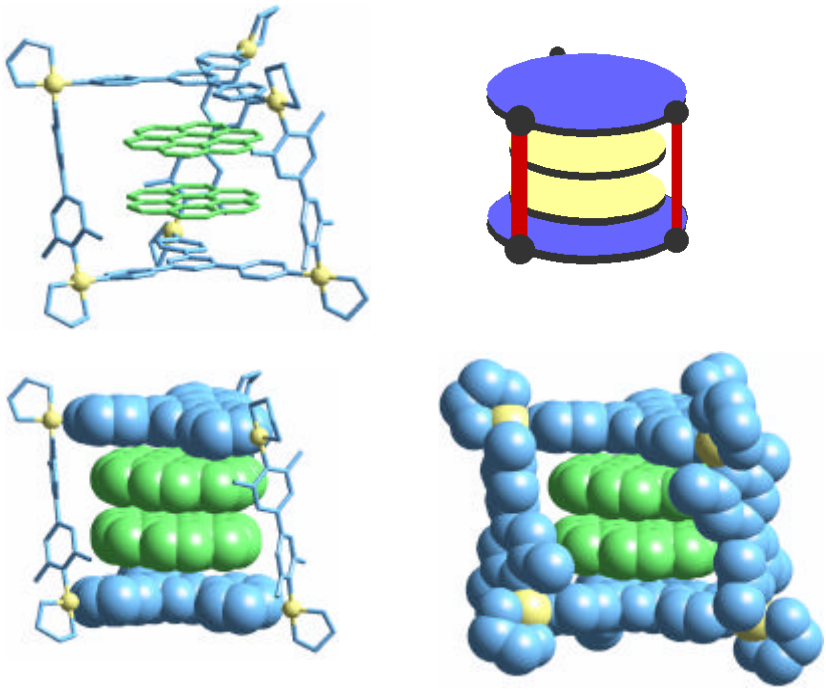


Figure S1. An Optimized Structure (MM2) of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$.

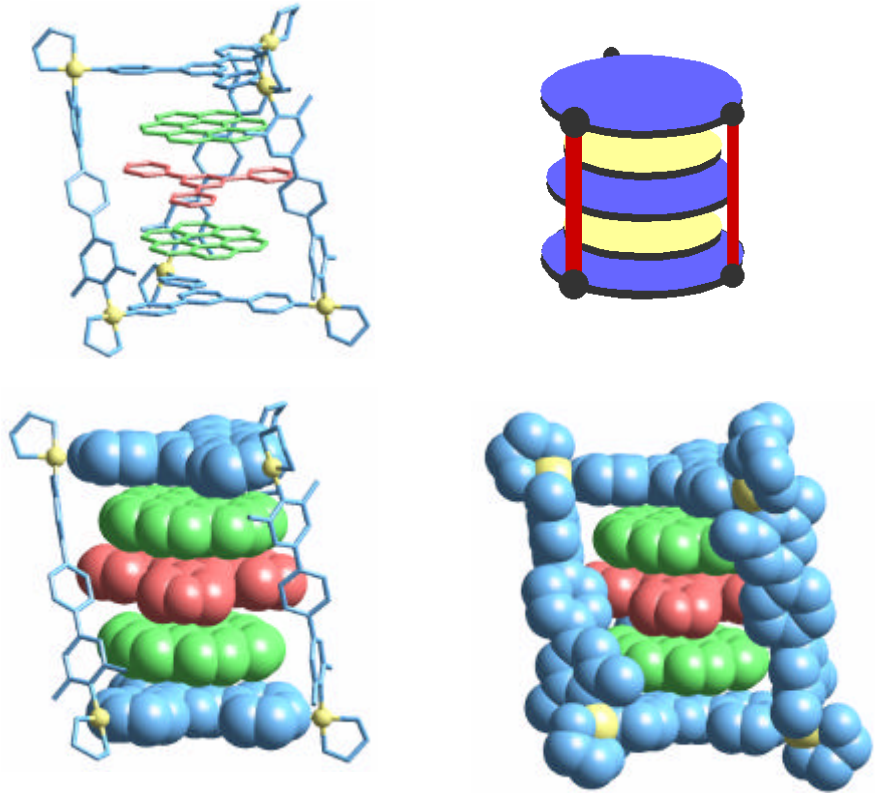


Figure S2. An Optimized Structure (MM2) of $[\mathbf{8}\supset(\mathbf{5}\bullet\mathbf{2}\bullet\mathbf{5})]^{12+}$.