Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Highly Fluorescent M_2L_4 Molecular Capsules with Anthracene Shells

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Contents

Materials and methods

NMR: Bruker AVANCE-400 (400 MHz)

GC MS: Shimadzu Parvum2/ULBON HR-1

MALDI-TOF MS: Shimadzu AXIMA-CFR Plus

ESI-TOF MS: Bruker micrOTOF II

FT IR: JASCO FT/IR-4200

UV-vis: JASCO V-670DS

Fluorescence: SHIMADZU RF-5300PC

X-ray single crystal structural analysis: Rigaku VariMax with RAPID

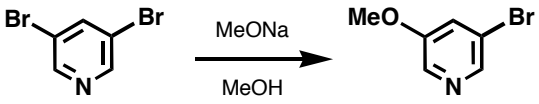
Elemental analysis: LECO CHNS-932 VTF-900

Absolute PL quantum yield: Hamamatsu C9920-02G with an integration sphere.

Time-resolved absorption and emission spectra analysis: Hamamatsu C7700-ABS-N with C7700-01high dynamic range streak camera and Continuum Minilite system.

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO kagaku KANTO CHEMICAL CO.,INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc.

Synthesis of 3-bromo-5-methoxypyridine ZL-63



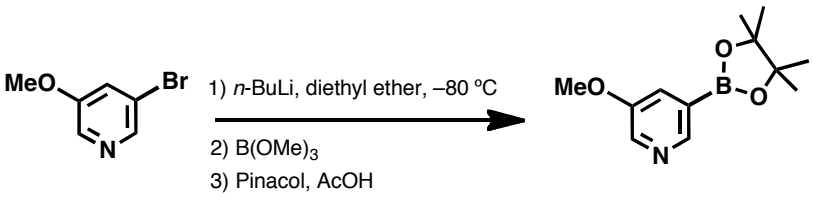
To a 50 mL autoclave reactor containing a magnetic stirring bar were added 3,5-dibromopyridine (9.962 g, 42.05 mmol) and an anhydrous MeOH solution (40 mL) of MeONa (4.559 g, 84.11 mmol). After the mixture was heated at 140 ºC for 48 h, the mixture was poured into H_2O (100 mL) and the crude product was extracted with dichloromethane. The organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 10:1) and then 3-bromo-5-methoxypyridine was obtained as a white solid (6.421 g, 34.15 mol; 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 3.86 (s, 3H), 7.36 (dd, J = 2.4, 1.6, 1H), 8.24 (d, J = 2.4, 1H), 8.28 (d, J = 1.6, 1H).

GC-MS: *m/z* Calcd. for C_6H_6BrNO 187, Found 187 $[M]^+$.

Ref.: D. Alagille *et al*., *Bioorg. Med. Chem.* **2005**, *13*, 197–209.

Synthesis of 5-methoxy-3-pyridineboronic acid pinacol ester ZL-90



A 200 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. Anhydrous diethyl ether (70 mL) and a 2.60 M solution of *n*-butyllithium in hexane (11.3 mL, 29.5 mmol) were added to this flask. A solution of 3-bromo-5-methoxypyridine (5.036 g, 26.78 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to the solution at –80 ºC. The solution was further stirred at –80 ºC for 1 h and then trimethyl borate (3.40 mL, 29.5 mmol) was added to the solution at the same temperature. The solution was warmed to room temperature for ca. 12 h. Pinacol (3.490 g, 29.5 mmol) and then AcOH (1.7 ml, 30 mmol) were added to the resultant mixture. The solution was stirred for 6 h at room temperature and then the mixture was concentrated under reduce pressure. The crude product was reprecipitated with hexane to afford 5-methoxy-3-pyridineboronic acid pinacol ester as a white solid (4.877 g, 21.12 mol; 83% yield).

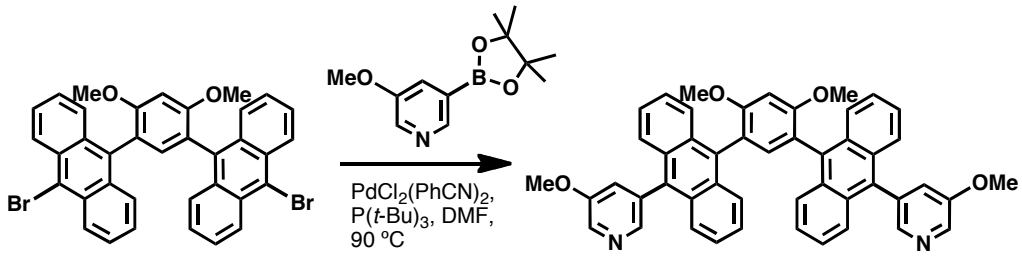
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.36 (s, 12H), 3.87 (s, 3H), 7.54 (dd, J = 3.2, 1.2, 1H), 8.37 (d, J = 3.2, 1H), 8.54 (d, J = 1.2, 1H).

^{11}B NMR (128 MHz, $CDCl_3$, rt, Bis(pinacolato)diboron): δ 30.78.

GC-MS: *m/z* Calcd. for $C_{12}H_{18}BNO_3$ 235, Found 235 $[M]^+$.

Ref.: D. J. Haydon *et al*., WO2009074812 (A1).

Synthesis of ligand 2 ZL-95



A 200 mL glass flask containing a magnetic stirring bar was filled with nitrogen. 1,5-Di(10-bromoanthracen-9-yl)-2,4-dimethoxybenzene (2.510 g, 3.871 mmol), 5-methoxy-3-pyridineboronic acid pinacol ester (3.340 g, 14.21 mmol), K_3PO_4 (5.100 g, 24.06 mmol), and degassed DMF (ca. 80 mL) were added to this flask. When $PdCl_2(PhCN)_2$ (0.300 g, 0.780 mmol) and degassed DMF (10 mL) were added to a 50 mL glass flask containing a magnetic stirring bar and the flask was filled with nitrogen, a hexane solution (0.192 g/mL) of tri-*tert*-buthylphosphine (1.60 mL, 1.52 mmol) was added to this flask. After stirring the mixture for 30 min at room temperature, the mixture was added to the 200 mL glass flask and then the resultant solution was further stirred at 90 ºC for 2 d. The mixture was concentrated under reduce pressure. The crude product was extracted with $CHCl_3$ and combined organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 2:1) to afford **2** as a yellow solid (2.500 g, 3.547 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 3.86 (s, 6H), 3.88 (s, 3H), 3.93 (s, 3H), 7.04 (s, 1H), 7.27 (s, 2H), 7.37 (m, J = 8.4, 6.4, 1.2, 4H), 7.40 (s, 1H), 7.44 (dd, J = 8.4, 6.4, 4H), 7.62 (d, J = 8.4, 4H), 7.99 (dd, J = 8.4, 1.2, 4H), 8.27 (s, 1H), 8.40 (s, 1H), 8.51 (d, J = 2.0, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 55.5, 56.0, 96.0, 119.1, 119.2, 123.2, 125.1, 125.4, 126.3, 127.0, 130.2, 130.3, 132.2, 134.3, 134.4, 135.4, 136.8, 144.0, 144.1, 155.5, 158.9, 158.9.

FT-IR (KBr, cm^{-1}): 3066, 2926, 2855, 1611, 1460, 1422, 1317, 1262, 1207, 1031, 873, 767.

MALDI-TOF MS (dithranol): *m/z* calcd. for $C_{48}H_{36}N_2O_4$ 704.27, found 704.22 $[M]^+$.

E.A.: Calcd. for $C_{48}H_{36}N_2O_4$•1.25H_2O: C, 79.26; H, 5.34; N, 3.85; O, 11.55. Found: C, 79.60; H, 4.94; N, 3.88; O, 11.58.

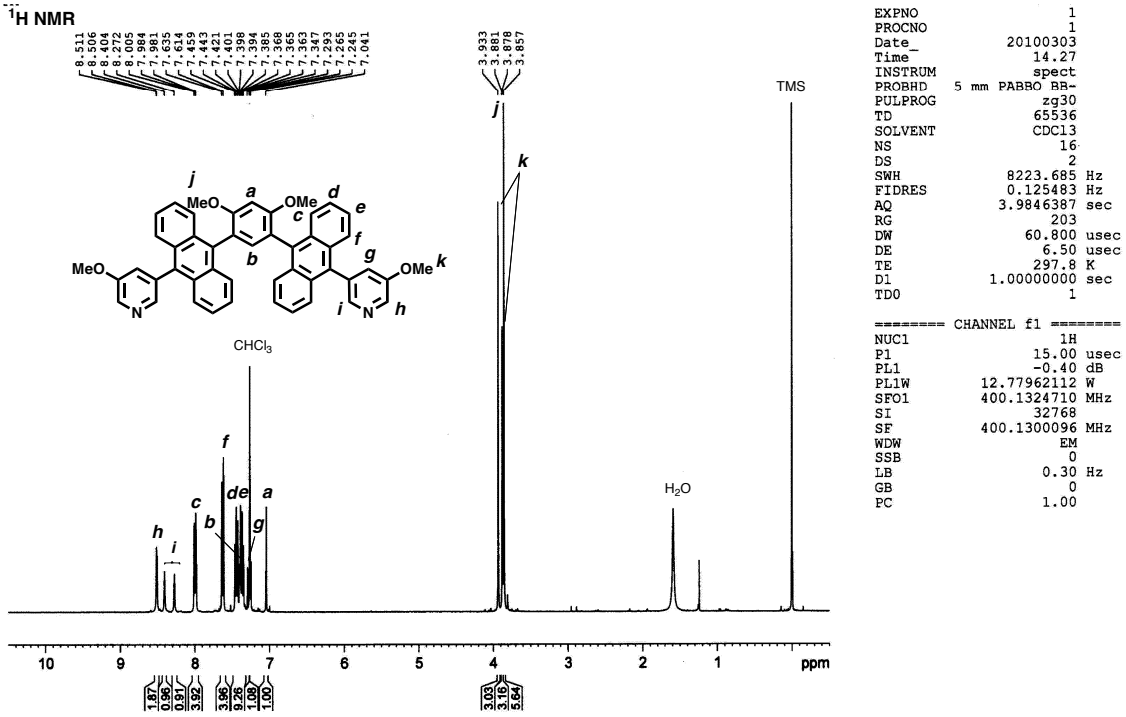


Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

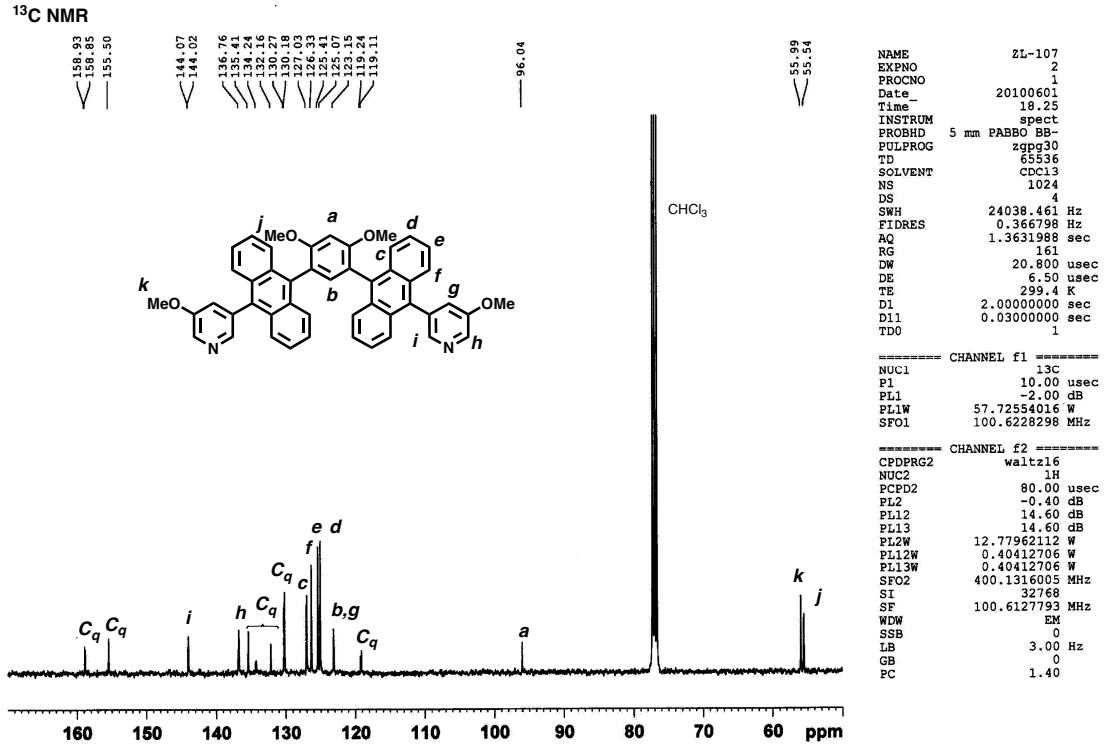


Fig. S2. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

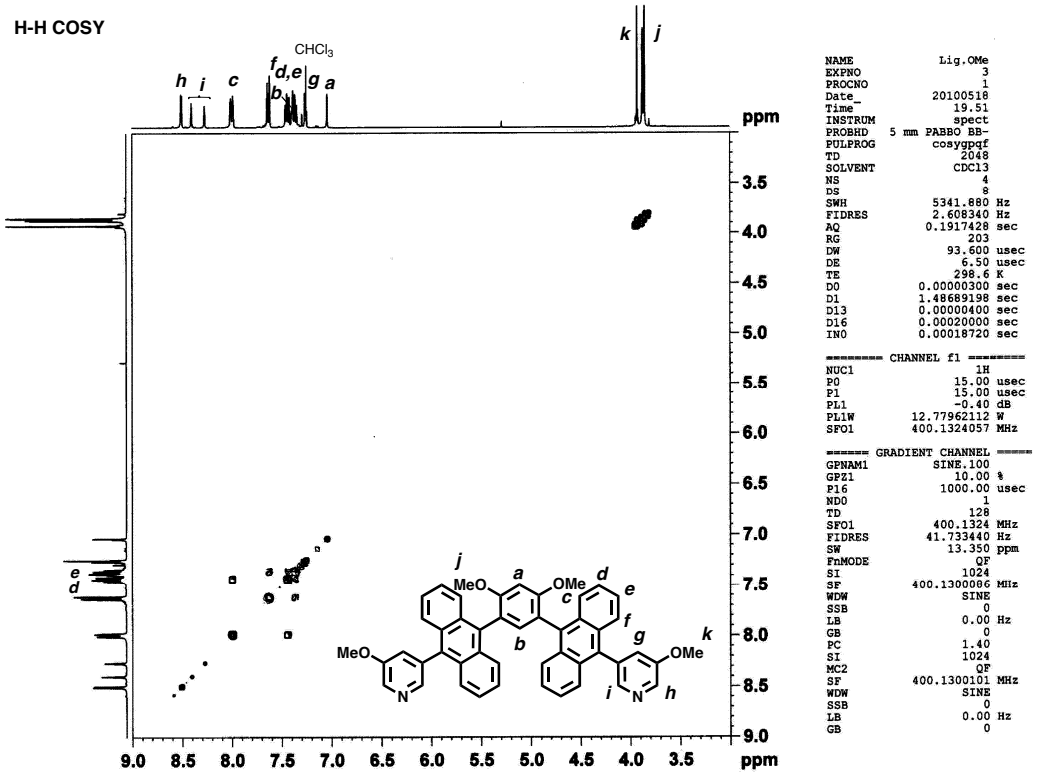


Fig. S3a. ^{1}H-^{1}H COSY (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

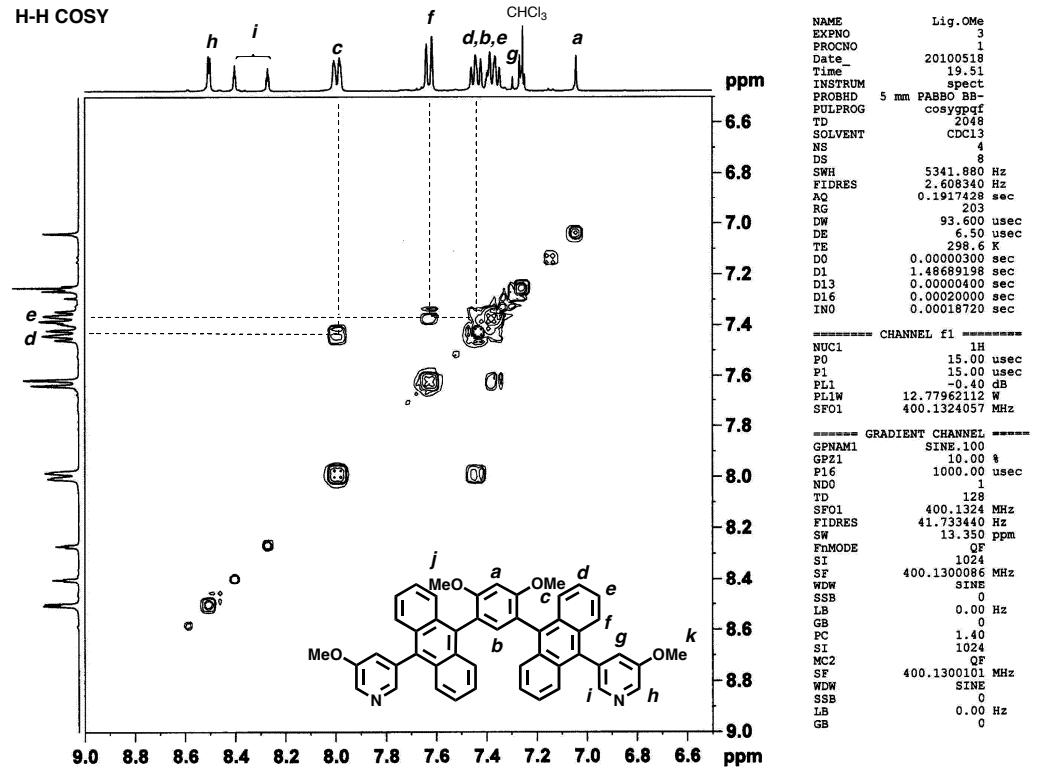


Fig. S3b. ^{1}H-^{1}H COSY (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

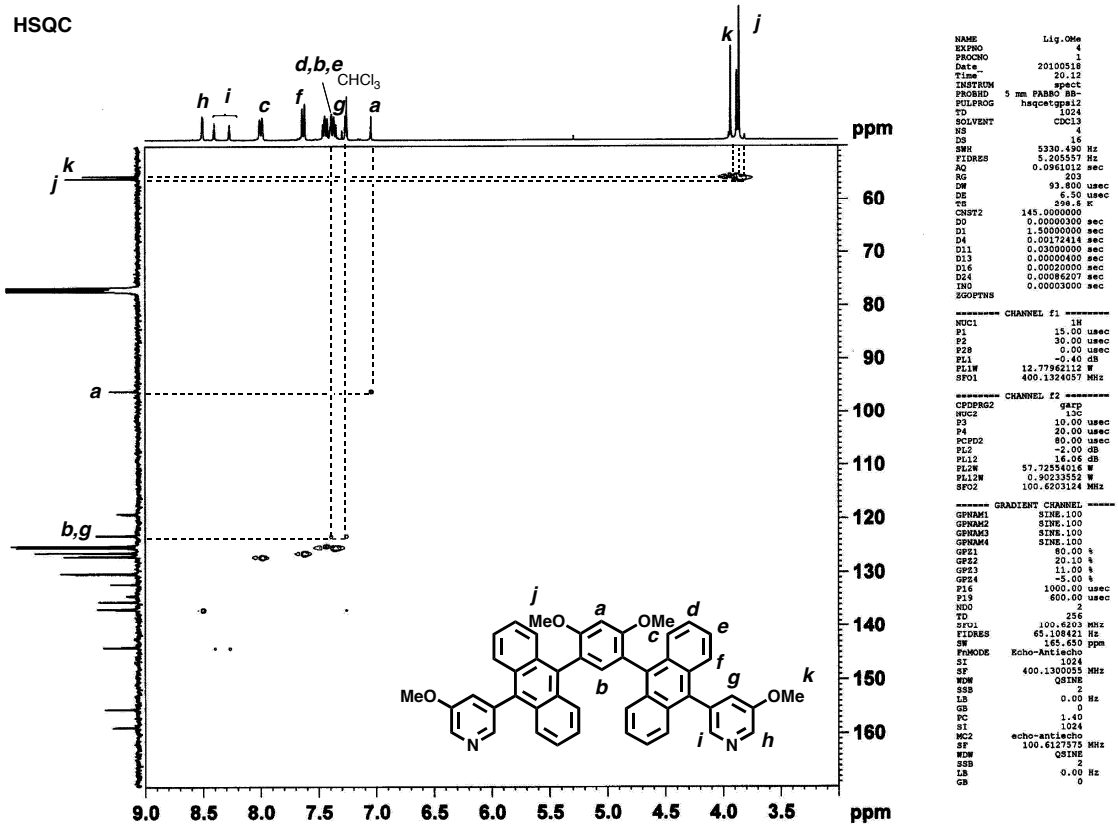


Fig. S4a. HSQC (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

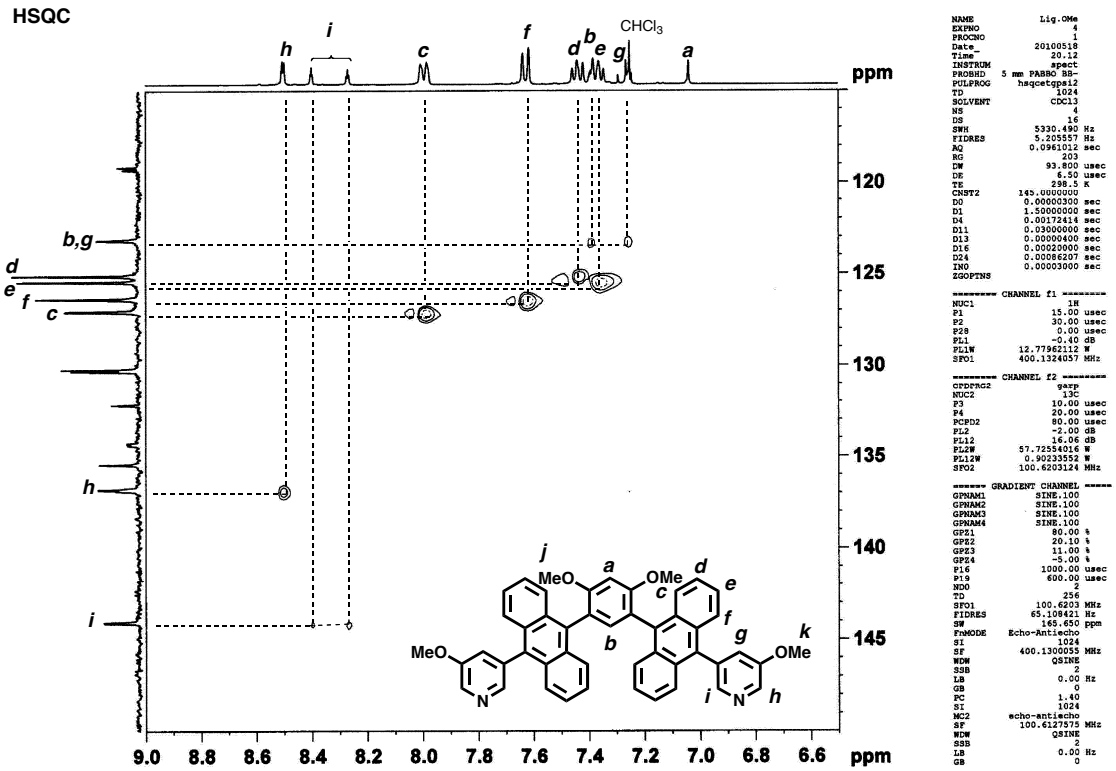
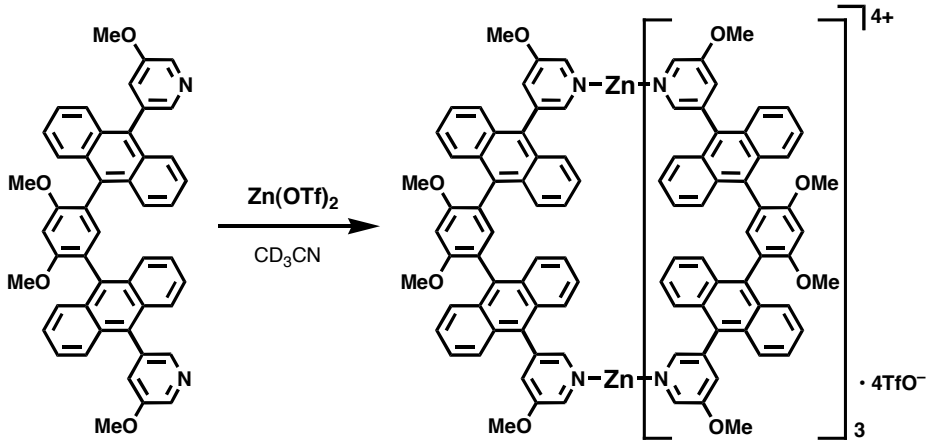


Fig. S4b. HSQC (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2**.

Synthesis of Zn(II)-capsule $\mathbf{1}^{Zn}$ ZL-107



Ligand **2** (21.3 mg, 30.2 μmol), $Zn(OTf)_2$ (5.96 mg, 15.5 μmol), and CD_3CN (0.50 mL) were added to a test tube containing a magnetic stirring bar. The mixture was stirred at 80 ºC for 1 h. ^{1}H NMR analysis of the resulted solution revealed the quantitative formation of Zn(II)-capsule $\mathbf{1}^{Zn}$. The mixture was concentrated under reduce pressure and then extracted with $CHCl_3$. After the filtration, the clear pale yellow solution was concentrated under reduce pressure to afford $\mathbf{1}^{Zn}$ as a yellow solid (24.4 mg, 6.88 μmol, 91%).

^{1}H NMR (400 MHz, CD_3CN, rt): δ 3.91 (s, 24H), 4.22 (s, 24H), 6.06 (s, 4H), 6.99 (br, 8H), 7.11 (d, J = 8.8, 16H), 7.24 (s, 4H), 7.37 (br, 24H), 7.62 (d, J = 8.8, 8H), 7.74 (br, 8H), 7.95 (d, J = 8.4, 8H), 8.10 (s, 8H), 8.50 (d, J = 2.4, 8H).

^{13}C NMR (100 MHz, CD_3CN, rt): δ 56.9, 57.8, 97.4, 119.7, 125.9, 126.3, 126.7, 127.2, 127.8, 128.3, 129.0, 130.3, 130.3, 130.9, 130.9, 131.3, 136.5, 137.4, 144.1, 158.3, 160.0.

FT-IR (KBr, cm^{-1}): 3064, 2940, 2842, 1586, 1506, 1460, 1266, 1207, 1173, 1031, 836, 640.

ESI-TOF MS (MeCN): m/z calcd. for $Zn_2C_{196}H_{144}N_8O_{28}F_{12}S_4$, found 737.5 ([$\mathbf{1}^{Zn}$–4•$TfO^-$]$^{4+}$), 747.7 ([$\mathbf{1}^{Zn}$+MeCN–4•$TfO^-$]$^{4+}$), 1032.9 ([$\mathbf{1}^{Zn}$–3•$TfO^-$]$^{3+}$), 1046.6 ([$\mathbf{1}^{Zn}$+MeCN –3•$TfO^-$]$^{3+}$), 1623.9 ([$\mathbf{1}^{Zn}$–2•$TfO^-$]$^{2+}$), 3396.8 ([$\mathbf{1}^{Zn}$–$TfO^-$]$^+$).

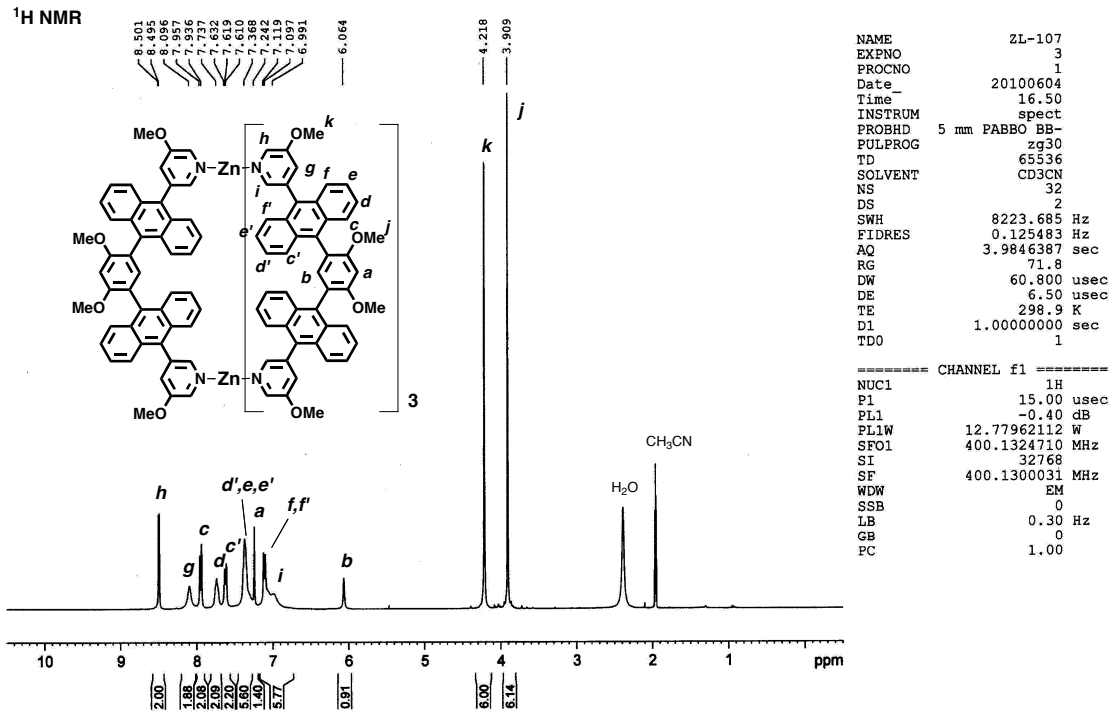


Fig. S5. ^{1}H NMR (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

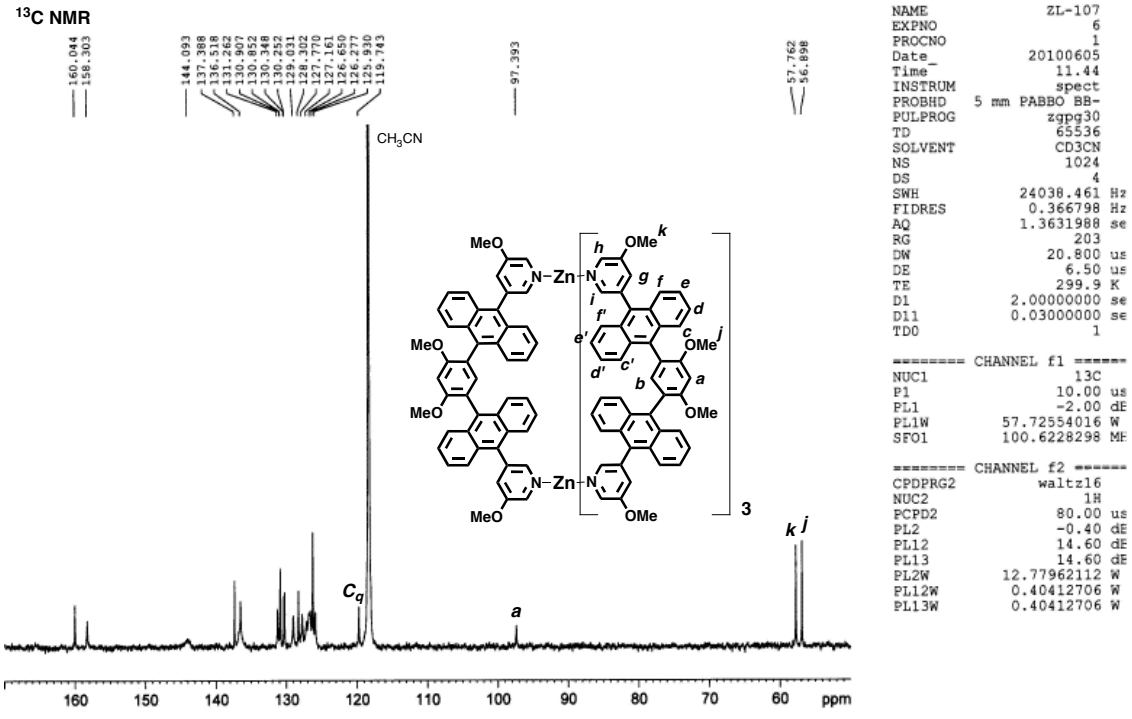


Fig. S6a. ^{13}C NMR (100 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

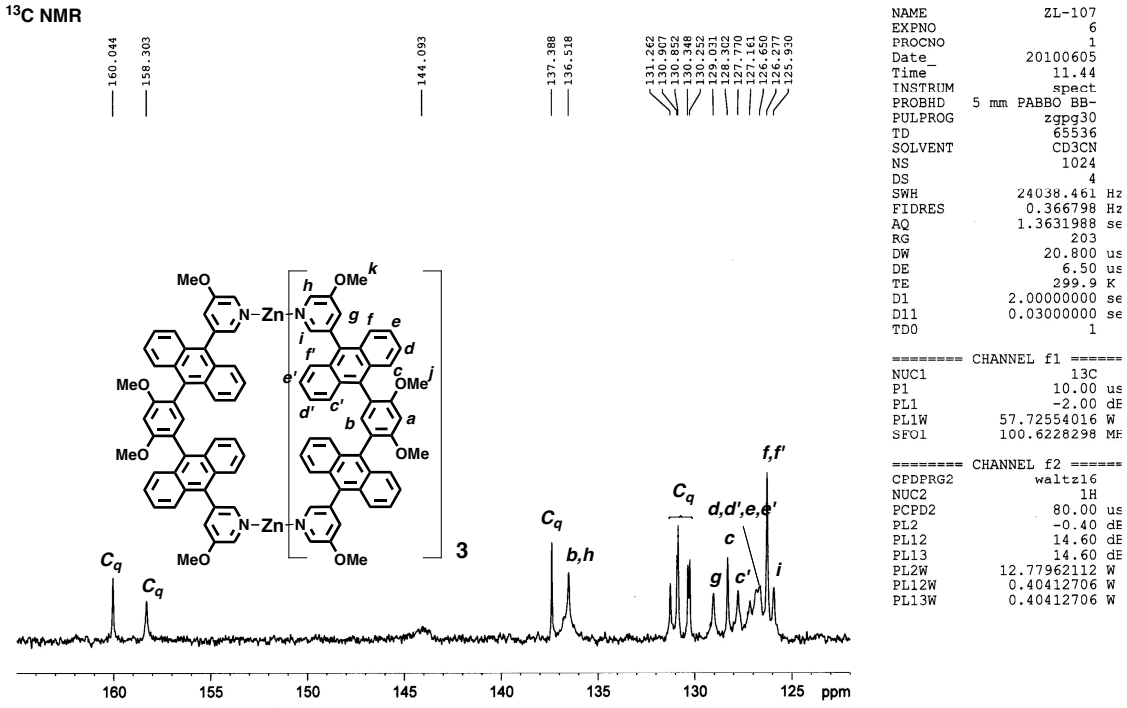


Fig. S6b. ^{13}C NMR (100 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

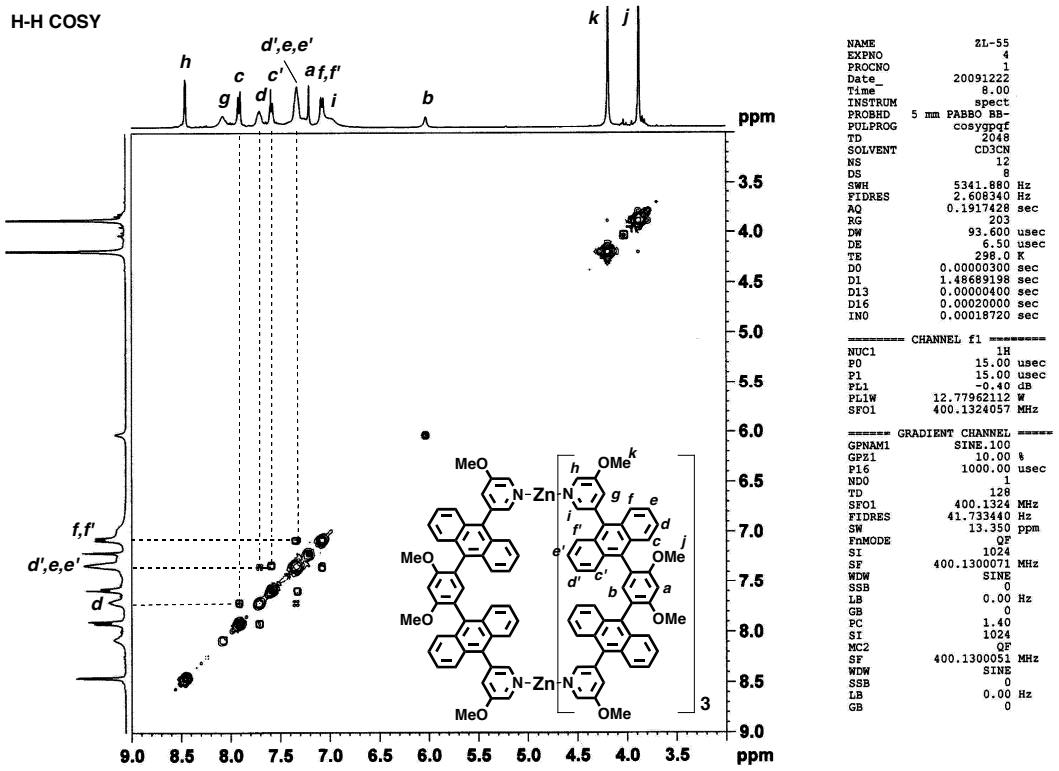


Fig. S7a. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

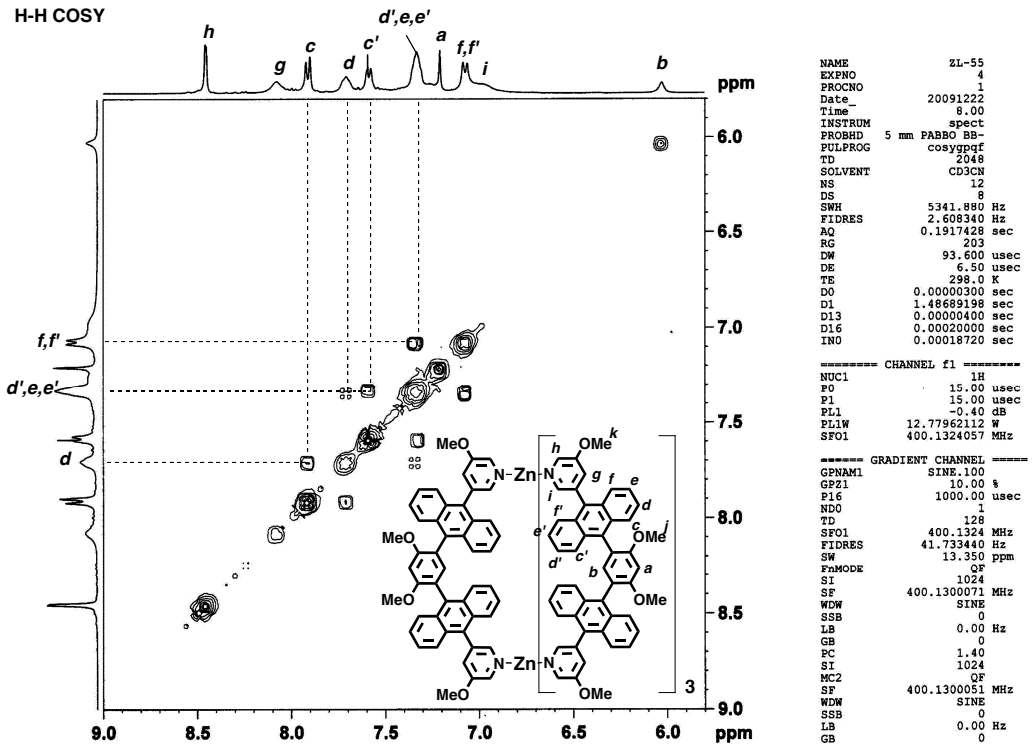


Fig. S7b. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

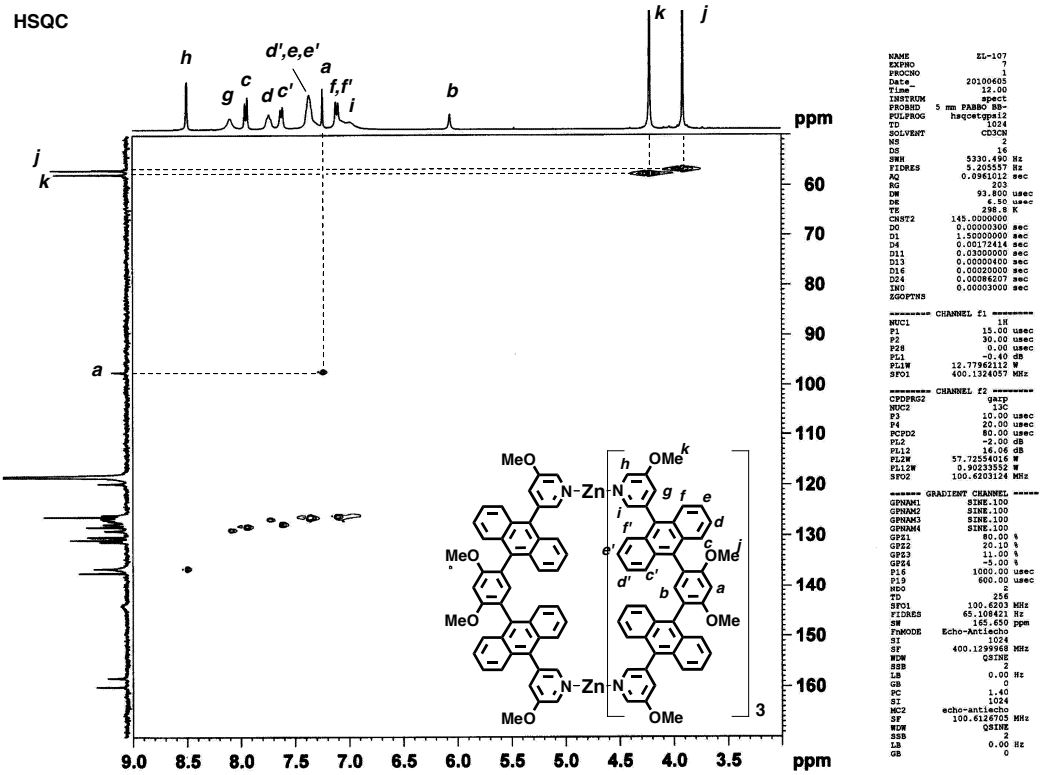


Fig. S8a. HSQC (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

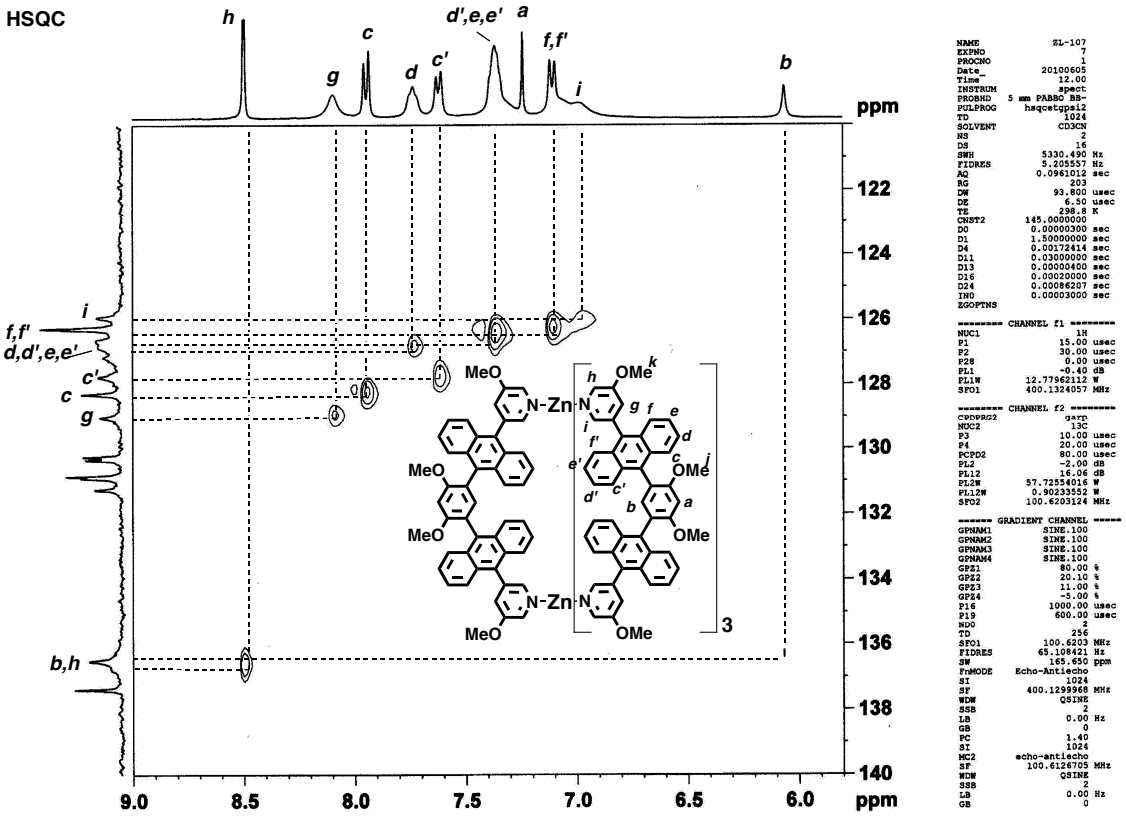


Fig. S8b. HSQC (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

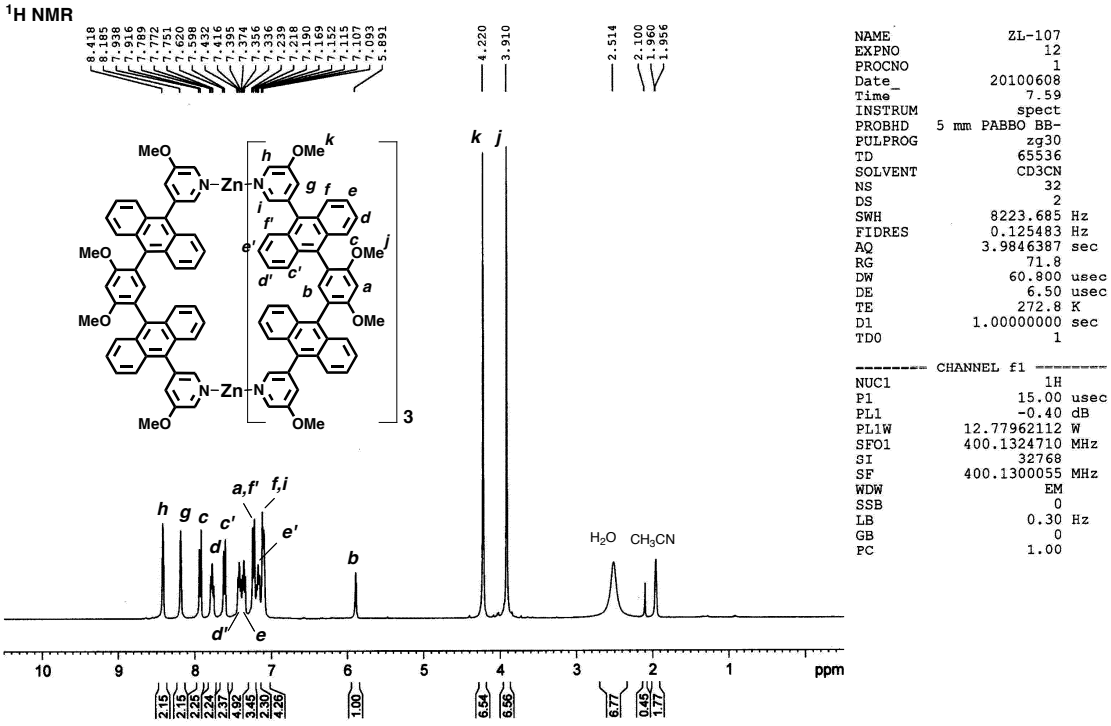


Fig. S9. ^{1}H NMR (400 MHz, CD_3CN, 0 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

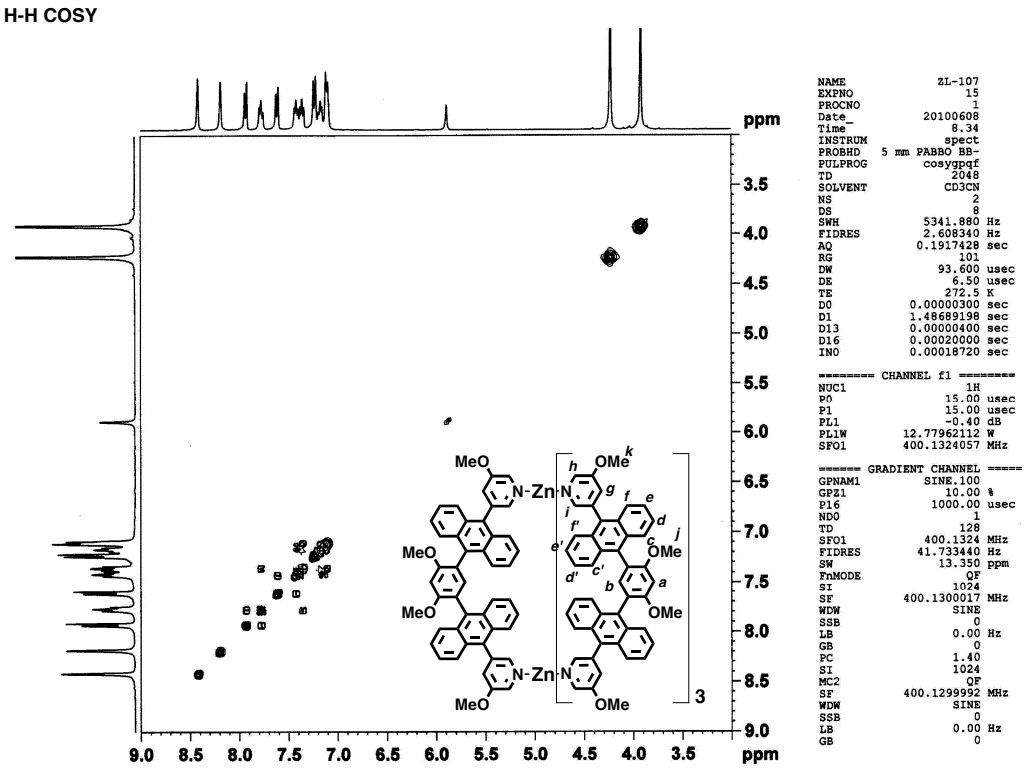


Fig. S10a. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, 0 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

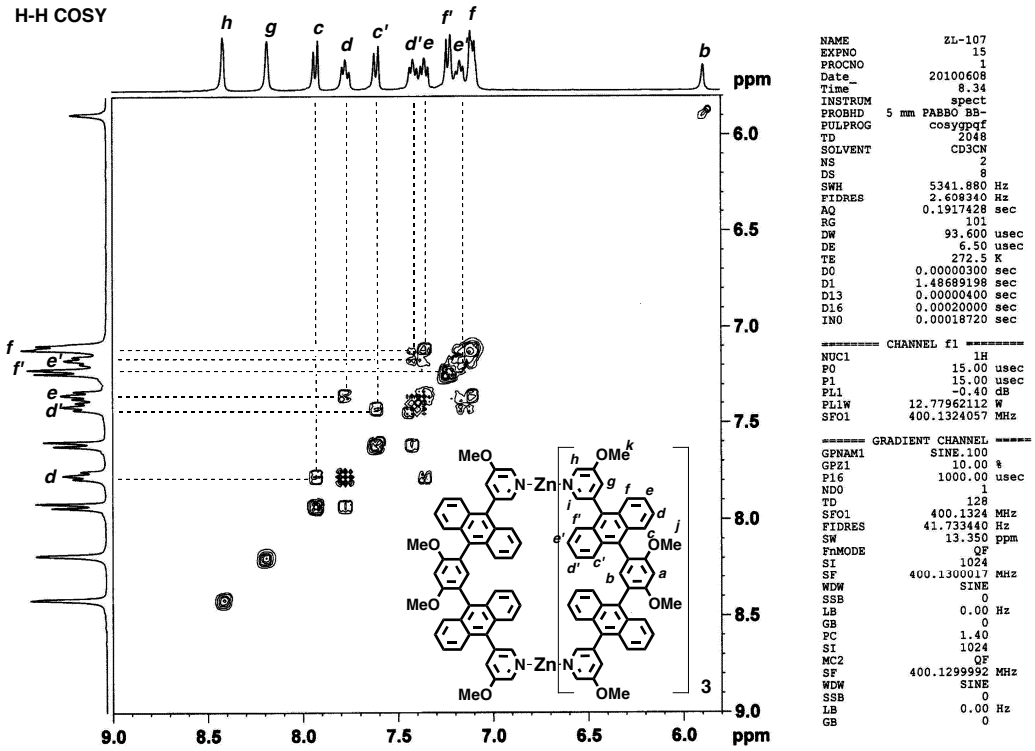


Fig. S10b. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, 0 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

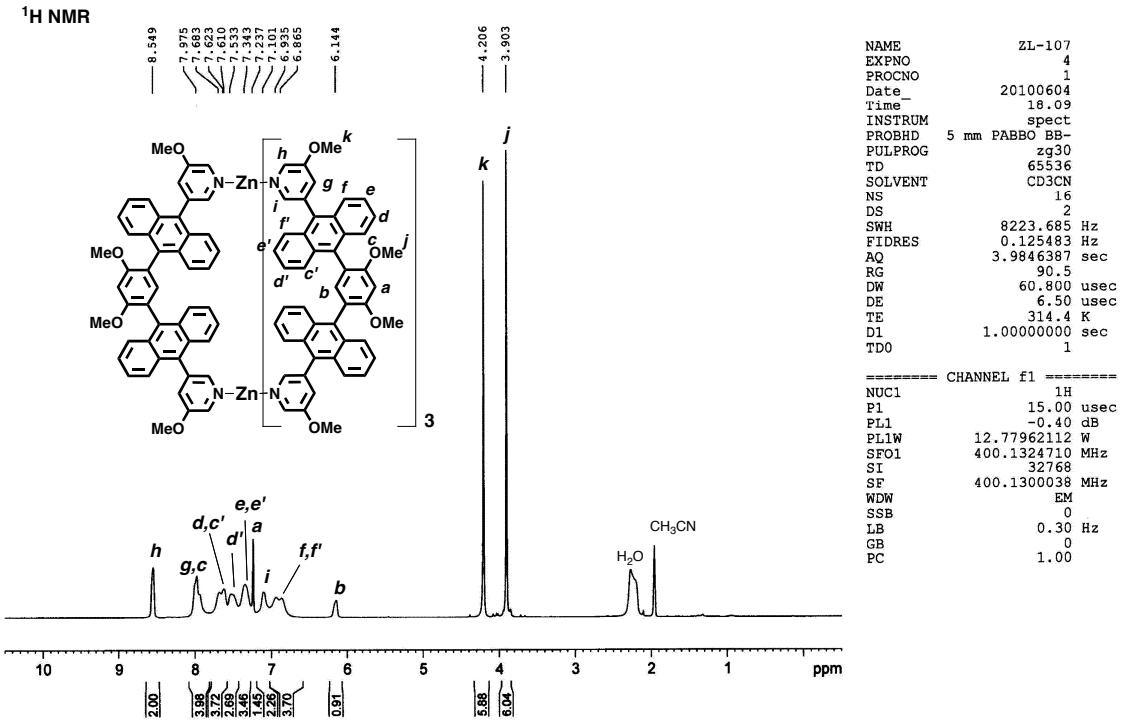


Fig. S11a. VT ^{1}H NMR (400 MHz, CD_3CN, 40 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

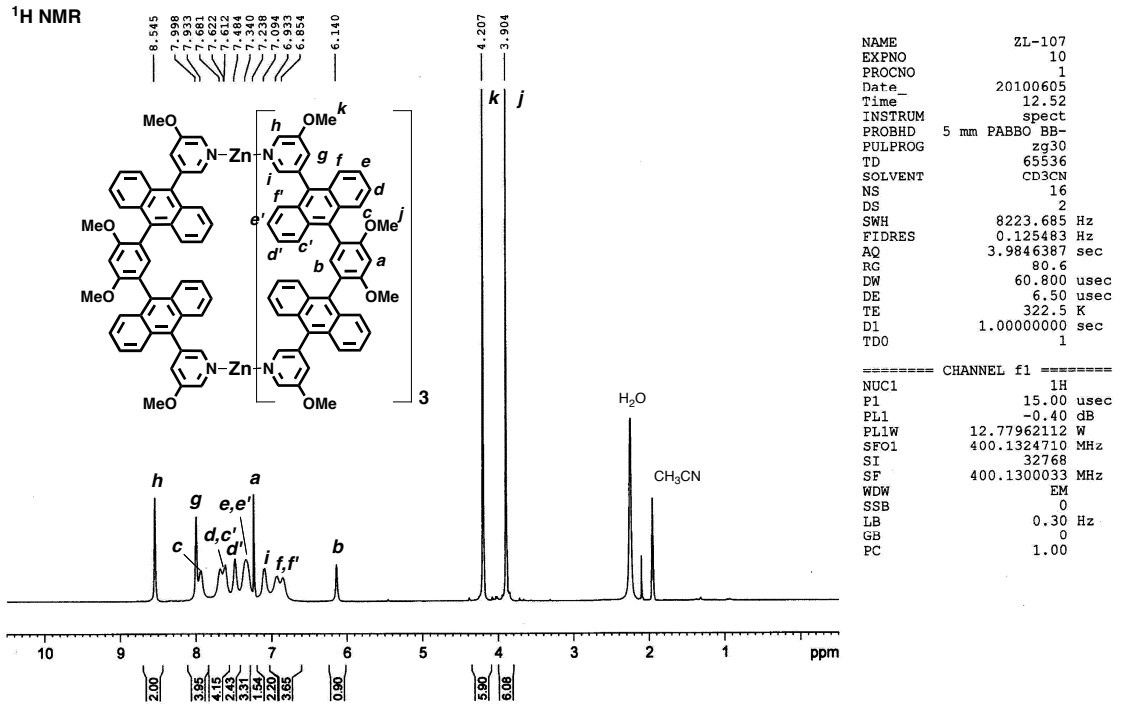


Fig. S11b. VT ^{1}H NMR (400 MHz, CD_3CN, 50 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

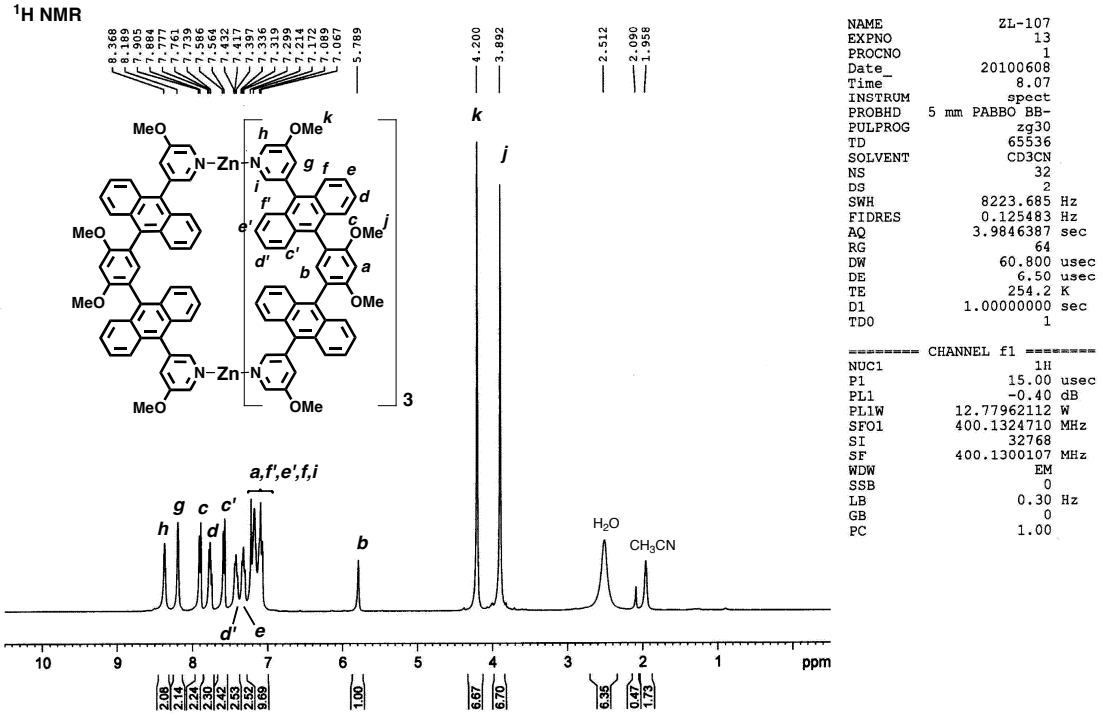


Fig. S11c. VT ^{1}H NMR (400 MHz, CD_3CN, –20 ºC) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

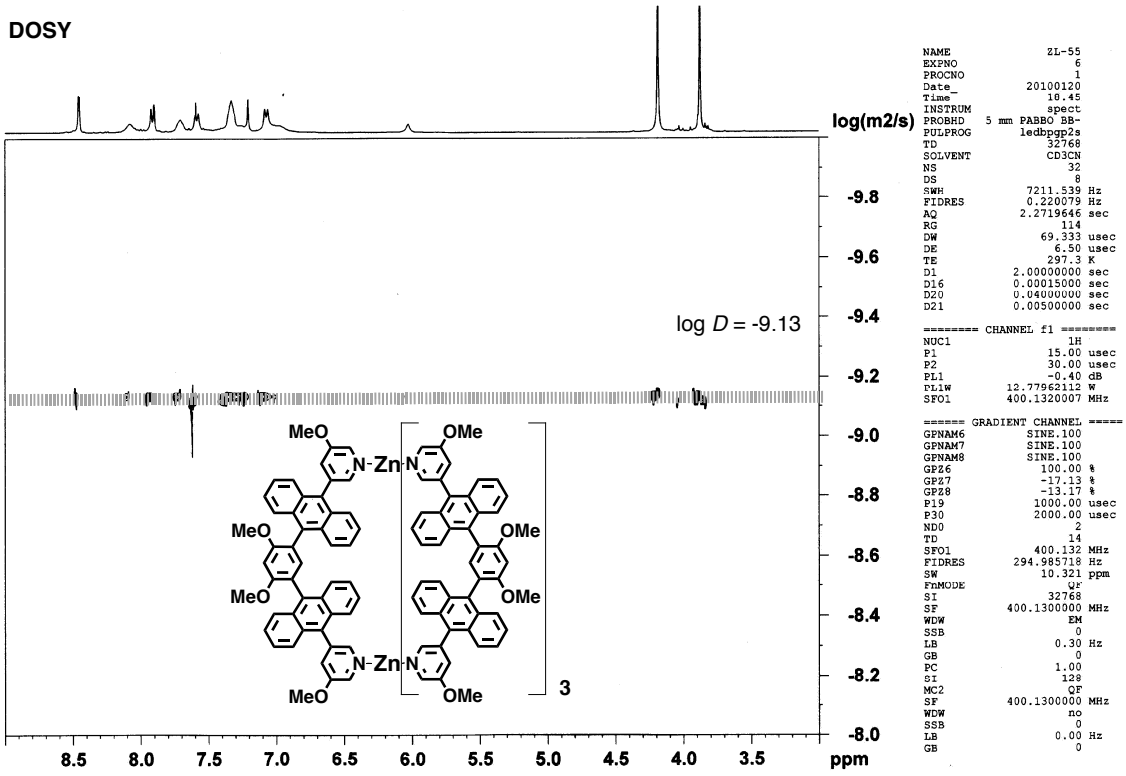


Fig. S12. ^{1}H DOSY (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule $\mathbf{1}^{Zn}$.

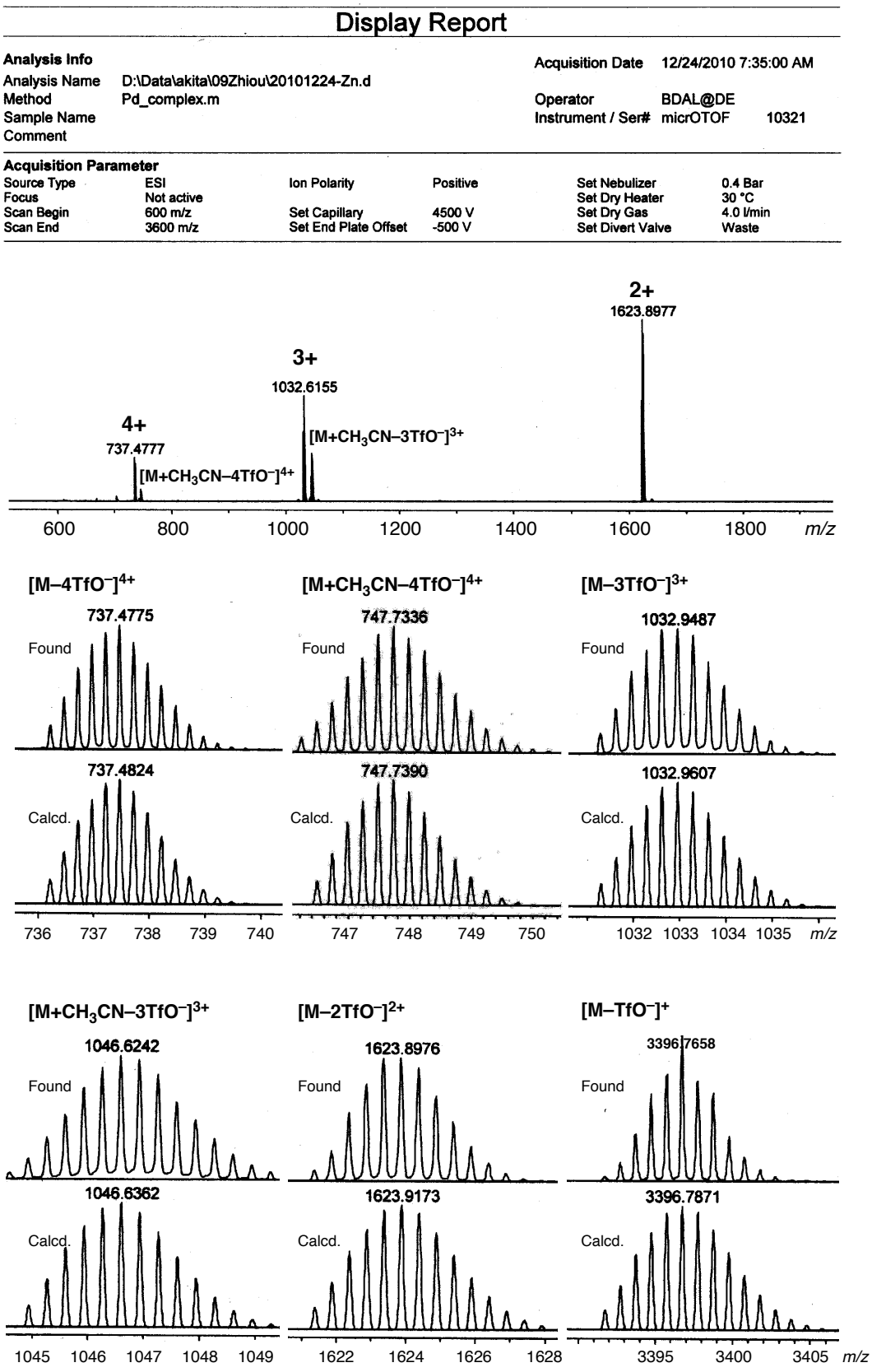
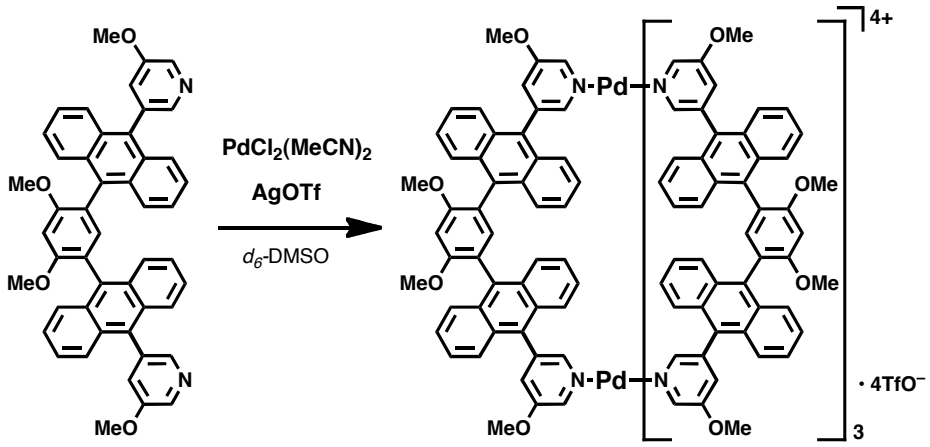


Fig. S13. ESI-TOF MS (MeCN) spectra of Zn(II)-capsule $\mathbf{1}^{Zn}$.

Synthesis of Pd(II)-capsule $\mathbf{1}^{Pd}$ ZL-54



Ligand **2** (11.5 mg, 16.3 μmol), $PdCl_2(MeCN)_2$ (2.8 mg, 8.4 μmol), AgOTf (5.4 mg, 21.0 μmol) and d_6-DMSO (0.50 mL) were added to a test tube containing a magnetic stirring bar. The mixture was stirred at 100 ºC for 1 h. ^{1}H NMR analysis of the resulted solution revealed the quantitative formation of Pd(II)-capsule $\mathbf{1}^{Pd}$.

^{1}H NMR (400 MHz, d_6-DMSO, r.t.): δ 3.82 (s, 24H), 4.19 (s, 24H), 6.32 (s, 1H), 6.68 (br, 32H), 7.28 (br, 20H), 7.73 (d, J = 8.8, 16H), 7.89 (s, 8H), 8.13 (s, 8H), 9.04 (s, 8H).

^{13}C NMR (100 MHz, d_6-DMSO, rt): δ 56.3, 57.6, 97.6, 119.5, 122.7, 125.0, 126.1, 126.4, 127.0, 128.0, 129.1, 139.5, 135.4, 135.7, 137.7, 140.5, 144.1, 157.9, 159.2.

ESI-TOF MS (MeCN): m/z calcd. for $Pd_2C_{196}H_{144}N_8O_{28}F_{12}S_4$, found 758.0 ($[\mathbf{1}^{Pd}–4•TfO^-]^{4+}$), 1060.3 ($[\mathbf{1}^{Pd}–3•TfO^-]^{3+}$), 1664.9 ($[\mathbf{1}^{Pd}–2•TfO^-]^{2+}$), 3478.8 ($[\mathbf{1}^{Pd}–TfO^-]^{+}$).

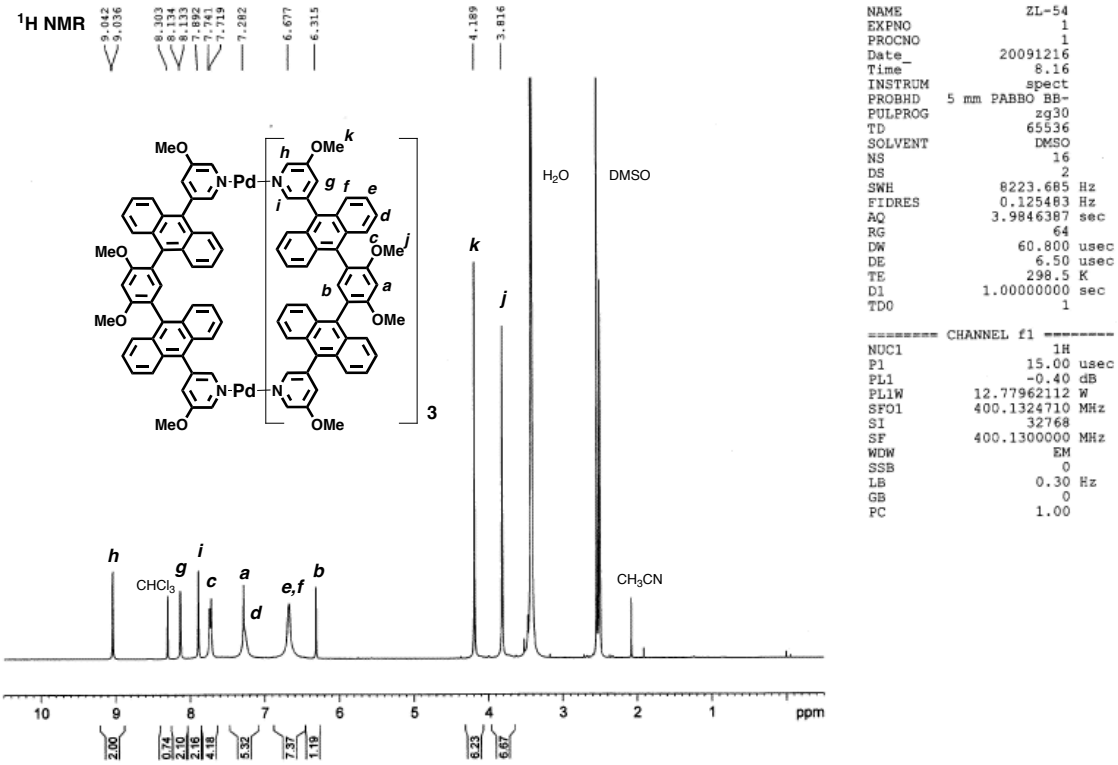


Fig. S14. ^{1}H NMR (400 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{Pd}$.

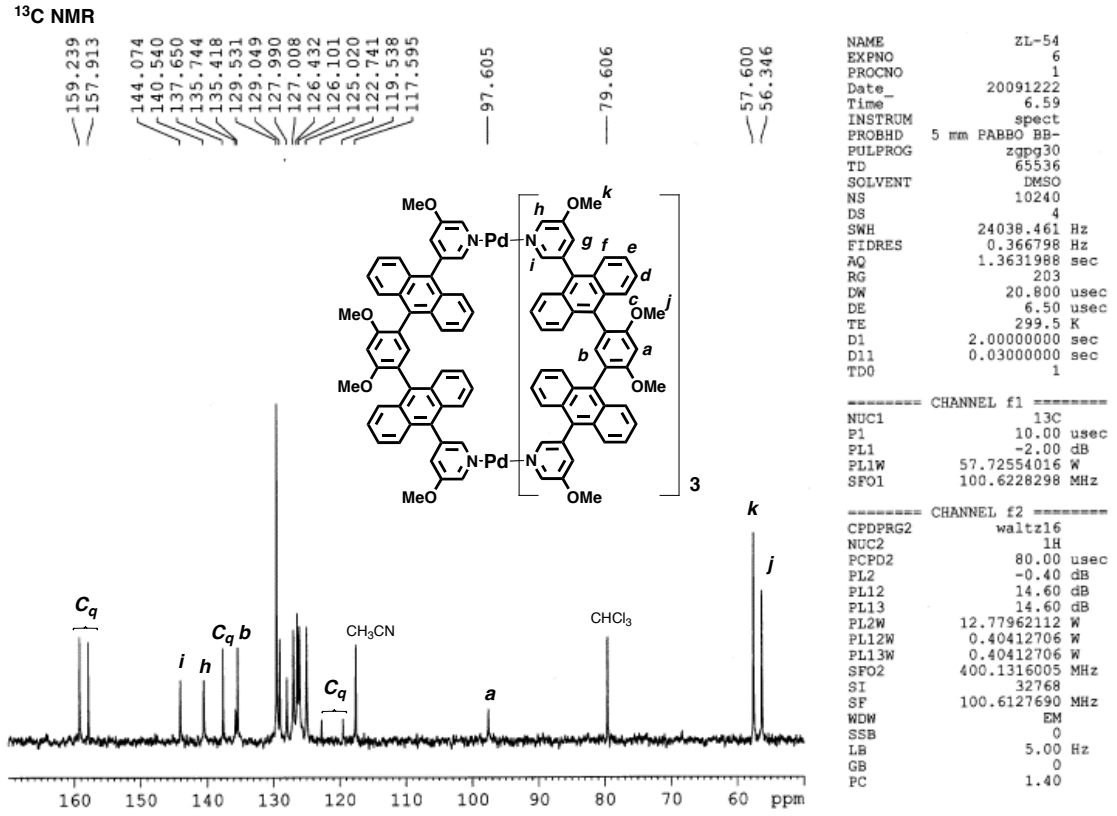


Fig. S15a. ^{13}C NMR (100 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{Pd}$.

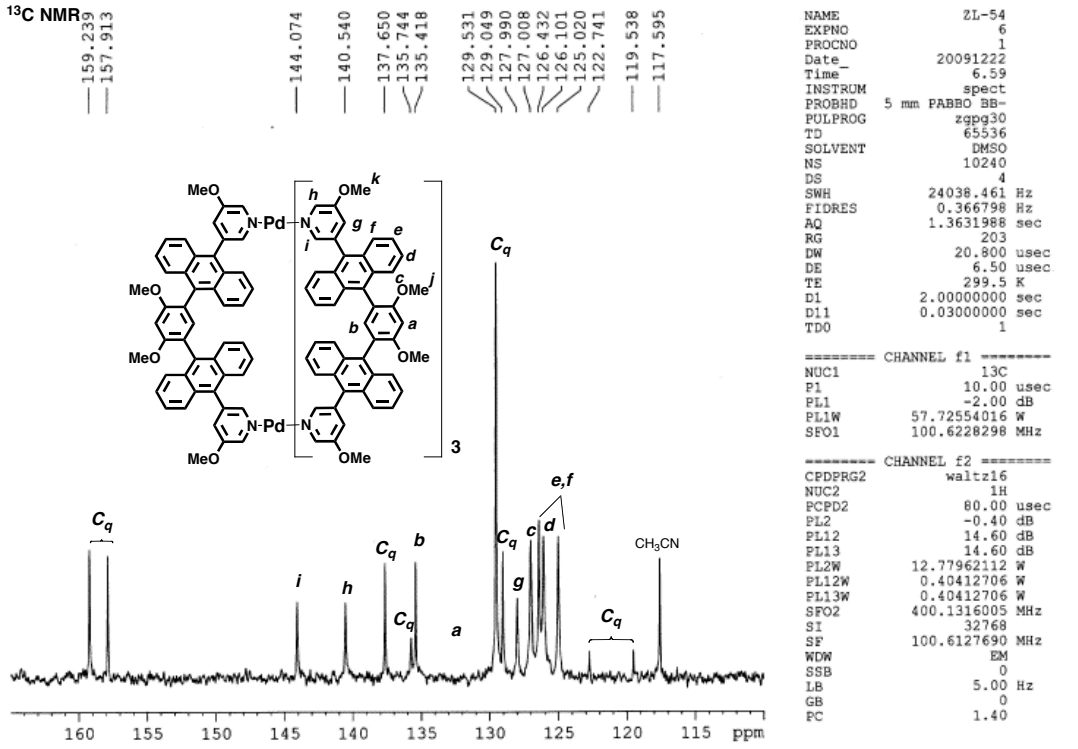


Fig. S15b. ^{13}C NMR (100 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{\mathbf{Pd}}$.

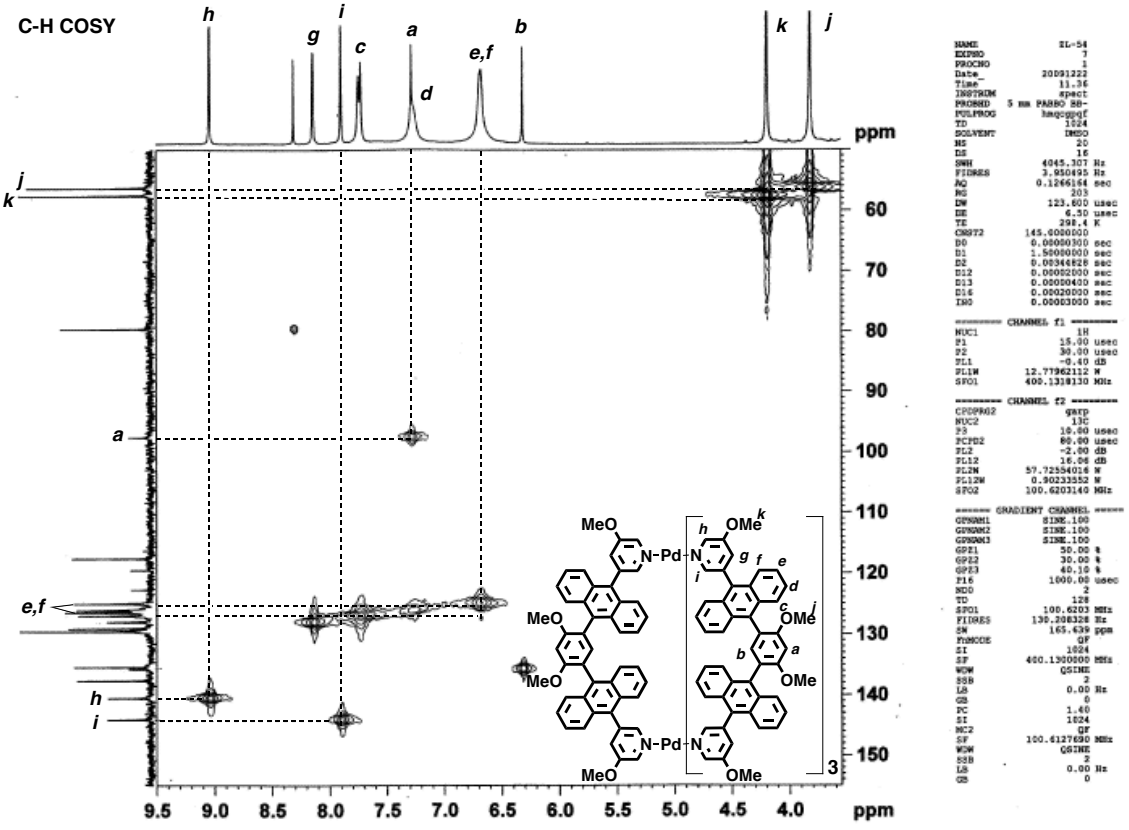


Fig. S16a. ^{13}C-^{1}H COSY (400 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{\mathbf{Pd}}$.

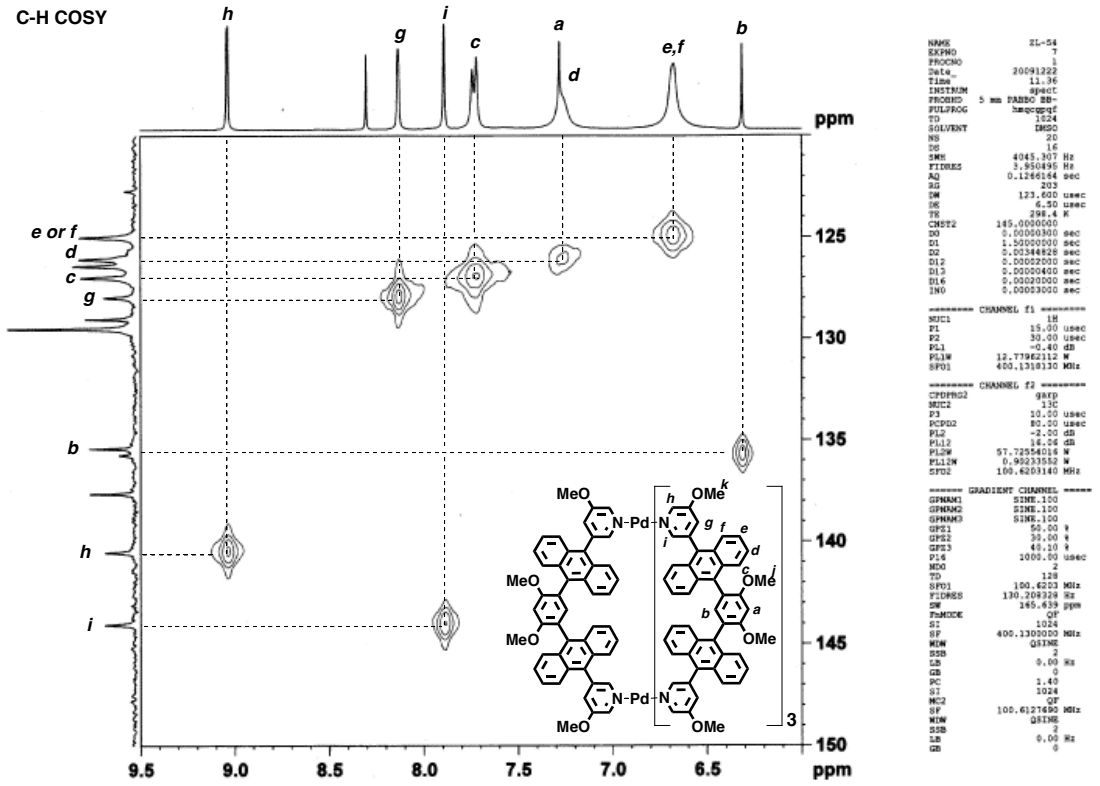


Fig. S16b. ^{13}C-^{1}H COSY (400 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{\mathbf{Pd}}$.

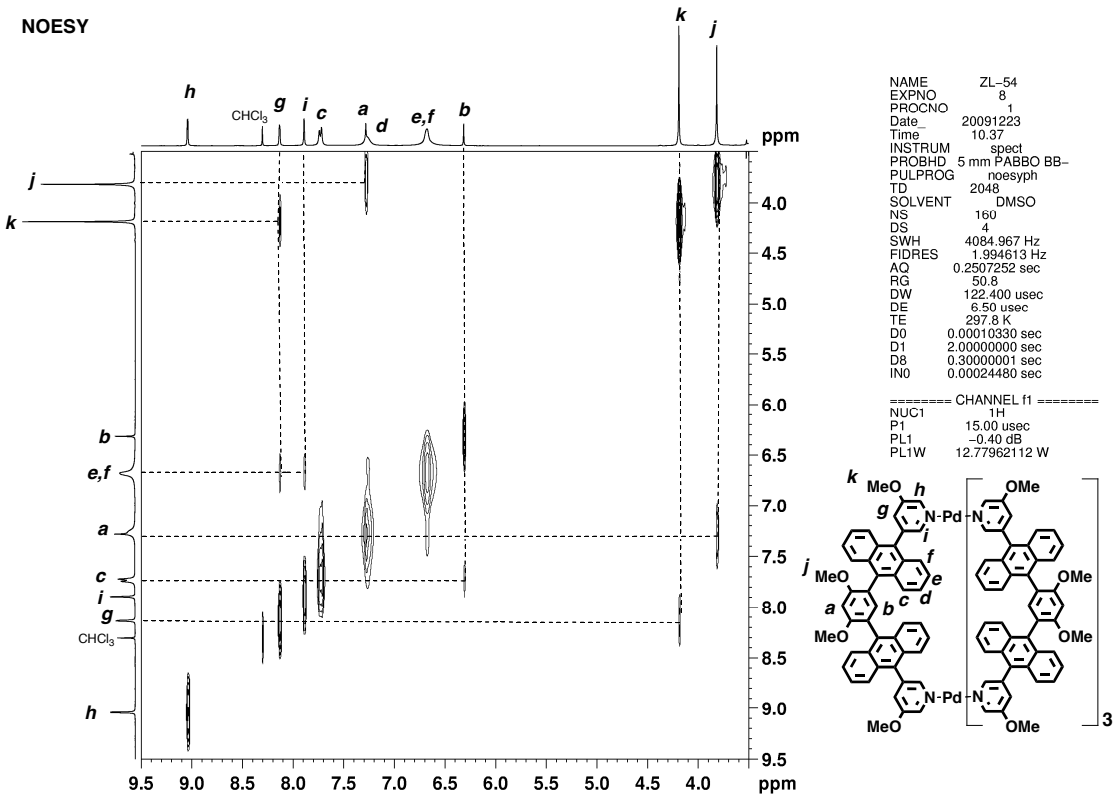


Fig. S17. NOESY (400 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{\mathbf{Pd}}$.

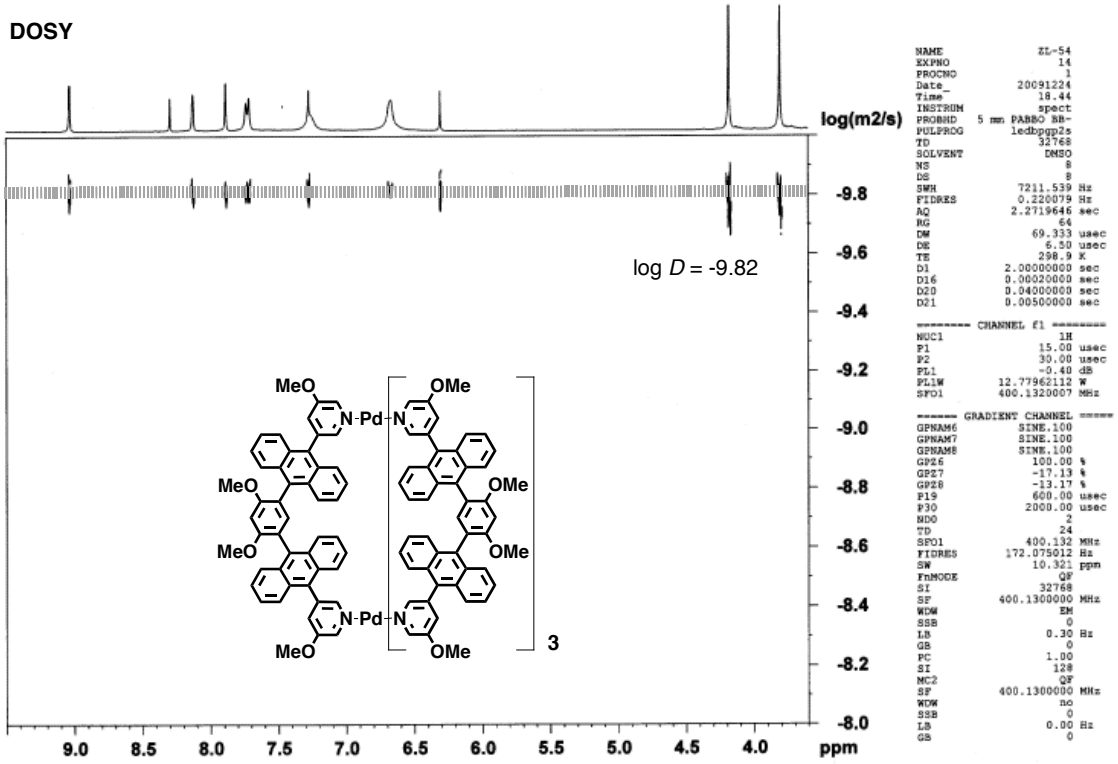
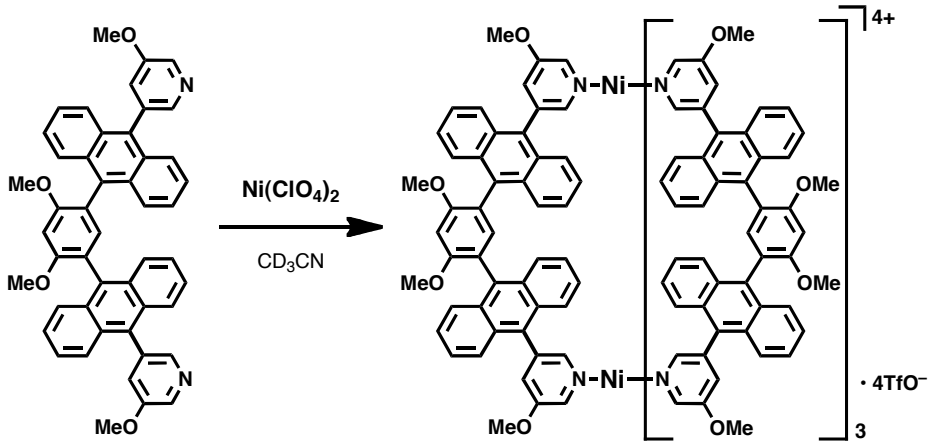


Fig. S18. ^{1}H DOSY (400 MHz, d_6-DMSO, r.t.) spectrum of Pd(II)-capsule $\mathbf{1}^{Pd}$.

Synthesis of Ni(II)-capsule 1^{Ni} ZL-57



Ligand **2** (9.7 mg, 13.8 μmol), $Ni(ClO_4)_2 \cdot 6H_2O$ (2.6 mg, 7.1 μmol) and CD_3CN (0.50 mL) were added to a test tube containing a magnetic stirring bar. The mixture was stirred at 80 ºC for 1 h. ^{1}H NMR and ESI-TOF MS analyses of the resulted

solution revealed the quantitative formation of Ni(II)-capsule $\mathbf{1}^{\mathbf{Ni}}$.

^{1}H NMR (400 MHz, CD_3CN, rt): δ 3.93, 6.81, 7.34, 7.51, 7.66, 7.87, 8.02.

^{13}C NMR (100 MHz, CD_3CN, rt): δ 56.9, 71.2, 97.4, 120.1, 123.6, 124.3, 125.3, 128.7, 129.0, 131.1, 133.1, 139.6, 140.3, 141.9, 151.3, 162.1.

FT-IR (KBr, cm^{-1}): 3064, 2939, 2841, 1585, 1506, 1460, 1316, 1266, 1206, 1119, 837, 770, 714, 628.

ESI-TOF MS (MeCN): *m/z* calcd. for $Ni_2C_{192}H_{144}N_8O_{32}Cl_4$, found 734.0 ($[\mathbf{1}^{\mathbf{Ni}}–4•ClO_4^-]^{4+}$), 1011.6 ($[\mathbf{1}^{\mathbf{Ni}}–3•ClO_4^-]^{3+}$), 1025.6 ($[\mathbf{1}^{\mathbf{Ni}}+MeCN–3•ClO_4^-]^{3+}$), 1567.4 ($[\mathbf{1}^{\mathbf{Ni}}–2•ClO_4^-]^{2+}$), 1587.9 ($[\mathbf{1}^{\mathbf{Ni}}+MeCN–2•ClO_4^-]^{2+}$), 3234.7 ($[\mathbf{1}^{\mathbf{Ni}} – ClO_4^-]^{+}$).

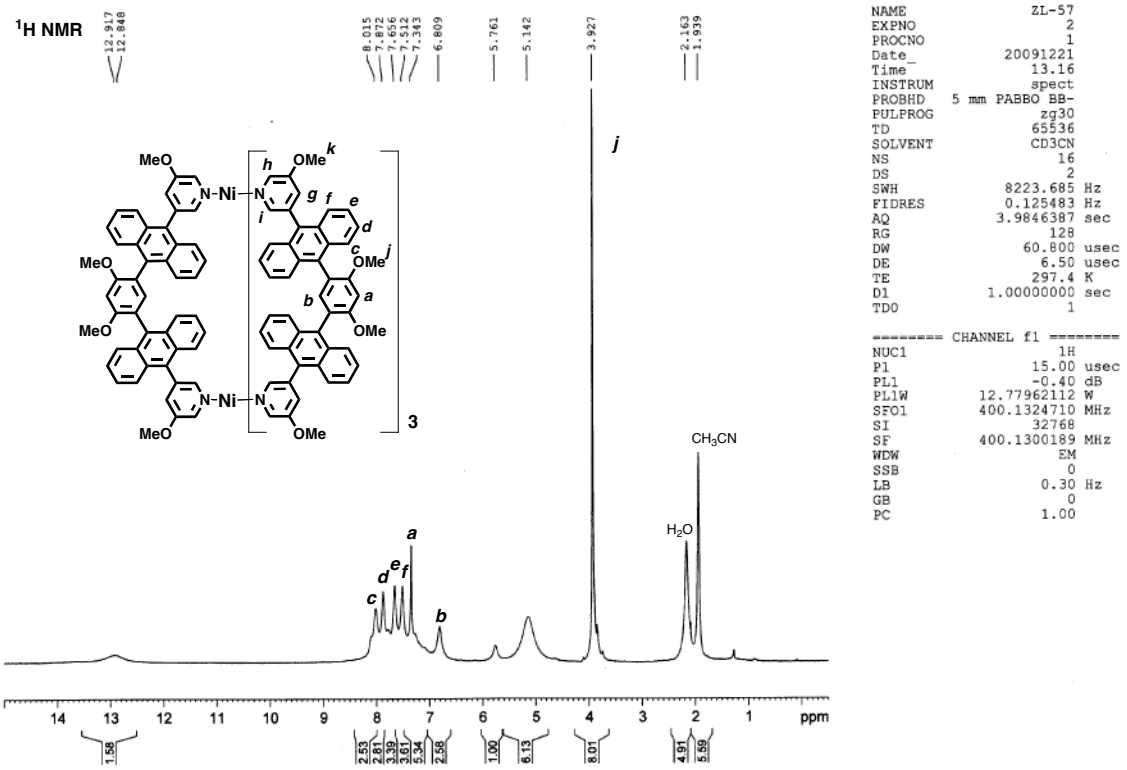


Fig. S19. ^{1}H NMR (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{\mathbf{Ni}}$.

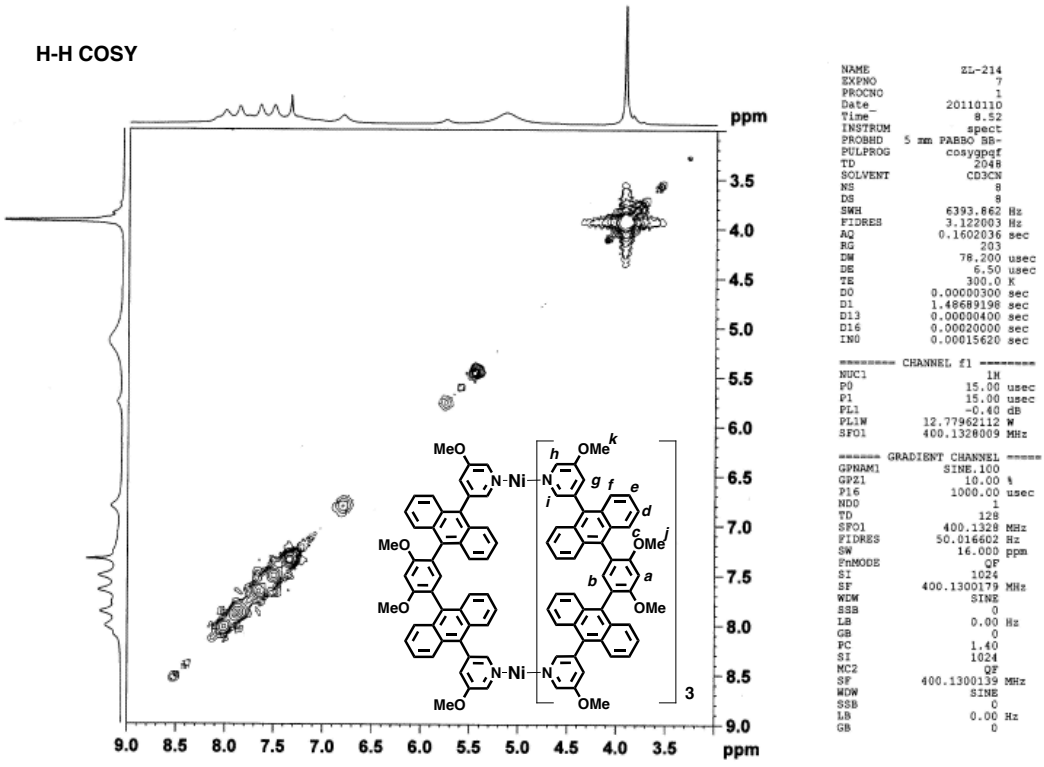


Fig. S20a. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

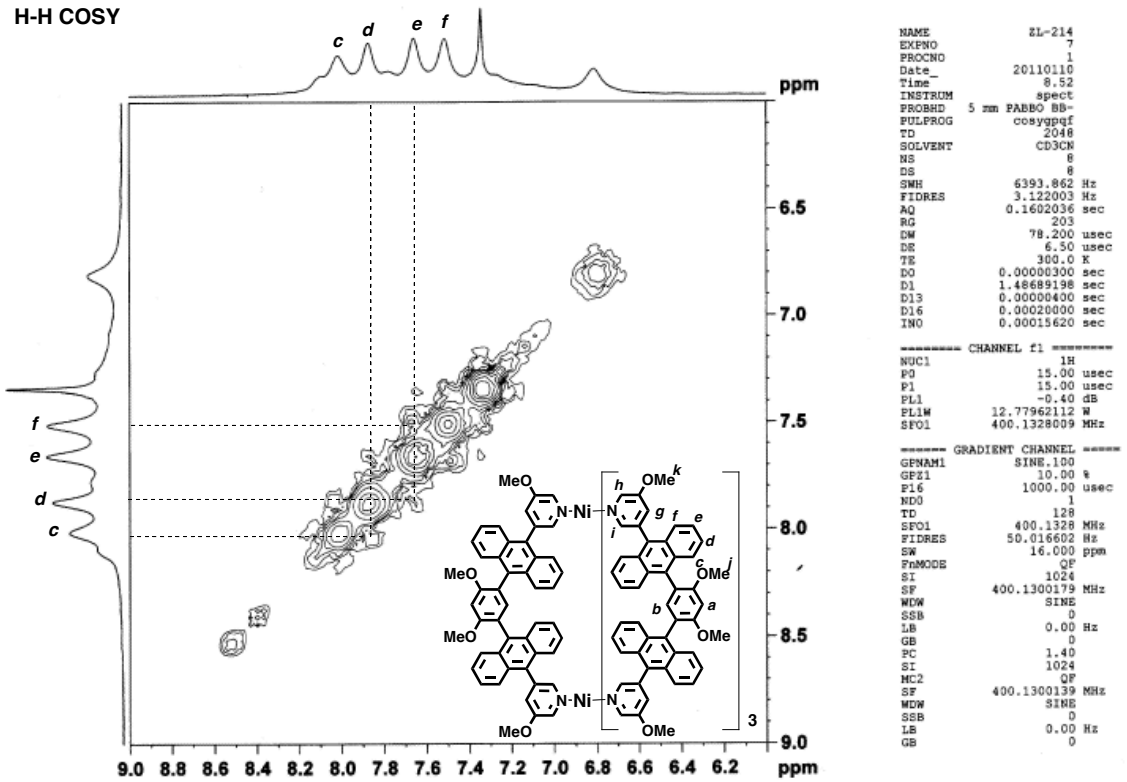


Fig. S20b. ^{1}H-^{1}H COSY (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

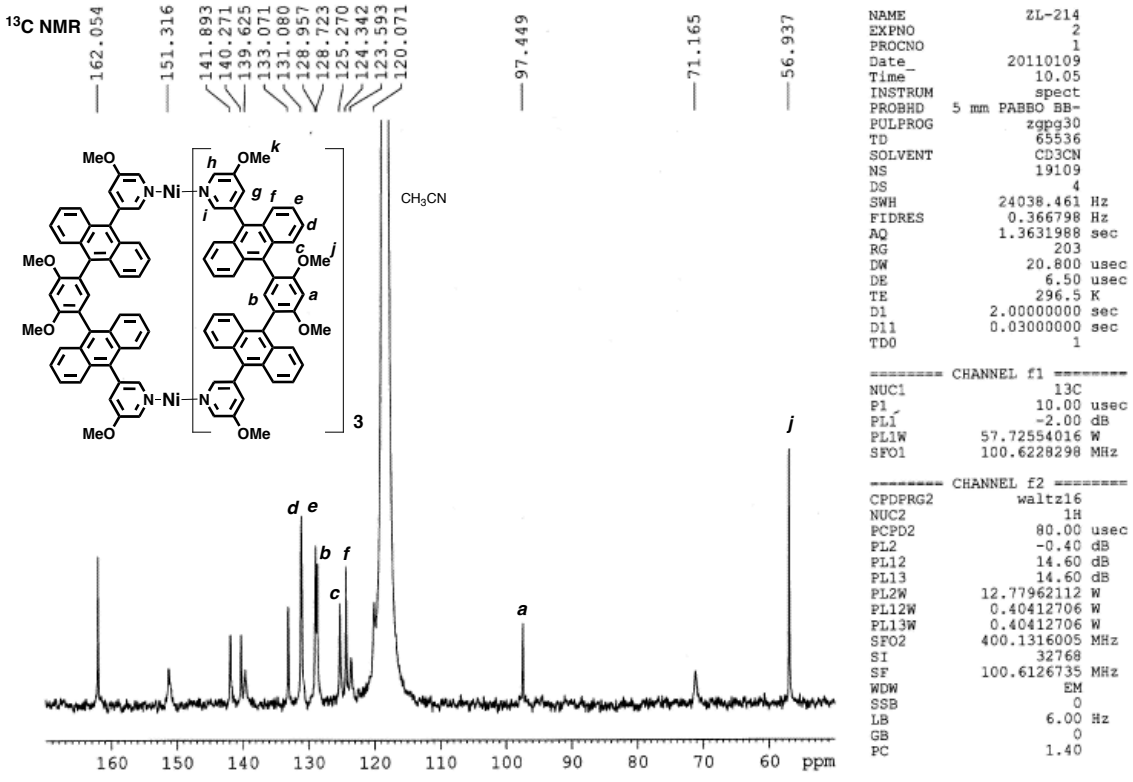


Fig. S21a. ^{13}C NMR (100 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

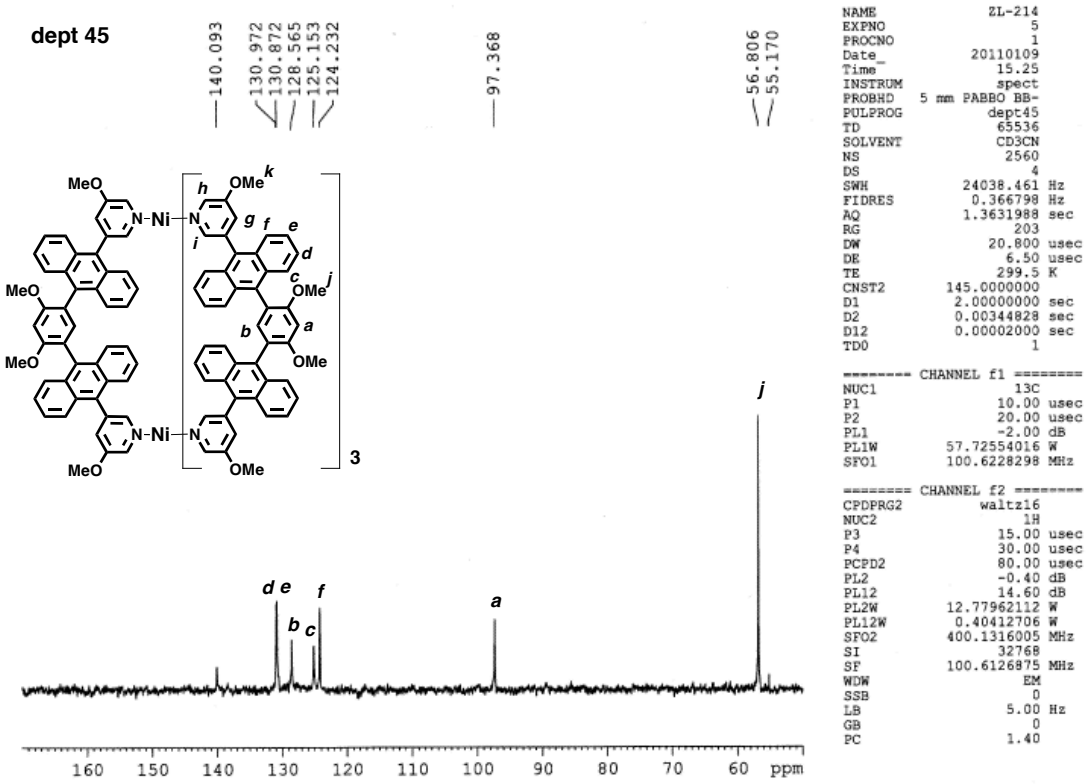


Fig. S21b. DEPT45 (100 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

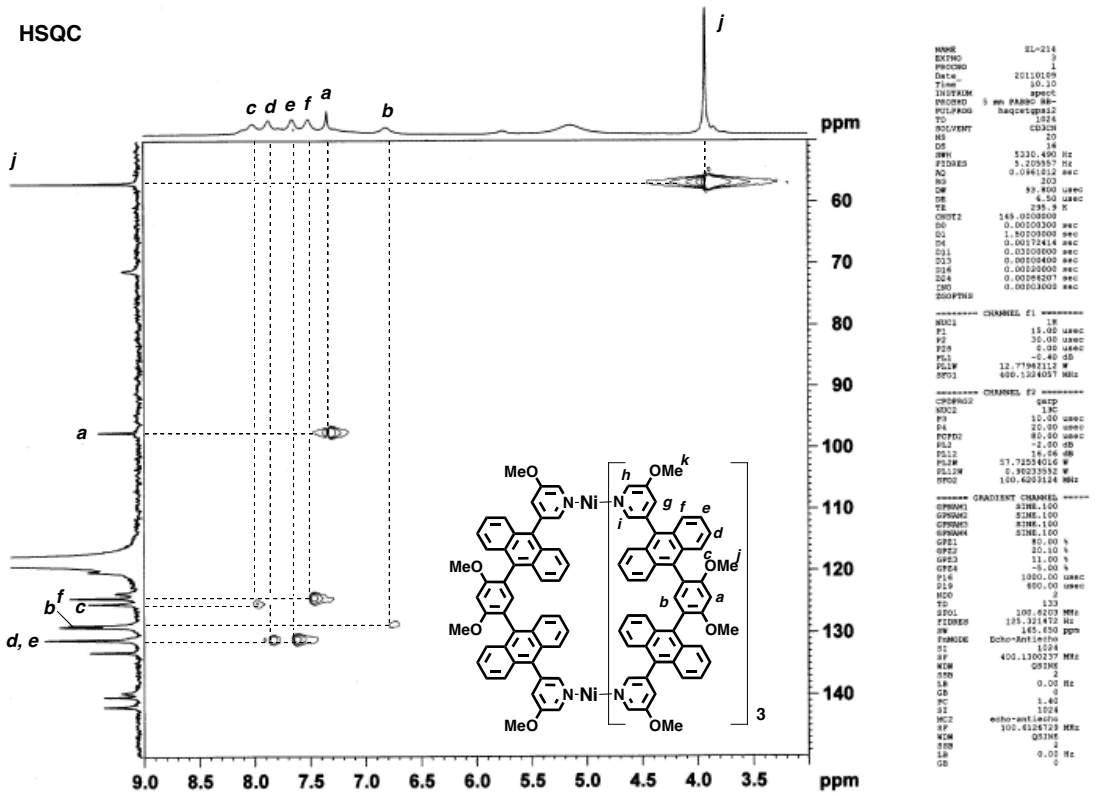


Fig. S22. HSQC (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

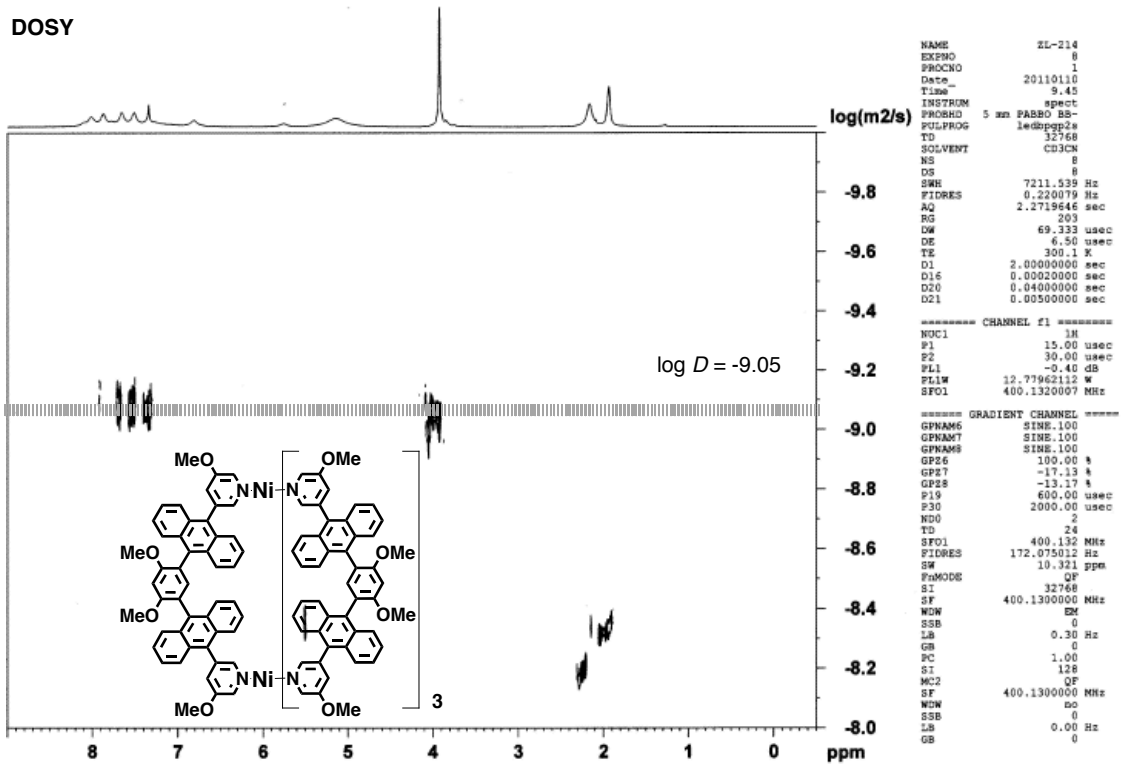


Fig. S23. ^{1}H DOSY (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule $\mathbf{1}^{Ni}$.

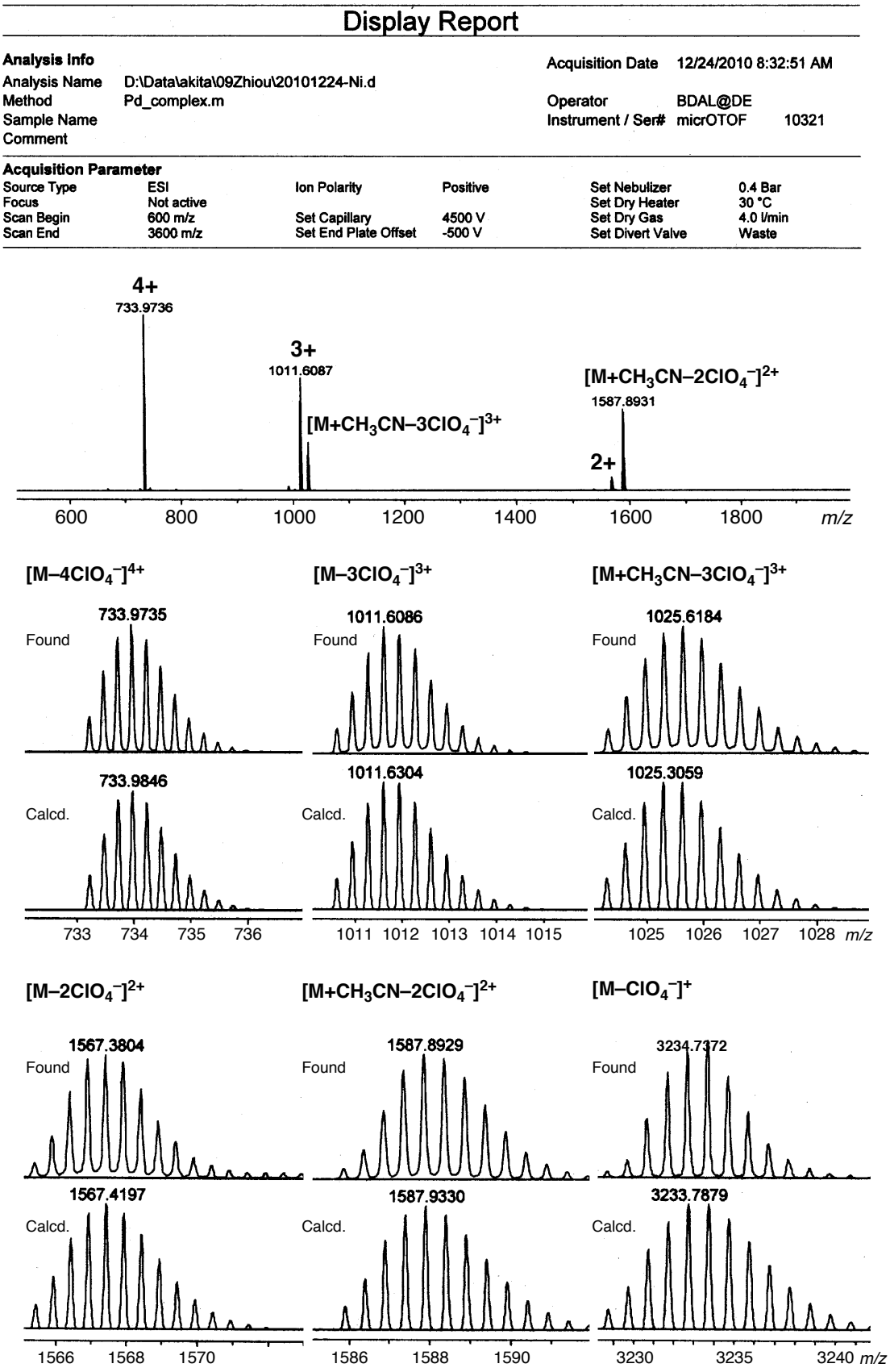
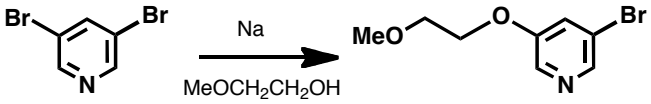


Fig. S24. ESI-TOF MS (MeCN) spectra of Ni(II)-capsule $\mathbf{1}^{Ni}$.

Synthesis of 3-bromo-5-(2-methoxyethoxy)pyridine ZL-112



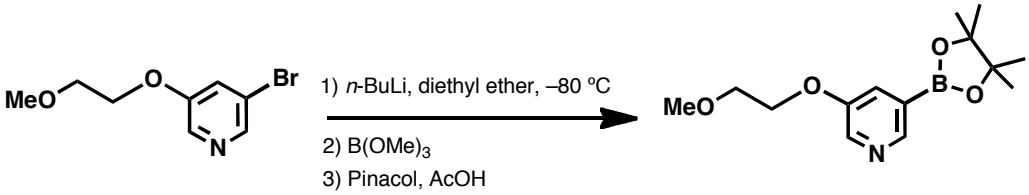
To a 100 mL round-bottom glass flask containing a magnetic stirring bar was added a 2-methoxyethanol solution (50 mL) of Sodium (0.558 g, 24.3 mmol) under a nitrogen atmosphere. After adding 3,5-dibromopyridine (2.89 g, 12.2 mmol) into the solution, the mixture was heated at 120 ºC for 48 h. The mixture was poured into H_2O (100 mL) and the crude product was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 7:1) and then 3-bromo-5-(2-methoxyethoxy)pyridine was obtained as a yellow solid (2.44 g, 10.5 mol; 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 3.45 (s, 3H), 3.76 (t, J = 4.8, 4.4, 2H), 4.16 (t, J = 4.8, 4.4, 2H), 7.40 (dd, J = 2.4, 1.6, 1H), 8.27 (d, J = 2.4, 1H), 8.29 (d, J = 1.6, 1H).

GC MS: m/z Calcd. for $C_8H_{10}BrNO_2$ 231, Found 231 $[M]^+$.

Ref.: Y. Sugihara *et al*., *J*. *Org*. *Chem*. **1996**, *61*, 6829–6834.

Synthesis of 5-(2-methoxyethoxy)-3-pyridineboronic acid pinacol ester ZL-133



A 200 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. Anhydrous diethyl ether (80 mL) and a 2.60 M solution of *n*-butyllithium in hexane (9.30 mL, 24.0 mmol) were added to this flask. A solution of 3-bromo-5-(2-methoxyethoxy)pyridine (5.08 g, 21.9 mmol) in anhydrous diethyl ether (ca. 20 mL) was added dropwise to the solution at –80 ºC. The solution was further stirred at –80 ºC for 1 h and then trimethyl borate

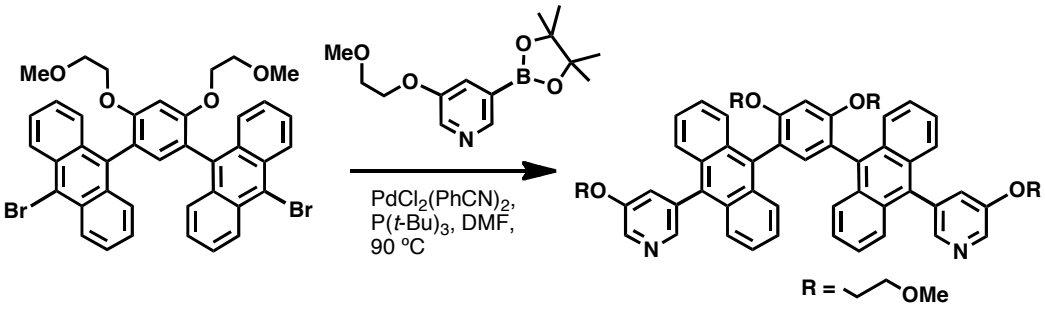
(2.80 mL, 24.0 mmol) was added to the solution at the same temperature. The solution was warmed to room temperature for ca. 12 h. Pinacol (2.84 g, 24.0 mmol) and AcOH (1.40 mL, 24.0 mmol) were added to the resultant mixture. The solution was stirred for 6 h at room temperature and then the mixture was concentrated under reduce pressure. The crude product was extracted with CH_2Cl_2 and combined organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was washed with diethyl ether to afford 5-(2-methoxyethoxy)-3-pyridineboronic acid pinacol ester as a white solid (2.37 g, 8.49 mol; 39% yield).

^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 1.35(s, 12H), 3.45 (s, 3H), 3.76 (t, J = 4.8, 4.4, 2H), 4.18 (t, J = 4.8, 4.4, 2H), 7.55 (dd, J = 2.8, 1.2, 1H), 8.41 (d, J = 2.8, 1H), 8.55 (d, J = 1.2, 1H).

ESI-TOF MS (MeCN): m/z Calcd. for $C_{14}H_{22}BNO_4$ 280.17, Found 280.16 $[M+H]^+$.

Ref.: S. Achim *et al*., WO200910488 (A1).

Synthesis of ligand 2' **ZL-71**



A 100 mL glass flask containing a magnetic stirring bar was filled with nitrogen. 1,5-Di(10-bromoanthracen-9-yl)-2,4-dimethoxyethoxybenzene (0.387 g, 0.530 mmol), 5-methoxyethoxy-3-pyridineboronic acid pinacol ester (0.440 g, 1.58 mmol), K_3PO_4 (0.674 g, 3.18 mmol), and degassed DMF (50 mL) were added to this flask. $PdCl_2(PhCN)_2$ (0.020 g, 0.053 mmol) and degassed DMF (5 mL) were added to a 50 mL glass flask containing a magnetic stirring bar. The flask was filled with nitrogen and then a hexane solution (0.192 g/mL) of tri-*tert*-buthylphosphine (0.11 mL, 0. 11 mmol) was added to this flask. After stirring the mixture for 30 min at room temperature, the mixture was added to the 100 mL glass flask, and then the resultant

solution was further stirred at 85 ºC for 24 h. The mixture was concentrated under reduce pressure. The crude product was extracted with $CHCl_3$ and combined organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 2:1) to afford ligand **2'** as a yellow solid (0.376 g, 0.427 mmol, 81% yield).

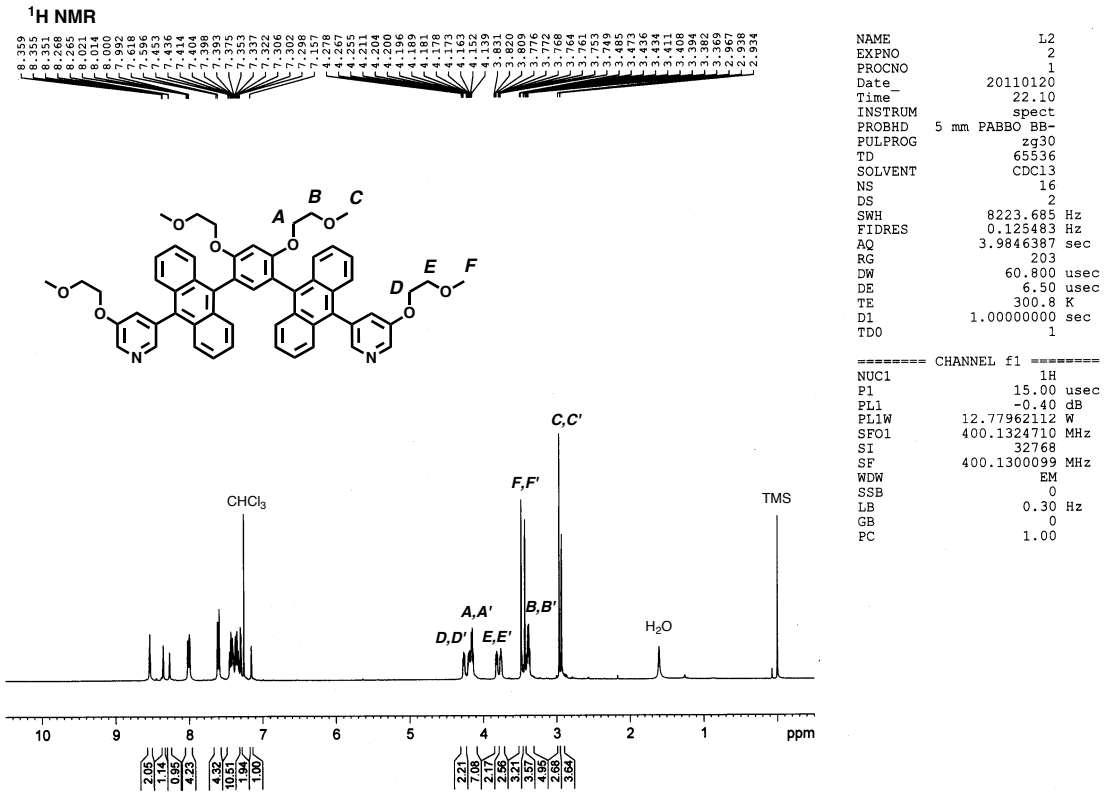
^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 2.93 (s, 3H), 2.97 (s, 3H), 3.38 (t, J = 5.2, 2H), 3.39 (t, J = 5.2, 2H), 3.44 (s, 3H), 3.49 (s, 3H), 3.77 (t, J = 1.6, 2H), 3.82 (t, J = 4.4, 2H), 4.15 (t, J = 5.2, 2H), 4.16 (t, J = 5.2, 2H), 4.20 (t, J = 1.6, 2H), 4.27 (t, J = 4.4, 2H), 7.16 (s, 1H), 7.30 (d, J = 1.6, 2H), 7.35 (dd, J = 8.8, 6.8, 4H), 7.40 (s, 1H), 7.44 (dd, J = 8.8, 6.8, 4H), 7.61 (d, J = 8.8, 4H), 8.01 (dd, J = 8.8, 3.2, 4H), 8.27 (s, 1H), 8.36 (s, 1H), 8.54 (d, J = 2.4, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 59.0, 59.3, 67.8, 67.9, 69.1, 69.2, 70.8, 100.2, 120.4, 124.0, 124.2, 125.1, 125.5, 126.3, 127.2, 130.2, 130.3, 132.1, 134.5, 135.5, 137.1, 137.4, 144.5, 154.9, 158.3.

FT-IR (KBr, cm^{-1}): 3060, 3039, 2925, 2879, 2817, 1582, 1504, 1422, 1381, 1314, 1260, 1194, 1126, 1057, 1026, 907, 863, 769, 718, 609.

MALDI-TOF MS (dithranol): m/z calcd. for $C_{56}H_{52}N_2O_8$ 880.37, found 880.58 $[M]^+$.

E.A.: Calcd. for $C_{56}H_{52}N_2O_8$•0.6$CHCl_3$: C, 71.36; H, 5.57; N, 2.94. Found: C, 71.57; H, 5.68; N, 2.93.

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PROCNO                1
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TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
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FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  203
DW                60.800 usec
DE                 6.50 usec
TE                300.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               -0.40 dB
PL1W        12.77962112 W
SFO1       400.1324710 MHz
SI               32768
SF         400.1300099 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
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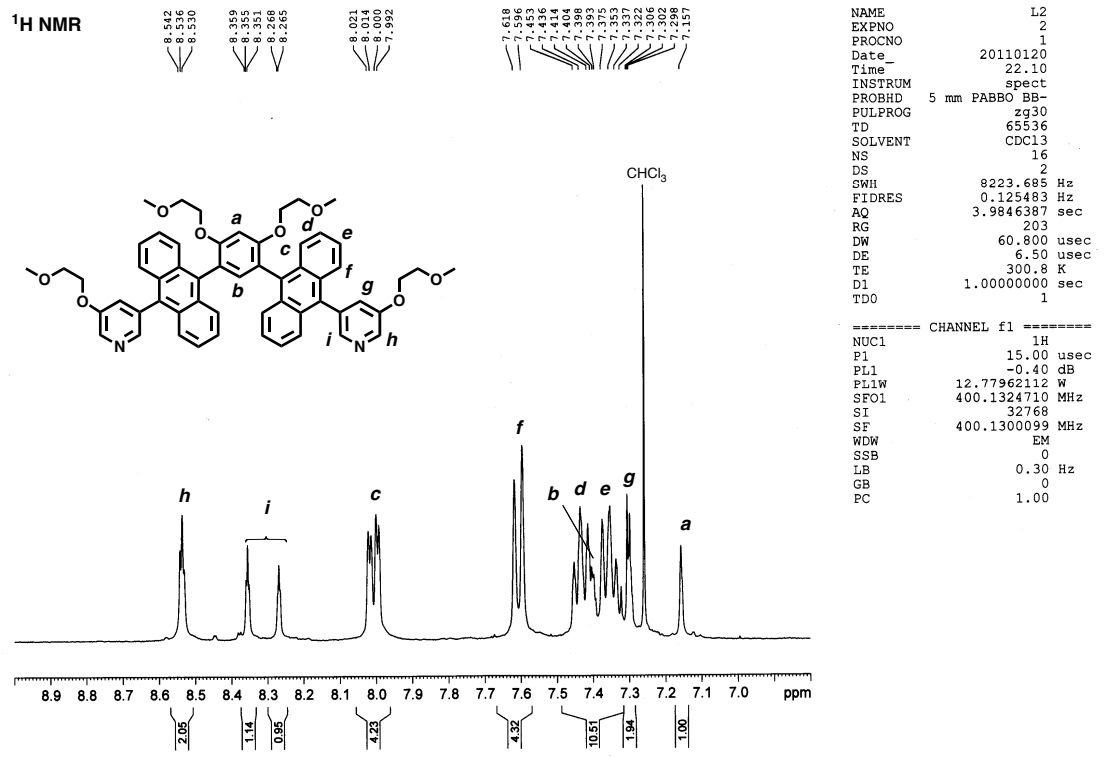
Fig. S25a. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

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EXPNO                 2
PROCNO                1
Date_          20110120
Time              22.10
INSTRUM           spect
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PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  203
DW                60.800 usec
DE                 6.50 usec
TE                300.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               -0.40 dB
PL1W        12.77962112 W
SFO1       400.1324710 MHz
SI               32768
SF         400.1300099 MHz
WDW                 EM
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PC                1.00
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Fig. S25b. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

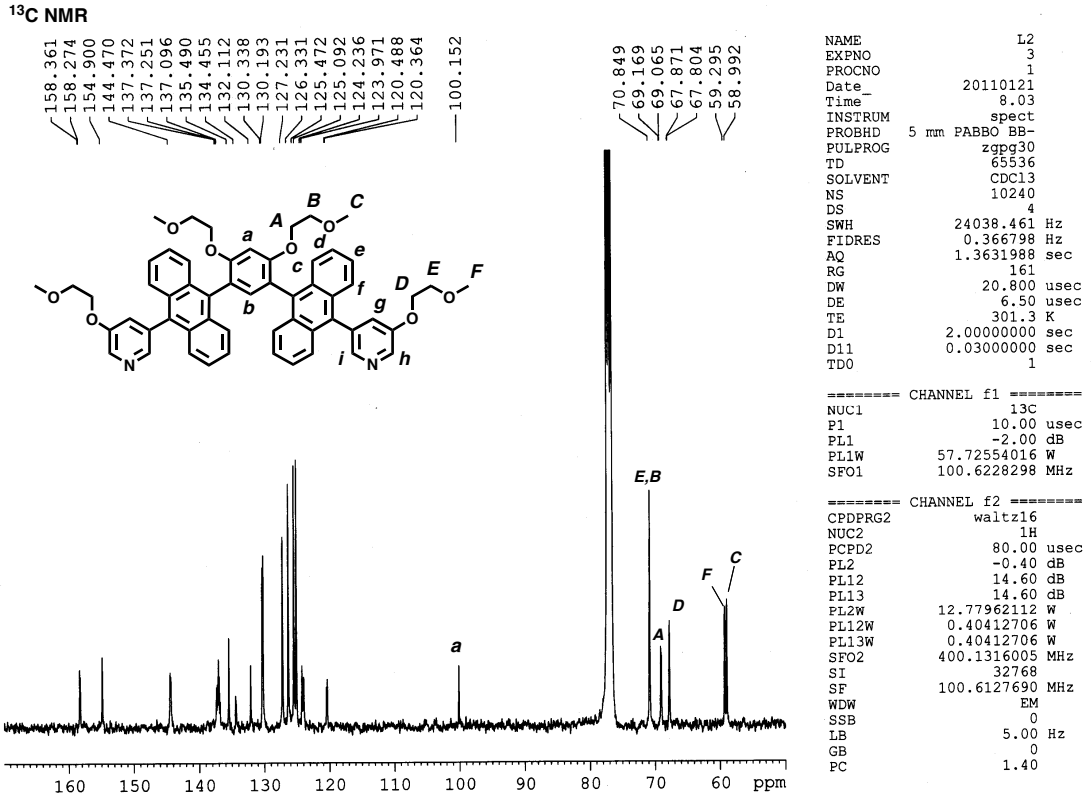


Fig. S26a. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

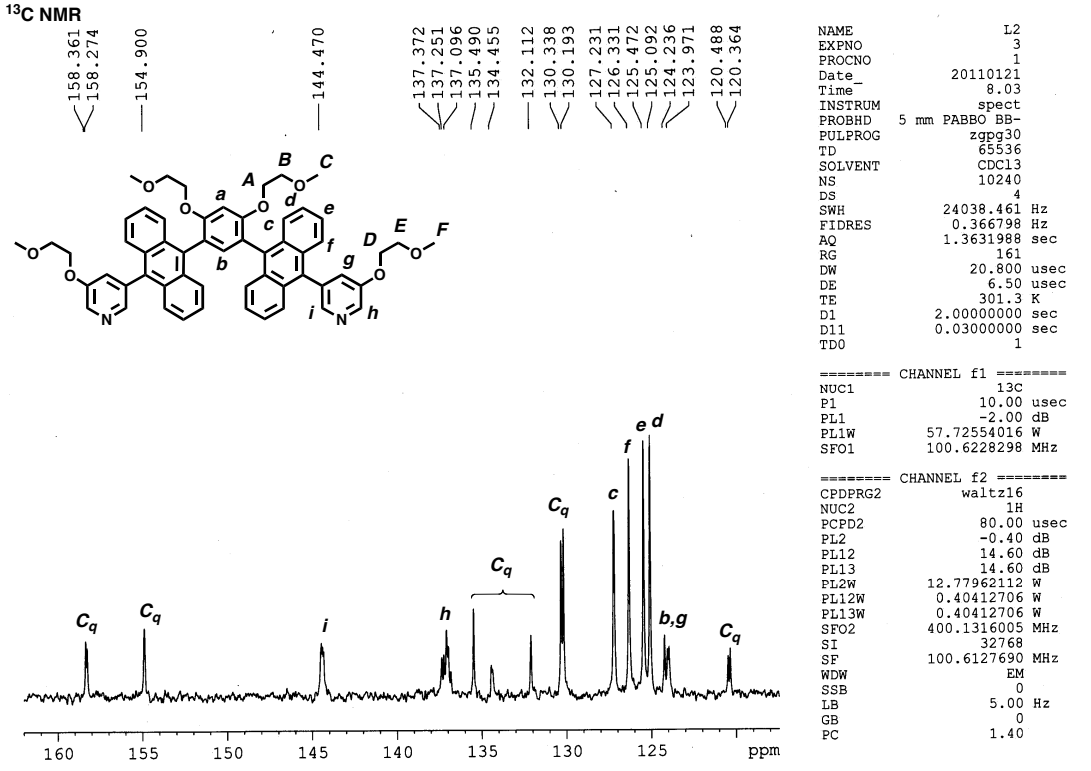


Fig. S26b. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

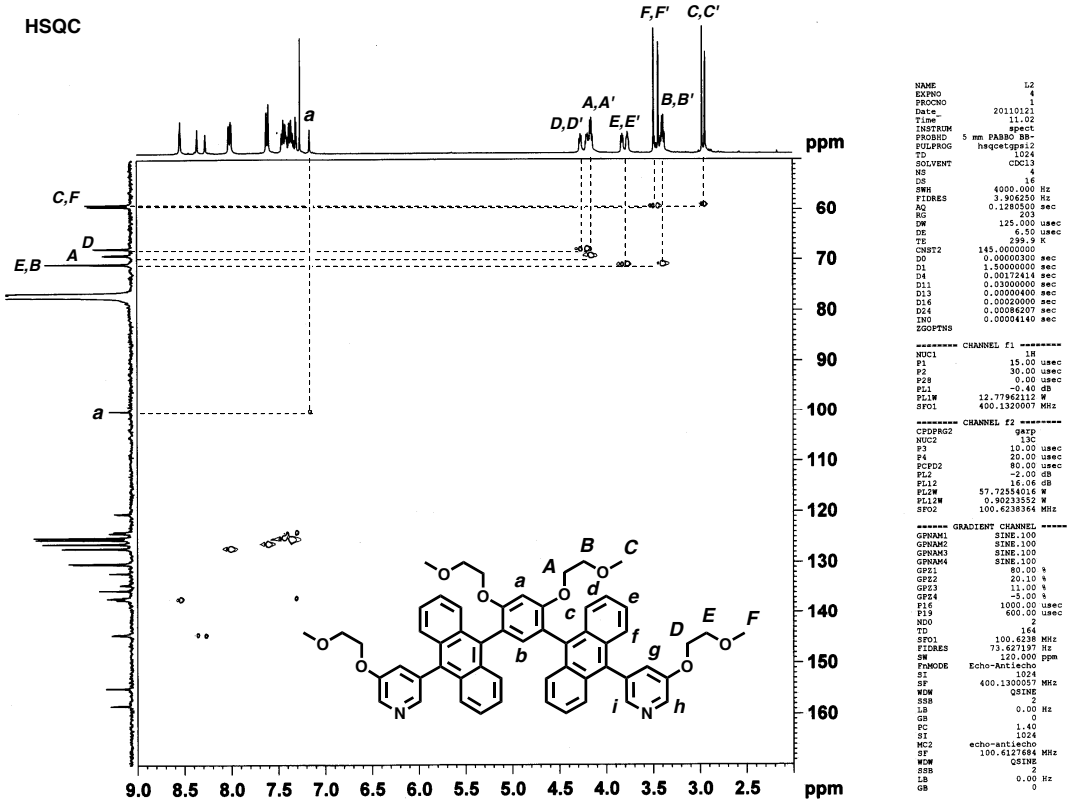


Fig. S27a. HSQC (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

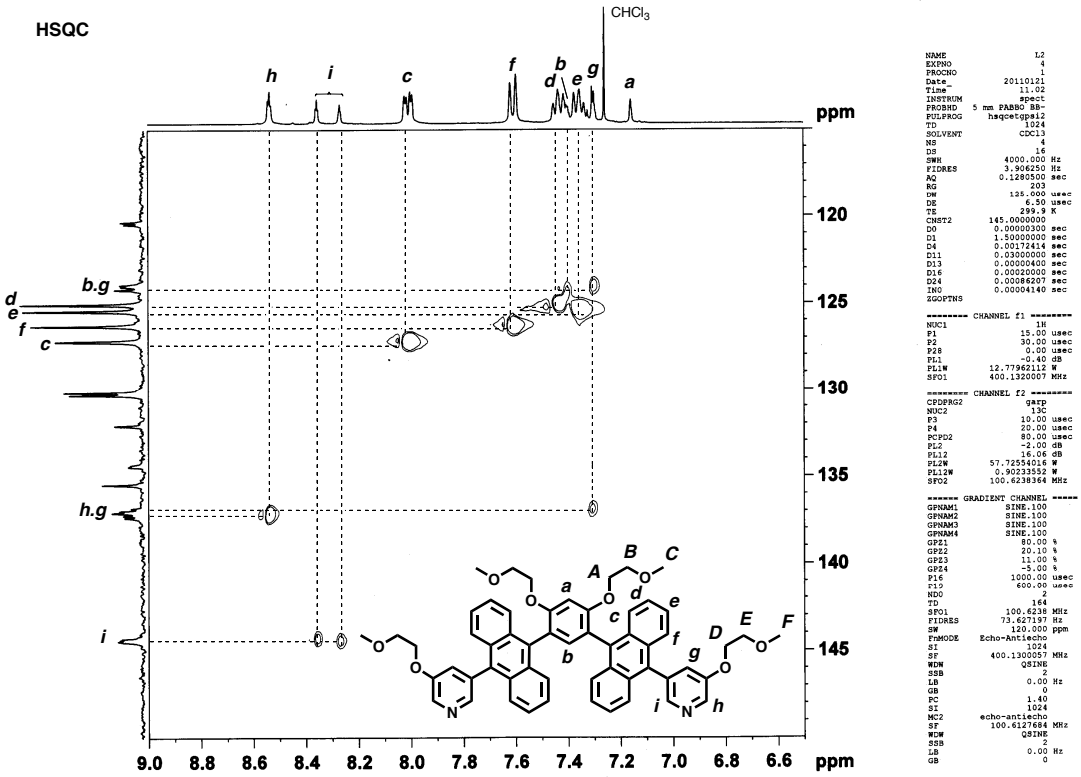
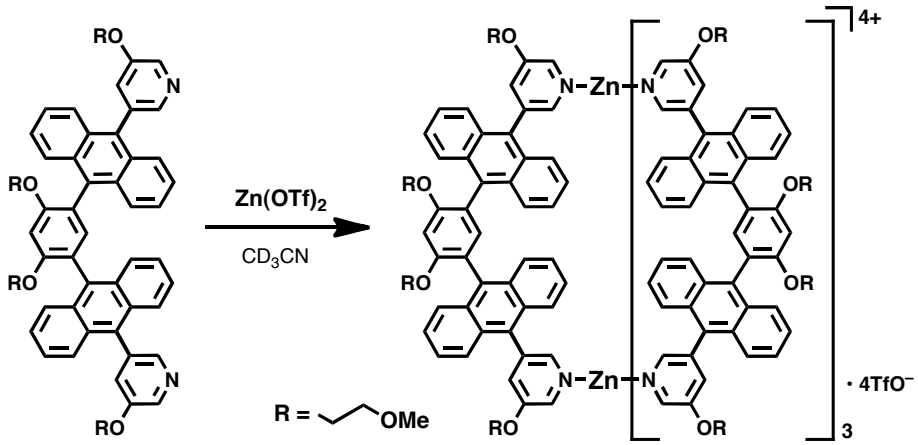


Fig. S27b. HSQC (400 MHz, $CDCl_3$, r.t.) spectrum of ligand **2'**.

Synthesis of Zn(II)-capsule 1'^{Zn} **ZL-74**



Ligand **2'** (11.0 mg, 12.5 μmol), $Zn(OTf)_2$ (3.3 mg, 9.1 μmol), and CD_3CN (0.50 mL) were added to a test tube containing a magnetic stirring bar. The mixture was stirred at 80 ºC for 1 h. ^{1}H NMR analysis of the resulted solution revealed the quantitative formation of Zn(II)-capsule **1'^{Zn}**.

^{1}H NMR (400 MHz, CD_3CN, r.t.): δ 3.05 (s, 24H), 3.42 (s, 24H), 3.42 (t, J = 5.2, 16H), 3.88 (t, J = 4.4, 16H), 4.23 (t, J = 5.2, 16H), 4.44 (t, J = 4.4, 8H), 4.63 (t, J = 4.4, 8H), 6.02 (s, 4H), 7.02 (br, 8H), 7.09 (d, J = 8.8, 16H), 7.26 (s, 4H), 7.32 (br, 16H), 7.42 (br, 8H), 7.62 (br, 8H), 7.70 (br, 8H), 7.95 (d, J = 8.4, 8H), 8.11 (s, 8H), 8.46 (d, J = 2.4, 8H).

ESI-TOF MS (MeCN): m/z calcd. for $Zn_2C_{228}H_{208}N_8O_{44}F_{12}S_4$, found 913.6 ([**1'^{Zn}**–4•TfO^-]$^{4+}$), 1267.7 ([**1'^{Zn}**–3•TfO^-]$^{3+}$), 1976.0 ([**1'^{Zn}**–2•TfO^-]$^{2+}$), 4101.9 ([**1'^{Zn}**–TfO^-]$^+$).

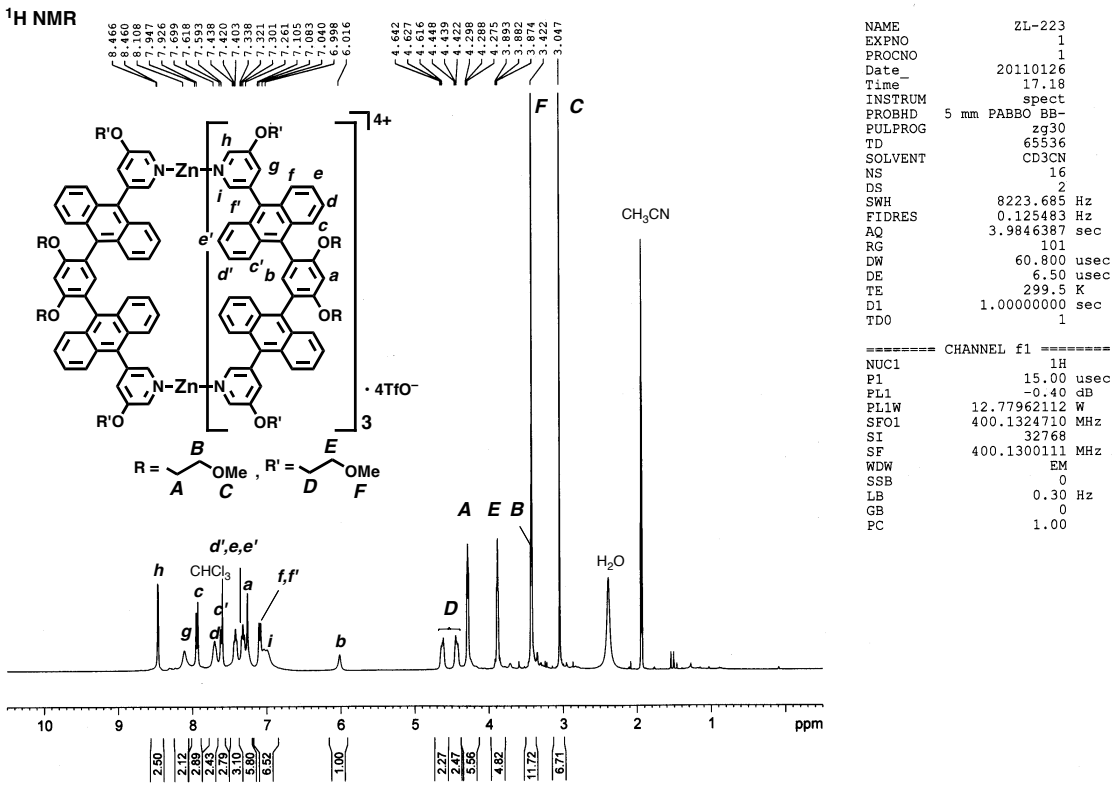


Fig. S28. ^{1}H NMR (400 MHz, CD_3CN, r.t.) spectrum of Zn(II)-capsule **1'^{Zn}**.

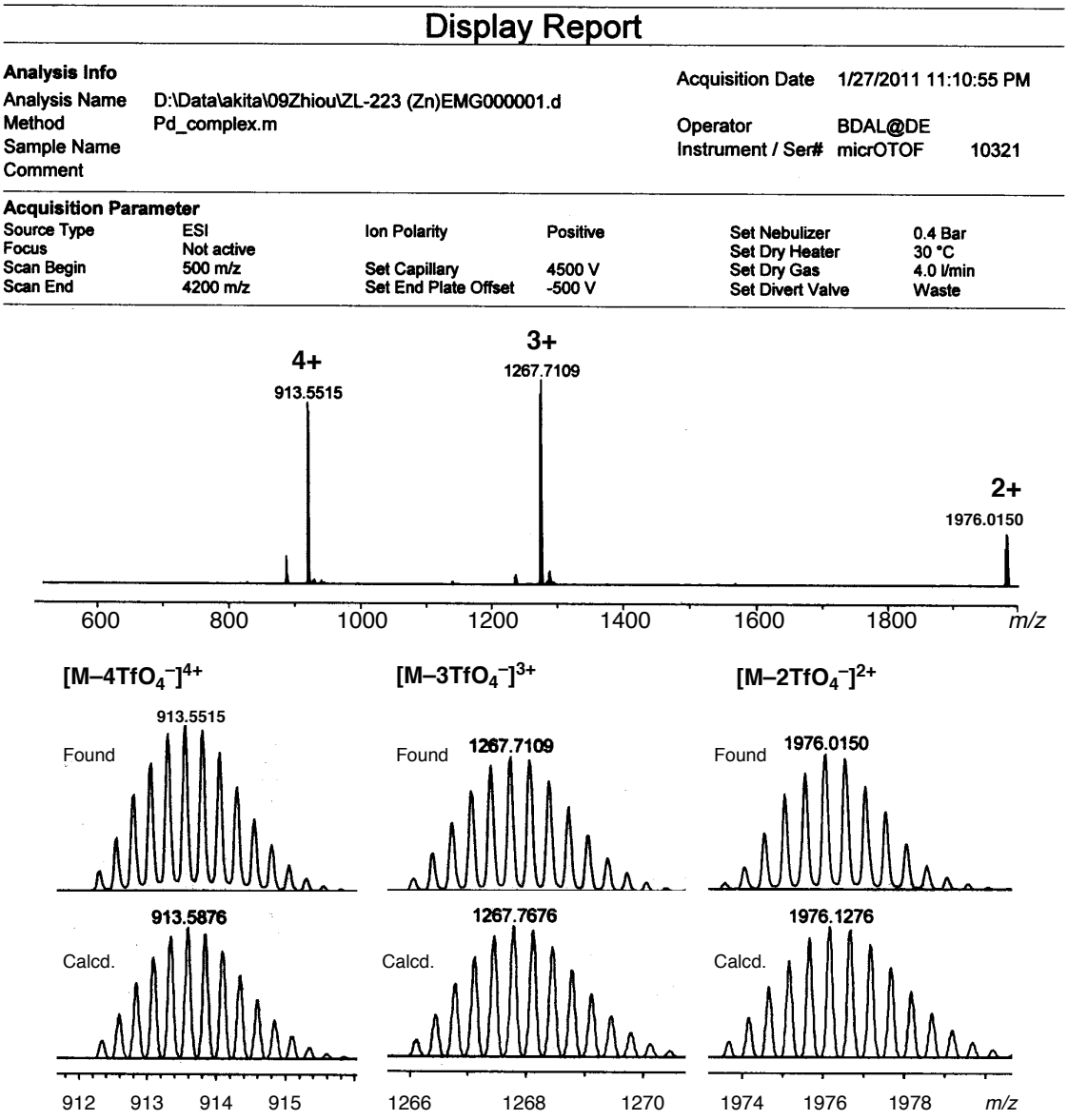
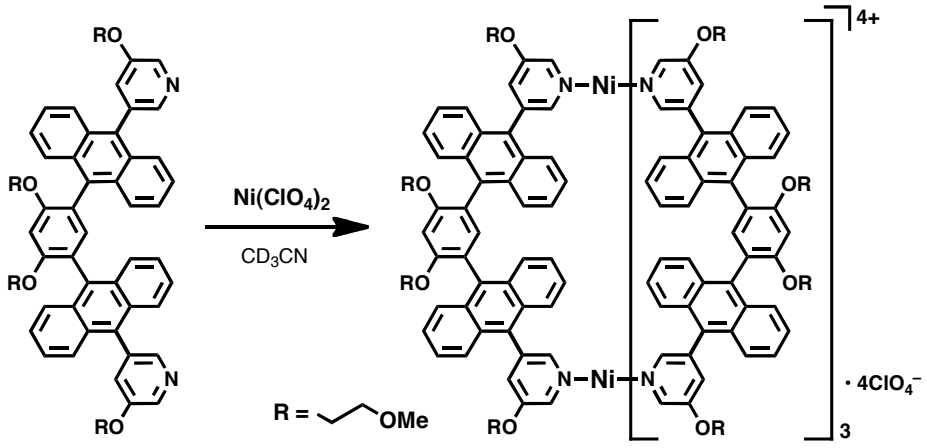


Fig. S29. ESI-TOF MS (MeCN) spectra of Zn(II)-capsule $\mathbf{1'}^{Zn}$.

Synthesis of Ni(II)-capsule 1'^{Ni} ZL-75



Ligand **2'** (10.6 mg, 12.0 μmol), $Ni(ClO_4)_2 \cdot 6H_2O$(2.8 mg, 7.7 μmol), and CD_3CN (0.50 mL) were added to a test tube containing a magnetic stirring bar. The mixture was stirred at 80 ºC for 1 h. ^{1}H NMR and ESI-TOF MS analyses of the resulted solution revealed the quantitative formation of Ni(II)-capsule **1'^{Ni}**. Pale yellow single crystals of **1'^{Ni}** were obtained by slow vapor diffusion of MeOH into a MeCN solution of capsule **1'^{Ni}**.

^{1}H NMR (400 MHz, CD_3CN, rt): δ 3.10, 3.46, 4.34, 6.79, 7.39, 7.49, 7.68, 7.90, 8.01.

ESI-TOF MS (MeCN): *m/z* calcd. for $Ni_2C_{224}H_{208}N_8O_{48}Cl_4$, found 910.0 ([**1'^{Ni}**–4•ClO_4^-]$^{4+}$), 1246.7 ([**1'^{Ni}**–3•ClO_4^-]$^{3+}$), 1260.4 ([**1'^{Ni}**+MeCN–3•ClO_4^-]$^{3+}$), 1920.1 ([**1'^{Ni}**–2•ClO_4^-]$^{2+}$), 1940.5 ([**1'^{Ni}**+MeCN–2•ClO_4^-]$^{2+}$), 3939.1 ([**1'^{Ni}**–ClO_4^-]$^+$), 3980.0 ([**1'^{Ni}**+MeCN– ClO_4^-]$^+$).

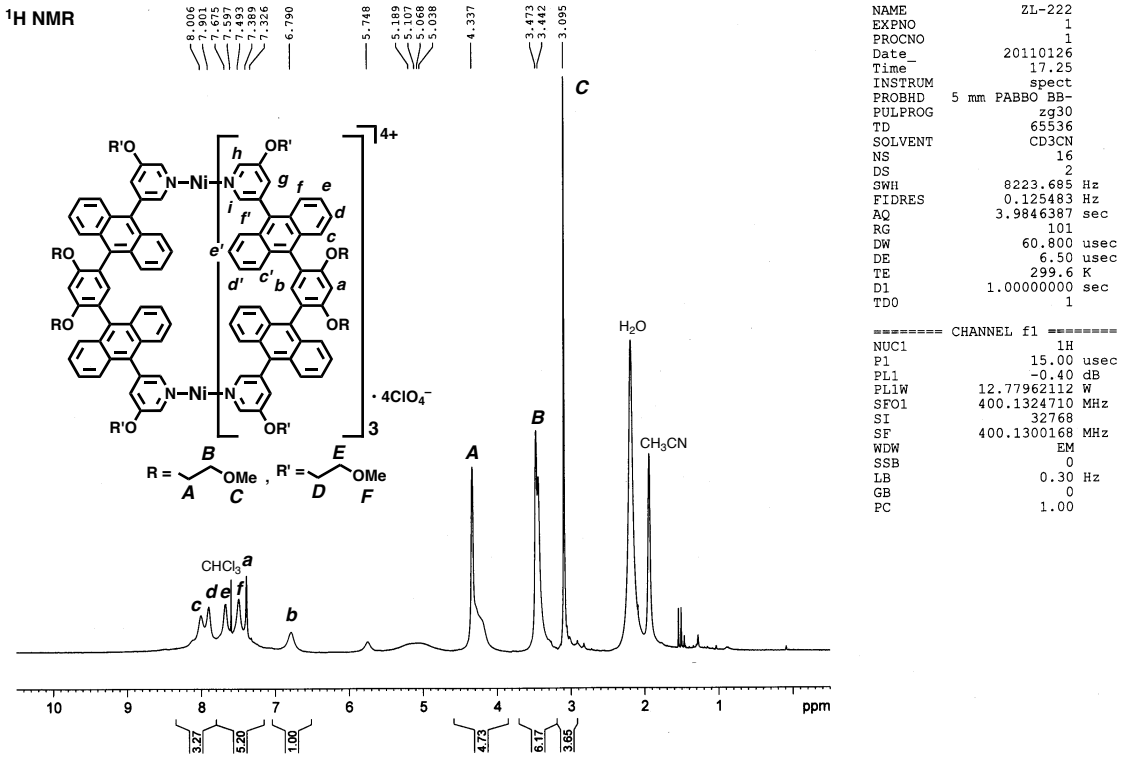


Fig. S30. ^{1}H NMR (400 MHz, CD_3CN, r.t.) spectrum of Ni(II)-capsule **1'**^{Ni}.

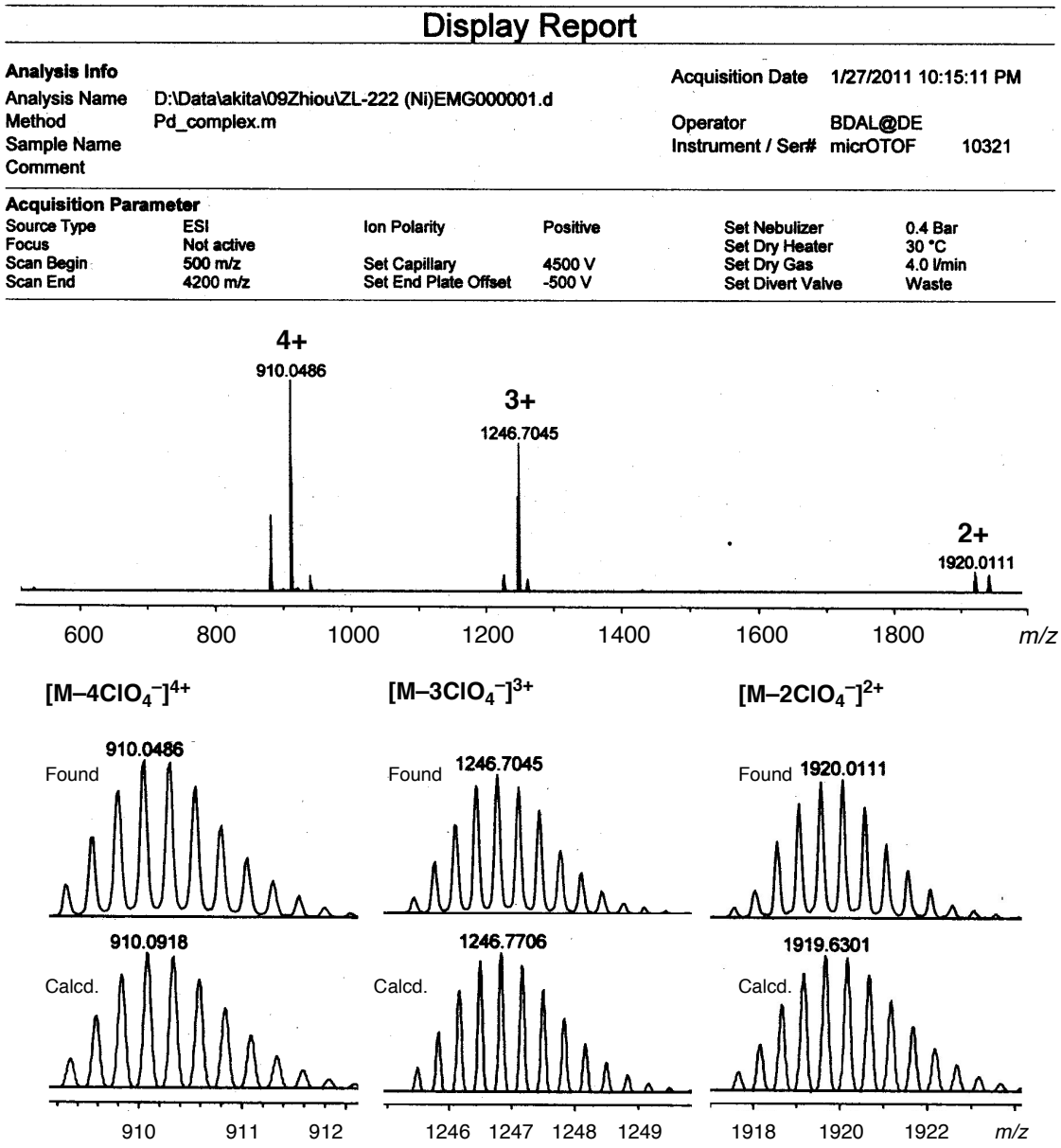


Fig. S31. ESI-TOF MS (MeCN) spectra of Ni(II)-capsule **1'**^{Ni}.

Table S1. Crystal data and structure refinement for Ni(II)-capsule **1'^{Ni}**.

Identification code	sc0663b
Empirical formula	$C_{234}H_{249}Cl_4N_9Ni_2O_{59}$
Formula weight	4390.78
Temperature	93(2) K
Wavelength	1.54187 Å
Crystal system	Tetragonal
Space group	*P*4nc
Unit cell dimensions	*a* = 19.4133(4) Å
	c = 29.968(2) Å
Volume	11294.4(9) Å^3
Z	2
Density (calculated)	1.291 Mg/m^3
Absorption coefficient	1.333 mm^{-1}
F(000)	4624
Crystal size	0.15 x 0.11 x 0.10 mm^3
Theta range for data collection	2.95 to 68.20°.
Index ranges	-22<=h<=23, -23<=k<=23, -36<=l<=36
Reflections collected	124070
Independent reflections	10352 [R(int) = 0.0448]
Completeness to theta = 68.20°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10352 / 43 / 745
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R_1 = 0.0573
R indices (all data)	R = 0.0662, wR_2 = 0.1606
Largest diff. peak and hole	0.592 and –0.603 e.Å^{-3}
Absolute structure	Flack (1983)
Flack parameter	–0.01(3)

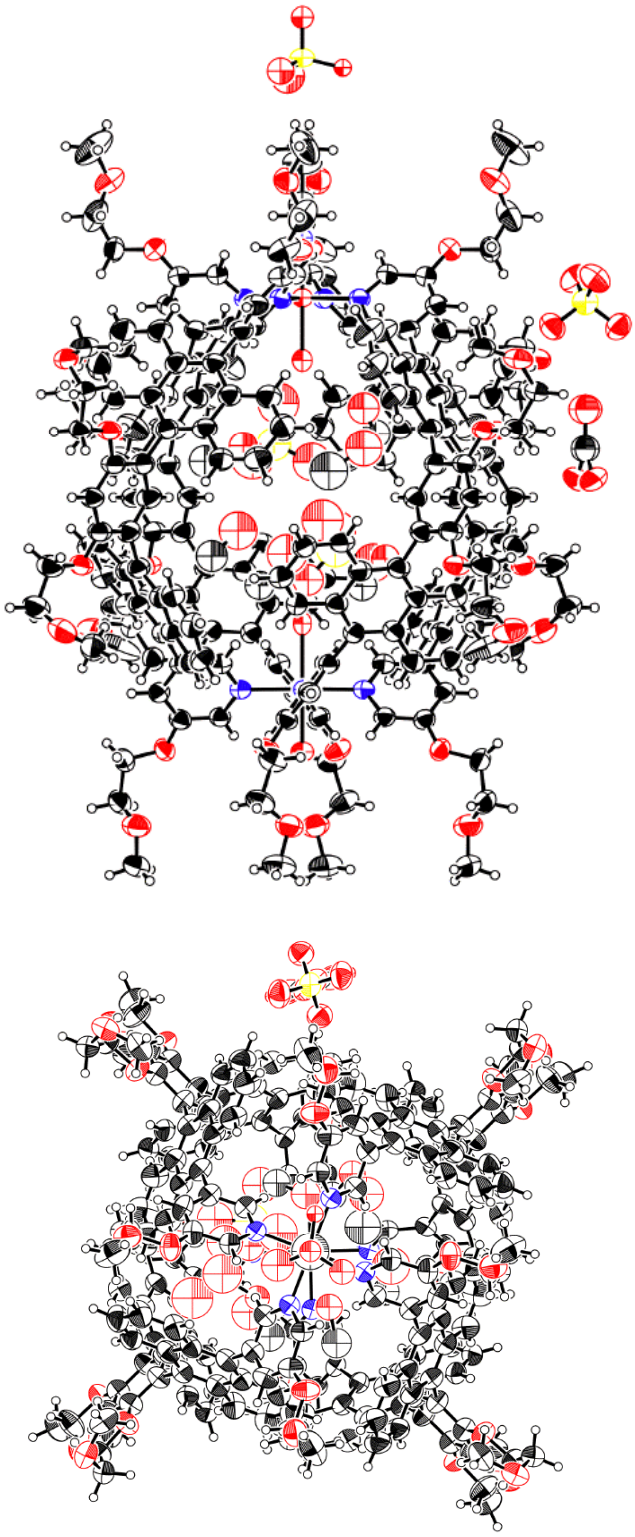


Fig. S32. ORTEP drawing of capsule $\mathbf{1'^{Ni}}$ (side and top views).

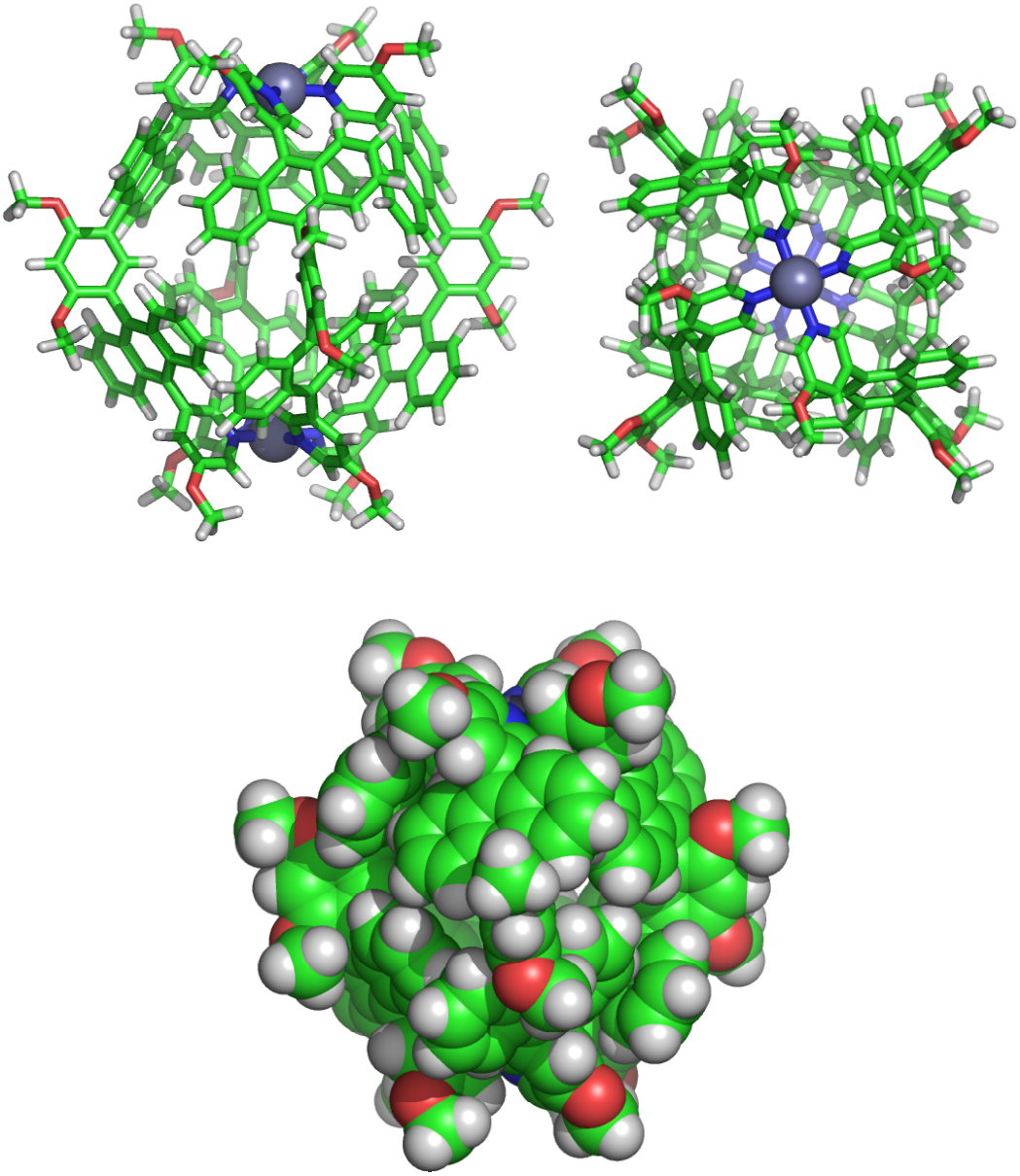


Fig. S33. Optimized structure of Zn(II)-capsule $\mathbf{1}^{Zn}$ (side and top views). The calculation was carried out with the use of the Material Studio molecular modeling package (ver. 4.4, Accelerys, San Diego, CA).