

- Electronic Supplementary Information -

**$\text{Pd}^{2+} \cdots \text{O}_3\text{SR}^-$ interaction encourages anion
encapsulation of a quadruply-stranded Pd complex to
achieve chirality or high solubility**

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Experimental Section

Materials and Instrumentations

All chemicals and solvents were purchased from Kanto Chemical Co., Ltd., Wako Pure Chemical Co., Ltd., and Tokyo Kasei Kogyo Co., Ltd., and were used as received without further purification. Melting points were measured on Yanaco Micro Melting Point Apparatus 3120. ^1H NMR (500MHz), ^{13}C NMR (125 MHz), and ^{19}F NMR (470 MHz) spectra were recorded on a JEOL α -500 spectrometer. Unless stated otherwise, the chemical shift values reported here are with respect to DMSO ($\delta = 2.48$ ppm (^1H), 39.5 ppm (^{13}C)) or monofluorobenzene ($\delta = -113.15$ ppm, (^{19}F)). ESI MS spectra were acquired on MarinerTM ESI-TOF Biospectrometry Workstation. Solution-state CD spectra were measured on a JASCO J-720 spectrometer.

Solid-state CD Measurements

Solid-state CD spectra were recorded using Universal Chiroptical Spectrophotometer (UCS-1).¹ A crystal of compounds $\mathbf{1}(d\text{-camS})_4$ (100 μg) or $\mathbf{1}(l\text{-camS})_4$ (108 μg) and dry KBr matrix were finely ground, and the powder was pressed at 4.8 MP/ cm^2 for 10 min to prepare a clear disk of 1 cm diameter. The KBr disk, held by a specially devised disk holder, was placed normal to a light beam. True CD spectra in the solid state were obtained by a specially devised set of procedures based on the Stokes-Mueller matrix method.¹

X-ray Crystallography

Single crystals of $\mathbf{1}(\text{ONs})_4$ were obtained from a DMF solution of $\mathbf{1}(\text{ONs})_4$ at ca. 70 °C. Single crystals of $\mathbf{1}(d\text{-camS})_4$ were obtained from a DMSO solution of $\mathbf{1}(d\text{-camS})_4$ at rt. X-ray crystallographic data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 103 K. Crystallographic parameters are listed in Table S1. The crystal structures were solved by direct method using the *SHELXS-97* program and refined by successive differential Fourier syntheses and full-matrix least-squares procedures using the *SHELXL-97* program.² Anisotropic thermal factors were applied to all non-hydrogen atoms. In the case of $\mathbf{1}(\text{ONs})_4$, the diffuse electron density due to the disordered and unidentified moieties was treated with the SQUEEZE routine within the PLATON software package,³ and the final d_{calc} , and Formula weight reflect known contents only. Computer graphics of the X-ray crystal structures were portrayed with Mercury 2.3 program.⁴

NMR Titrations.

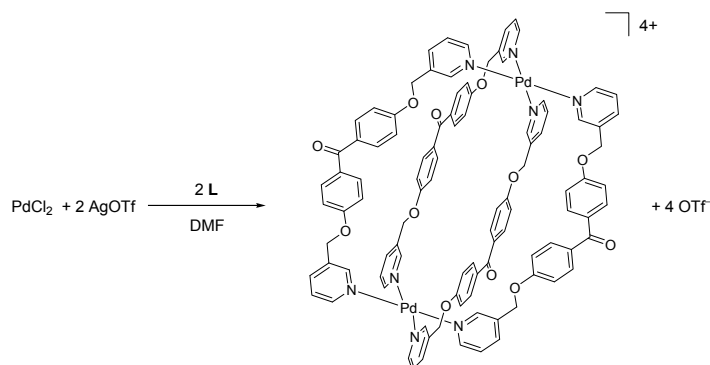
All titrations were performed with the starting concentration of $\mathbf{1}(\text{OTf})_4$ at 1.0 mM (DMSO- d_6) and the addition of appropriate aliquots of titrant (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 equiv) to the NMR sample with a 40-200 μl Finn timer[®] (ThermoLabsystems) as appropriate. α -pyridyl protons H_a and H_b of $\mathbf{1}$ were followed during the course of the titration, and the data were fitted and analyzed to give association constants ($\log_{10}(K_{a1})$ and $\log_{10}(K_a)$) using WinEQNMR2 program.⁵

Table S1. Crystallographic parameters

Crystal	1 (ONs) ₄	1 (<i>d</i> -camS) ₄
Formula	[Pd ₂ (C ₂₅ H ₂₀ N ₂ O ₃) ₄] (ONs) ₄ ·(DMF) ₄	[Pd ₂ (C ₂₅ H ₂₀ N ₂ O ₃) ₄] (<i>d</i> -camS) ₄ ·(DMSO) ₆
Formula weight	2919.81	3192.4
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 1 (#1)
<i>a</i> / Å	14.075(6)	14.6994(11)
<i>b</i> / Å	16.502(7)	16.5936(12)
<i>c</i> / Å	19.601(8)	17.1117(12)
α /°	92.546(7)	83.298(1)
β /°	108.332(7)	85.992(1)
γ /°	109.447(7)	63.960(1)
<i>V</i> / Å ³	4018(3)	3723.7(5)
<i>D</i> _{calc.} /g cm ⁻³	1.21	1.42
<i>Z</i>	1	1
$2\theta_{\max}$ /°	52.8	55.8
μ (MoK α)/mm ⁻¹	0.344	0.461
Temperature /K	103	103
Crystal form	block	block
Crystal size /mm ³	0.2 × 0.1 × 0.05	0.2 × 0.2 × 0.2
Crystal colour	colourless	colourless
<i>h</i> range	-17 → 17	-19 → 8
<i>k</i> range	-20 → 20	-21 → 19
<i>l</i> range	-24 → 23	-22 → 21
# of total reflections	32666	23115
# of unique reflections	16175	19148
# of observed reflections	10148	17459
<i>R</i> _{int}	0.0722	0.0168
Criterion for observed reflections	<i>I</i> > 2σ(<i>F</i> _o)	<i>I</i> > 2σ(<i>F</i> _o)
<i>R</i> 1 (observed)	0.0737	0.0361
<i>wR</i> 2 (observed)	0.1735	0.0953
<i>G. O. F.</i>	0.983	1.057
# of parameters used	892	1875
$\Delta\rho_{\max}$ (eÅ ⁻³)	+1.152	+1.515
$\Delta\rho_{\min}$ (eÅ ⁻³)	-0.766	-0.637
Flack's parameter	-	-0.018(13)
CCDC number	742382	827758

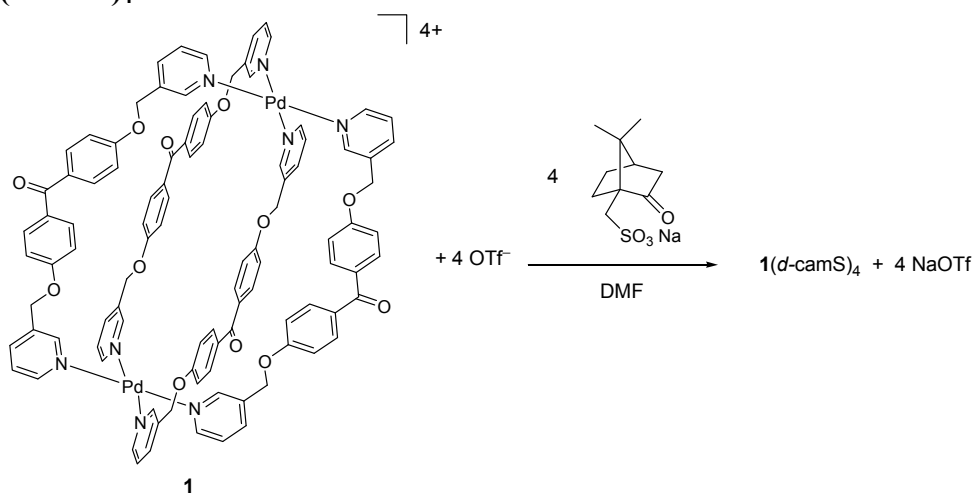
Experimental Detail

Synthesis of **1**(OTf)₄



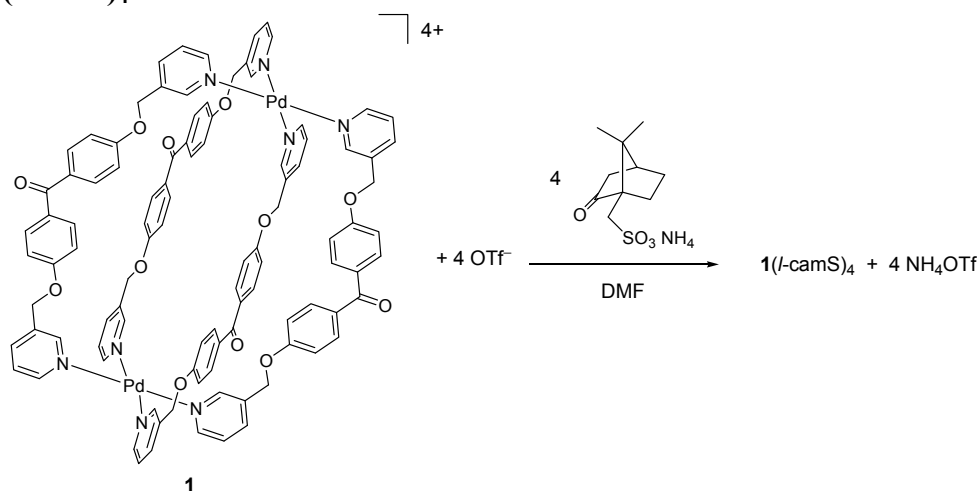
PdCl_2 (44.4 mg, 2.50×10^{-1} mmol) was dissolved in DMF (4 mL) and stirred for 1 h at room temperature with AgOTf (129 mg, 5.00×10^{-1} mmol). After removal of AgCl by filtration addition of compound **L**⁶ (208 mg, 5.25×10^{-1} mmol) to the filtrate, the mixture was stirred for 1 h at 70 °C. Et₂O (20 mL) was added to the resultant pale yellow solution. White precipitate was isolated by filtration and washed with CH₂Cl₂ and dried in vacuo to give **1**(OTf)₄ in 91 % yield (272 mg, 1.14×10^{-1} mmol). ¹H NMR (500 MHz, DMSO-*d*₆, rt): δ 9.40 (s, 8H), 9.33 (d, $J = 5.8$ Hz, 8H), 8.16 (d, $J = 7.6$ Hz, 8H), 7.82 (dd, $J = 5.8, 7.6$ Hz, 8H), 7.54 (d, $J = 8.5$ Hz, 16H), 7.10 (d, $J = 8.5$ Hz, 16H), 5.29 (s, 16H); ¹³C NMR (125 MHz, DMSO-*d*₆, rt): δ 193.01, 160.92, 150.61, 149.09, 139.79, 136.22, 131.65, 130.74, 127.12, 114.35, 66.57; ¹⁹F NMR (470 MHz, DMSO-*d*₆, rt): δ -77.8 (s); MS (ESI, m/z) calcd for C₁₀₀H₈₀N₈O₁₂Pd₂(OTf)₄: 2394.87; Found: 1047.8 [**1**+(OTf)₂]²⁺, 649.5 [**1**+(OTf)]³⁺, 449.4 **1**. (**1** = C₁₀₀H₈₀N₈O₁₂Pd₂ = [Pd₂L₄]⁴⁺).

Synthesis of **1**(*d*-camS)₄



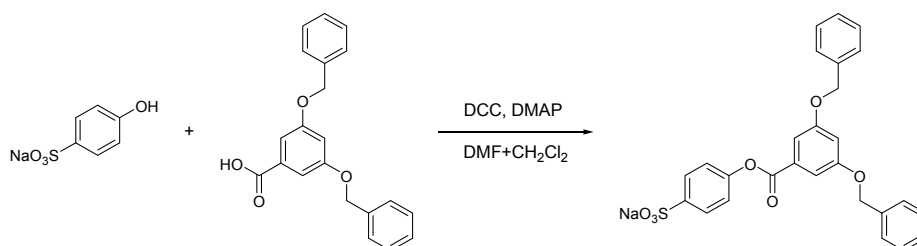
Sodium *d*-camphorsulfonate (13.7 mg, 5.40×10^{-2} mmol) was added to **1**(OTf)₄ (32.3 mg, 1.35×10^{-2} mmol) at room temperature in DMF (2 mL). Upon addition, the mixture was stirred at 60 °C for 1.5 h, after which white precipitate was isolated by filtration and washed several times with small quantities of distilled water and dried in vacuo to give **1**(*d*-camS)₄ in 75 % yield (27.4 mg, 1.01×10^{-2} mmol).

Synthesis of **1**(*l*-camS)₄



Ammonium *l*-camphorsulfonate (13.1 mg, 5.27×10^{-2} mmol) was added to **1**(OTf)₄ (31.5 mg, 1.31×10^{-2} mmol) at room temperature in DMF (2 mL). Upon addition, the mixture was stirred at 60 °C for 1.5 h, after which white precipitate was isolated by filtration and washed several times with small quantities of distilled water and dried in vacuo to give **1**(*l*-camS)₄ in 68 % yield (24.1 mg, 8.9×10^{-3} mmol).

Synthesis of Na(DenS)



Sodium *p*-hydroxybenzenesulfonate (0.18 g, 7.7×10^{-1} mmol) in dry DMF (5 mL) was added slowly to 3,5-bis(benzyloxy)benzoic acid (0.26 g, 7.8×10^{-1} mmol)⁷ and *N,N'*-dicyclohexylcarbodiimide (0.16 g, 7.7×10^{-1} mmol) at 0 °C in dry CH₂Cl₂ (10 mL). The solution was stirred at rt for 22 h and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography using silica gel (CH₂Cl₂:MeOH = 9:1, v/v) to give a white powder. Repeated crystallization from methanol-CH₂Cl₂ mixed solvent solutions gave colourless crystals of Na(DenS)(H₂O)_{1.5} in 30 % yield (0.12 g, 2.26×10^{-1} mmol). ¹H NMR (500 MHz, DMSO-*d*₆, rt): δ 7.66 (d, $J = 5.8$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 4H), 7.39 (t, $J = 7.3$ Hz, 4H), 7.33 (m, 4H), 7.20 (d, $J = 8.5$ Hz, 2H), 7.04 (t, $J = 2.1$ Hz, 1H), 5.19 (s, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 164.01, 159.44, 150.37, 145.78, 136.45, 130.65, 128.05, 127.84, 127.63, 127.27, 126.84, 121.05, 108.40, 69.64; Elemental Analysis calcd. for C₂₇H₂₁O₇S Na(H₂O)_{1.5}: C, 60.10; H, 4.48; Found: C, 60.17; H, 4.66; Melting Point: > 300 °C (decomp.).

Supporting Figures

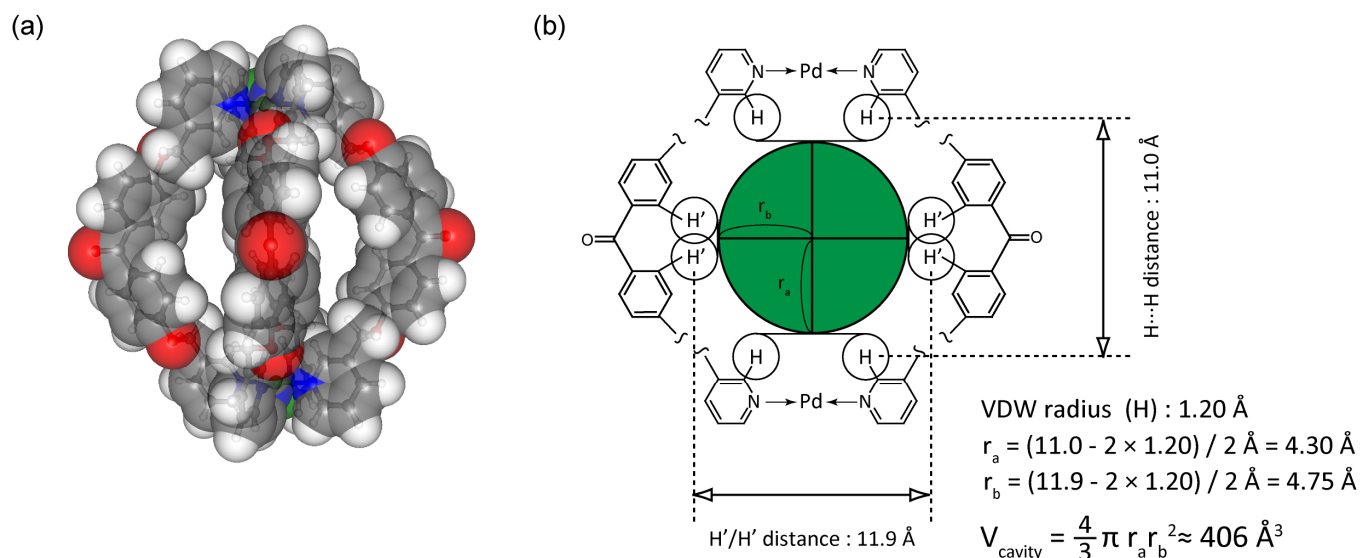


Fig. S1 (a) An energy minimized structure (universal force field method) of **1**.^{6,8} Colour scheme: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen), green (palladium). (b) Cavity volume of **1**.

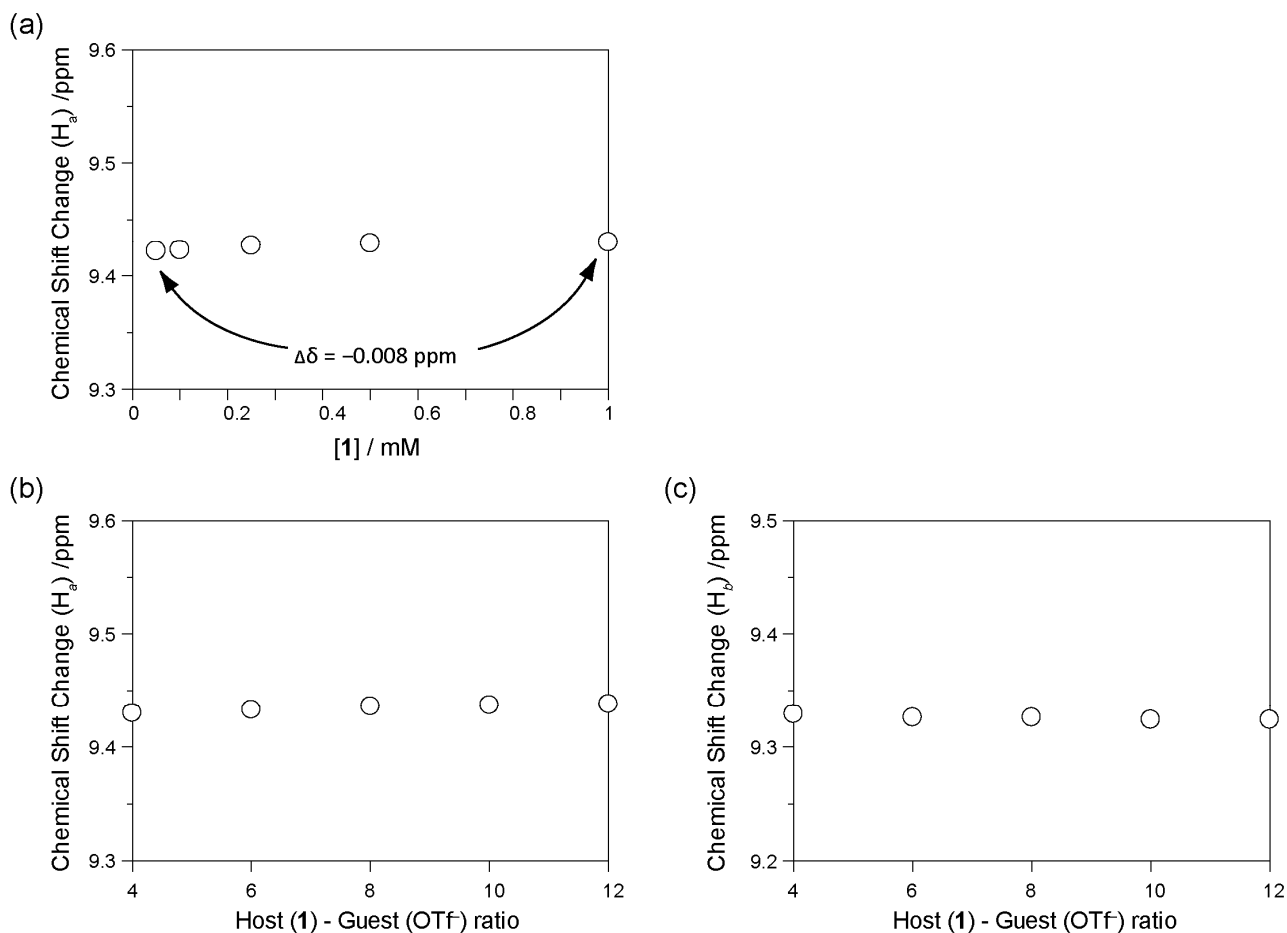


Fig. S2 (a) Chemical shift change of H_a upon dilution ($[1]_{\text{start}} = 1.0 \text{ mM}$, $[\text{OTf}^-]_{\text{start}} = 4.0 \text{ mM}$). (b) and (c) NMR titrations (OTf^-) monitoring H_a and H_b , respectively. $[1] = 1.0 \text{ mM}$.

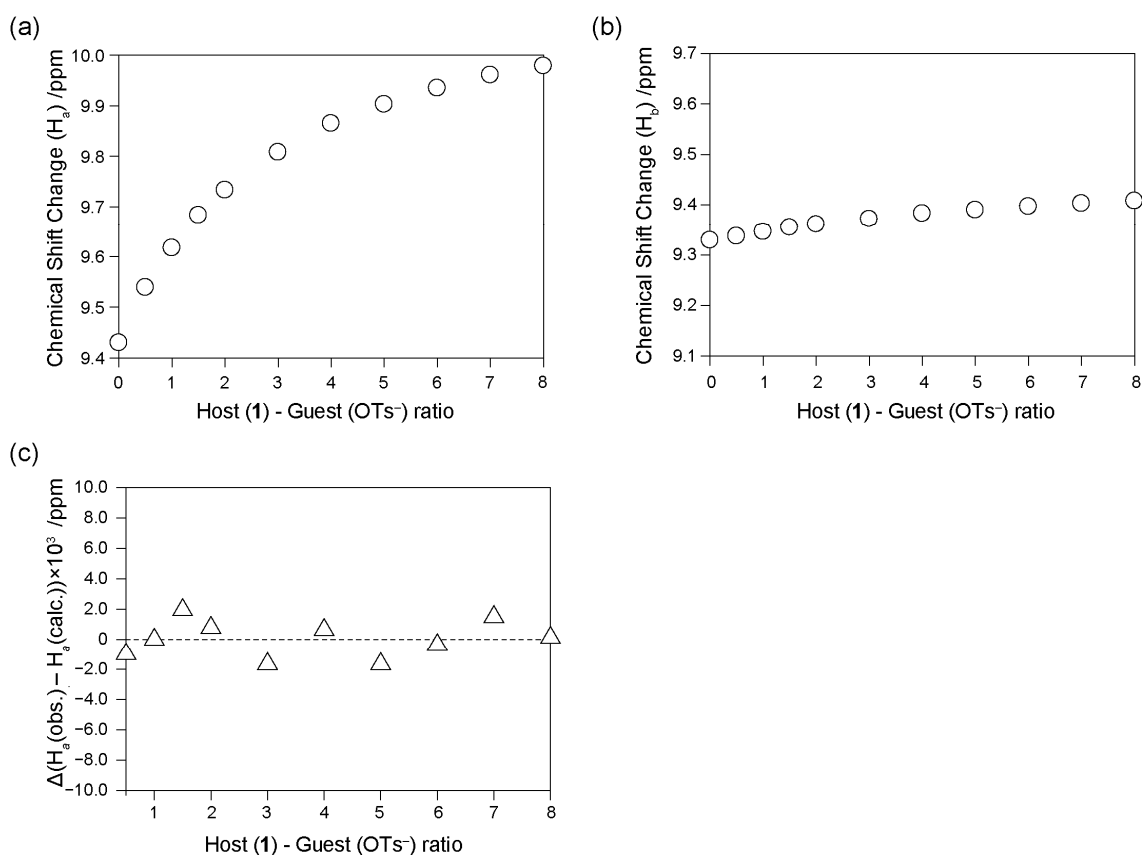


Fig. S3 ¹H NMR titration (OTs⁻) monitoring (a) H_a and (b) H_b . [1] = 1.0 mM. (c) $H_a(\text{obs.}) - H_a(\text{calc.})$. $H_a(\text{calc.})$ were calculated using WinEQNMR2 program⁵ (see also p. S20).

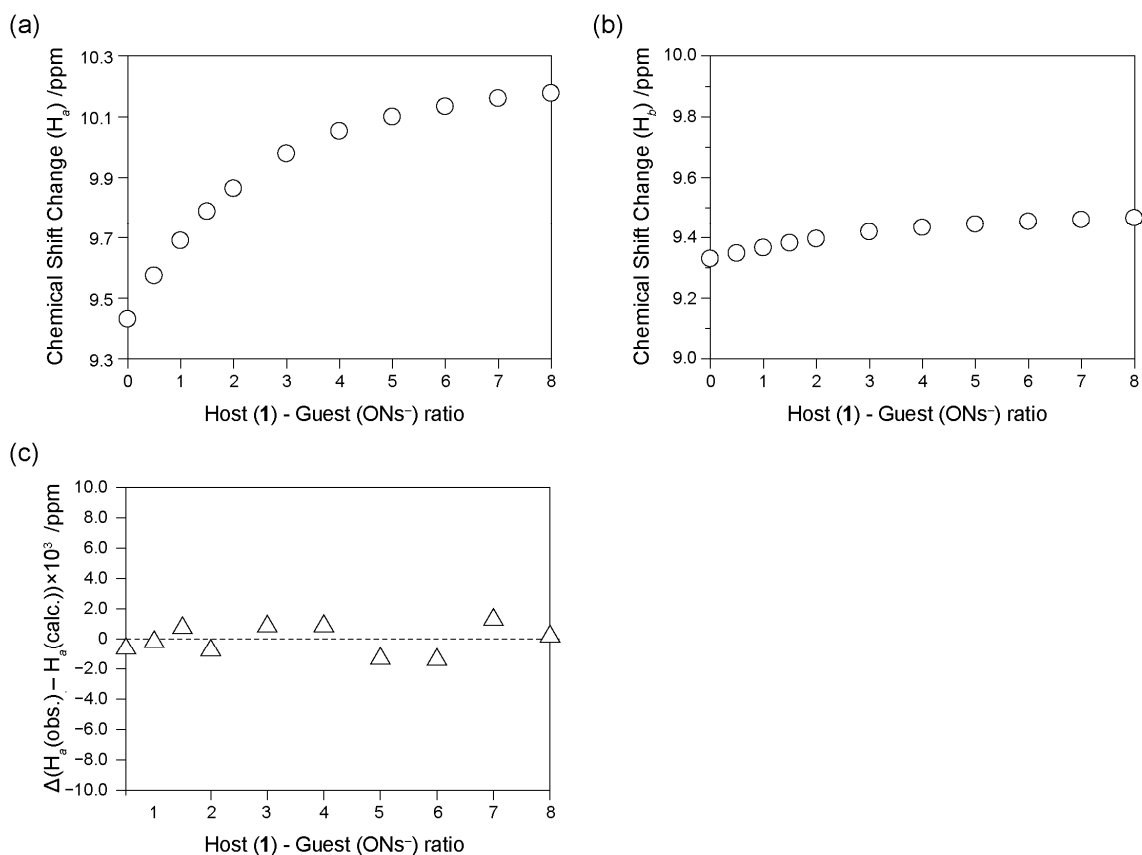


Fig. S4 ¹H NMR titration (ONs⁻) monitoring (a) H_a and (b) H_b . [1] = 1.0 mM. (c) $H_a(\text{obs.}) - H_a(\text{calc.})$. $H_a(\text{calc.})$ were calculated using WinEQNMR2 program⁵ (see also p. S21).

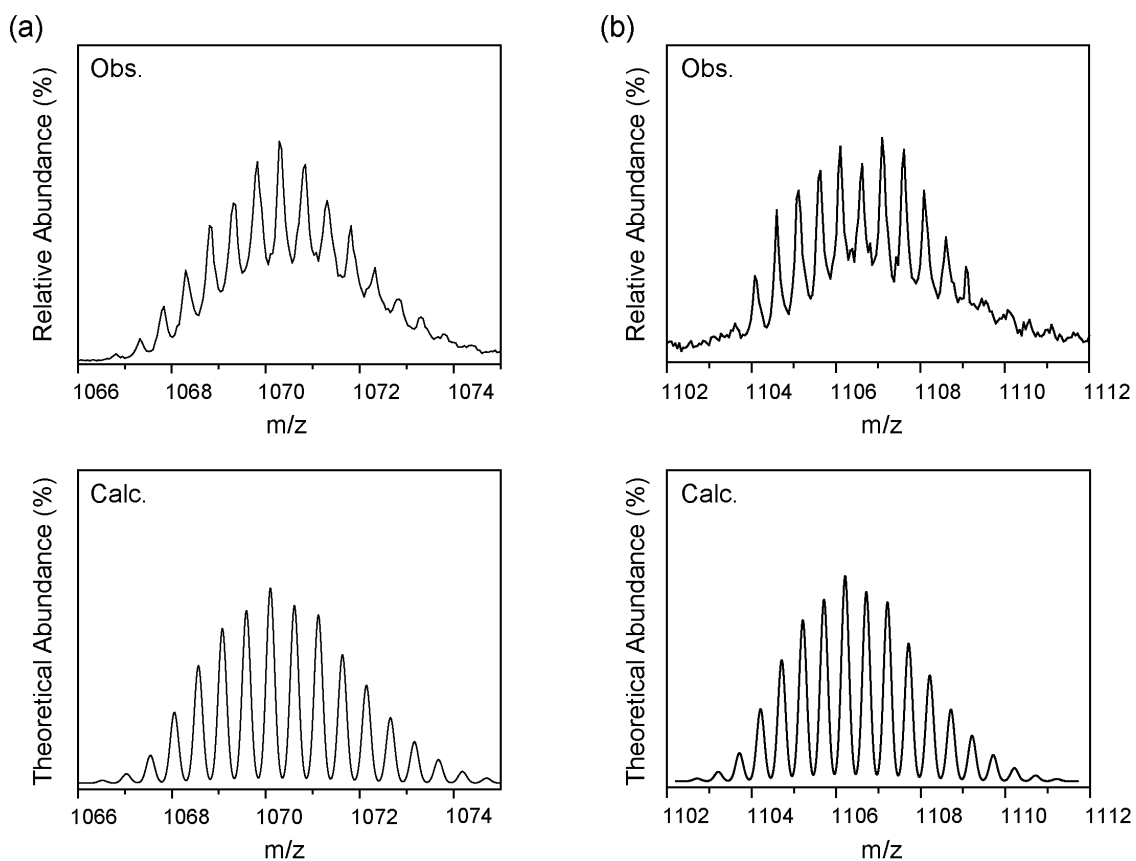


Fig. S5 Observed and calculated ion peaks of (a) $[1+(OTs)_2]^{2+}$ and (b) $[1+(ONs)_2]^{2+}$.

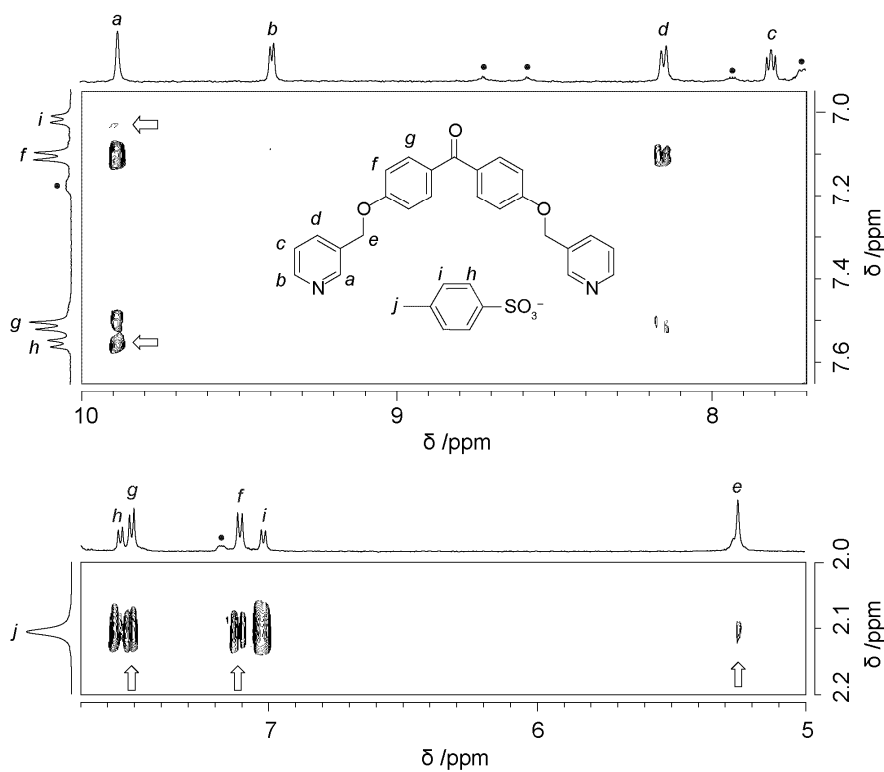


Fig. S6 Partial views of the 2D NOESY spectrum (500 MHz, $DMSO-d_6$, rt) of **1** with 4 equiv OTs^- . Mixing time = 1000 ms. The arrows denote NOEs.

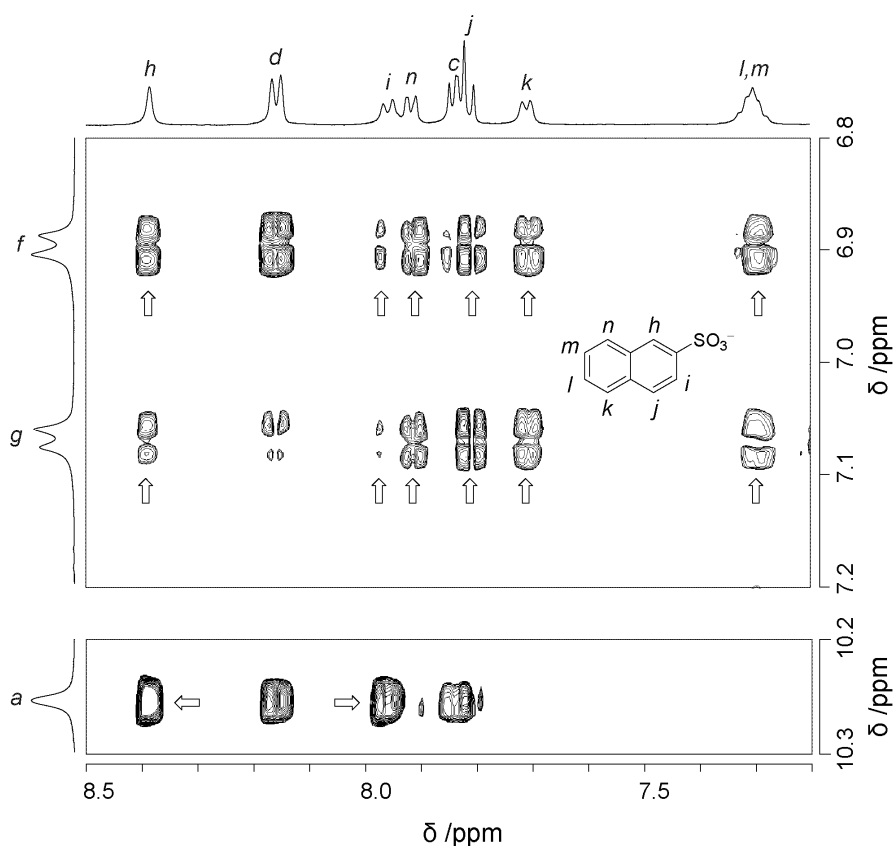


Fig. S7 Partial views of the 2D NOESY spectrum (500 MHz, DMSO-*d*₆, rt) of **1** with 4 equiv ONs⁻. Mixing time = 1000 ms. The arrows denote NOEs.

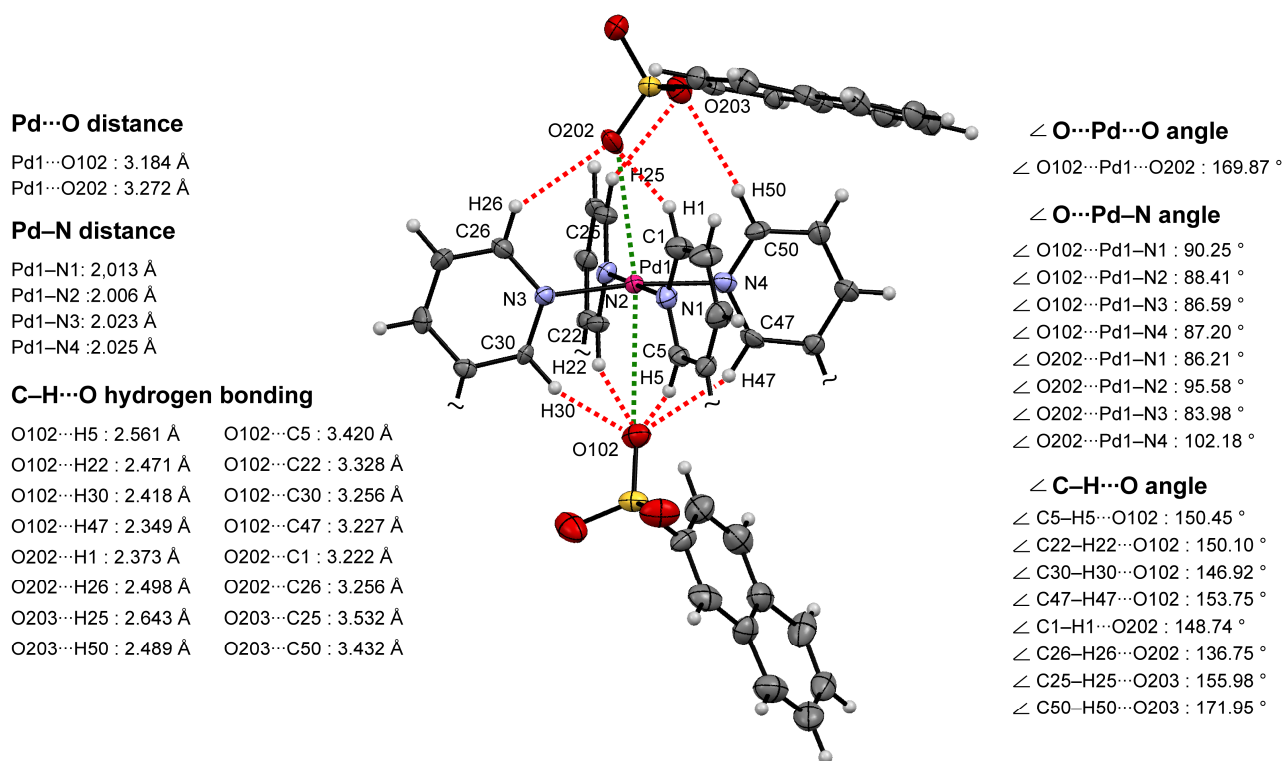


Fig. S8 Coordination environment around the Pd²⁺ centre of **1D**(ONs)₂ with atomic numbering scheme. Red dotted lines denote C-H...O hydrogen bonding. Colour scheme: gray (carbon), white (hydrogen), light blue (nitrogen), red (oxygen), orange (sulphur), purple (palladium).

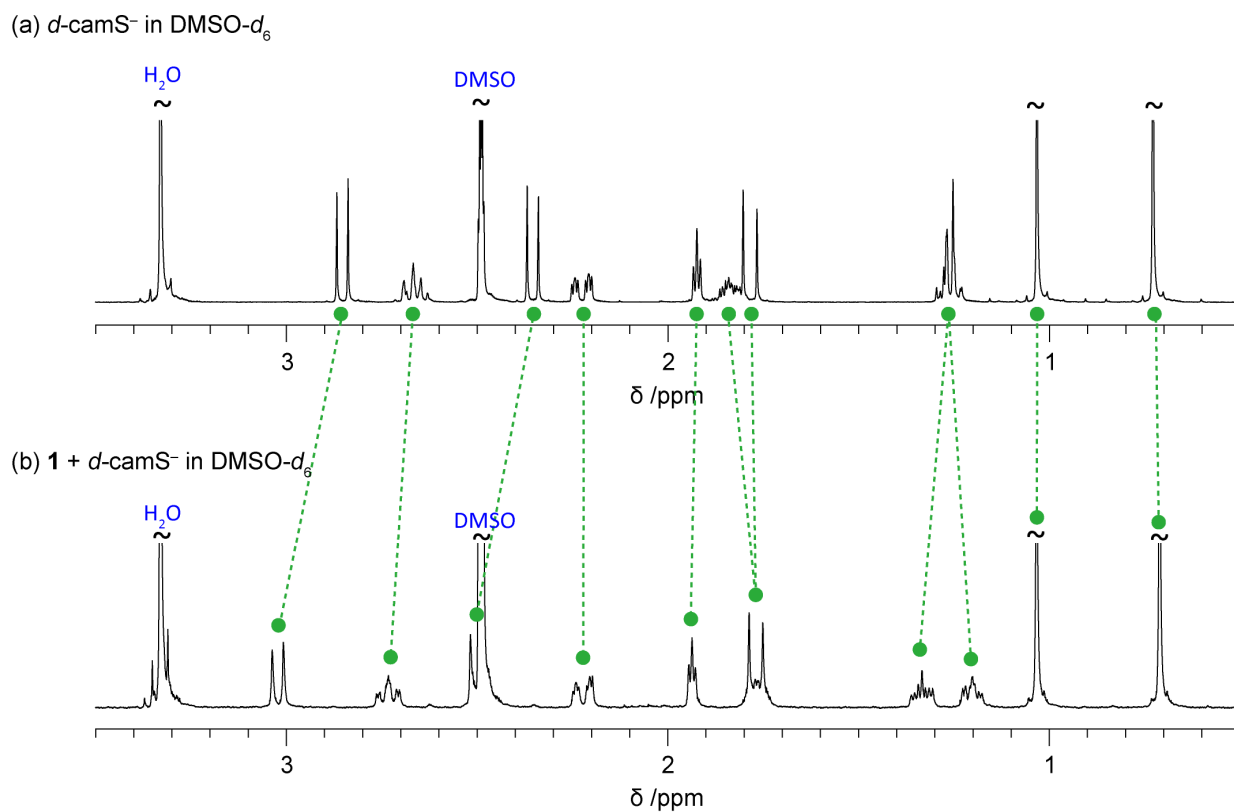


Fig. S9 Chemical shift change of $d\text{-camS}^-$ upon host-guest complexation (500 MHz, $\text{DMSO-}d_6$, rt). (a) $d\text{-camS}^-$. (b) **1** + $d\text{-camS}^-$ ($[\mathbf{1}] = 1.25 \text{ mM}$, $[d\text{-camS}^-] = 5.0 \text{ mM}$).

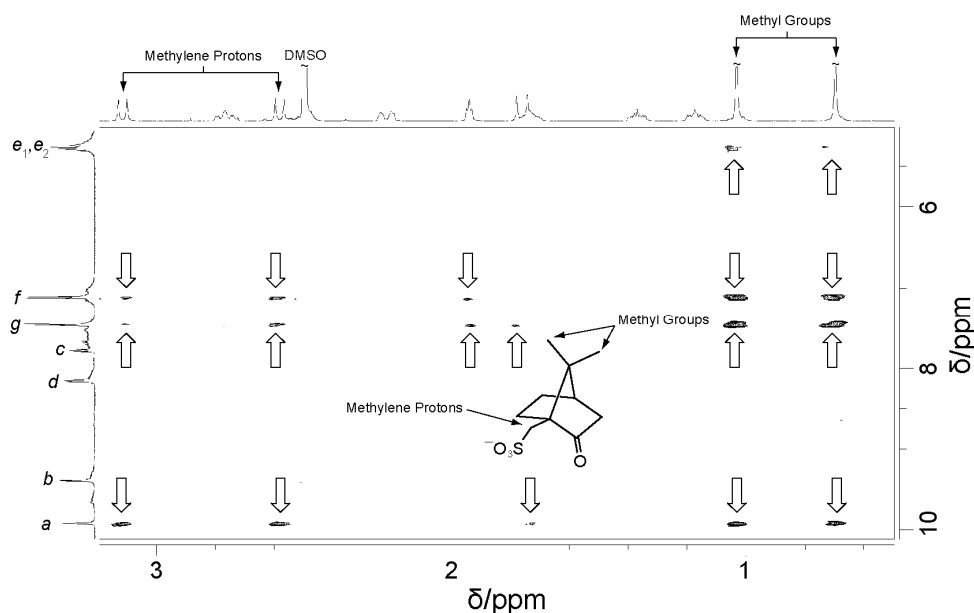


Fig. S10 A partial view of the 2D NOESY NMR spectrum (500 MHz, $\text{DMSO-}d_6$, rt) of **1** with 4 equiv $d\text{-camS}^-$. ($[\mathbf{1}] = 2.5 \text{ mM}$ and $[d\text{-camS}^-] = 10.0 \text{ mM}$). Mixing time = 1000 ms.

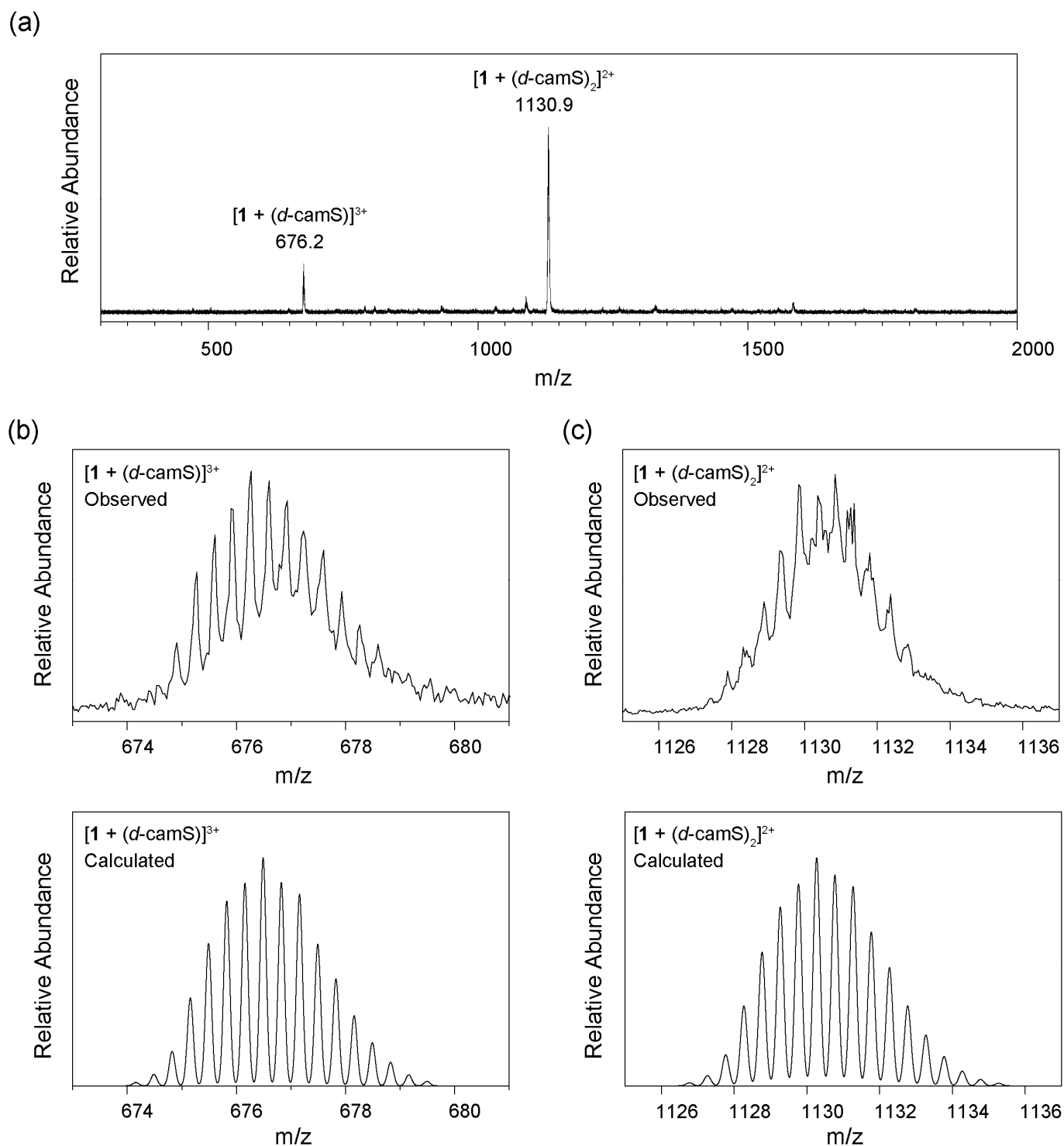


Fig. S11 (a) ESI MS spectrum of the DMSO- d_6 solution containing $\mathbf{1}_{\text{major}} \rightarrow (d\text{-cam})_2$ and $\mathbf{1}_{\text{minor}} \rightarrow (d\text{-cam})_2$ (See also Fig. 1d). (b) and (c) Observed and calculated ion peaks of $[1 + (d\text{-camS})]^{3+}$ and $[1 + (d\text{-camS})_2]^{2+}$, respectively.

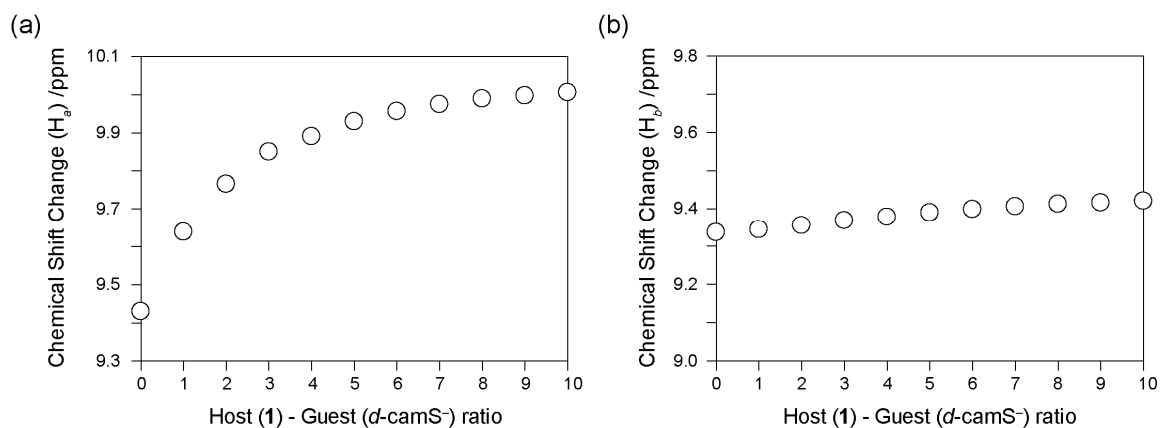


Fig. S12 ^1H NMR titration (d -camS $^-$) monitoring (a) H_a and (b) H_b . [$\mathbf{1}$] = 2.5 mM.

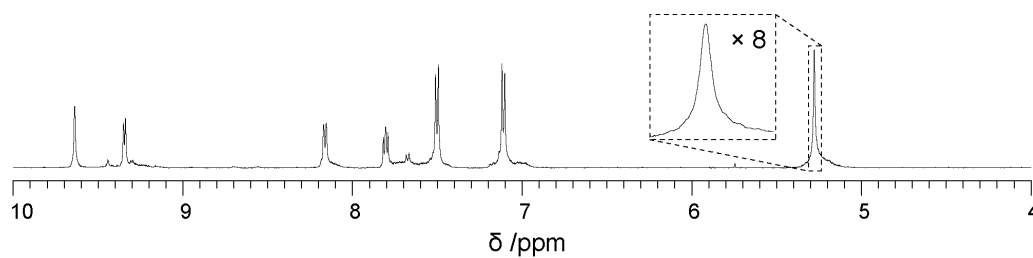


Fig. S13 ^1H NMR spectrum (500 MHz, DMSO- d_6 , rt) of $\mathbf{1}$ with 1 equiv d -camS $^-$. ([$\mathbf{1}$] = 2.5 mM and [d -camS $^-$] = 2.5 mM).

Pd...O distance

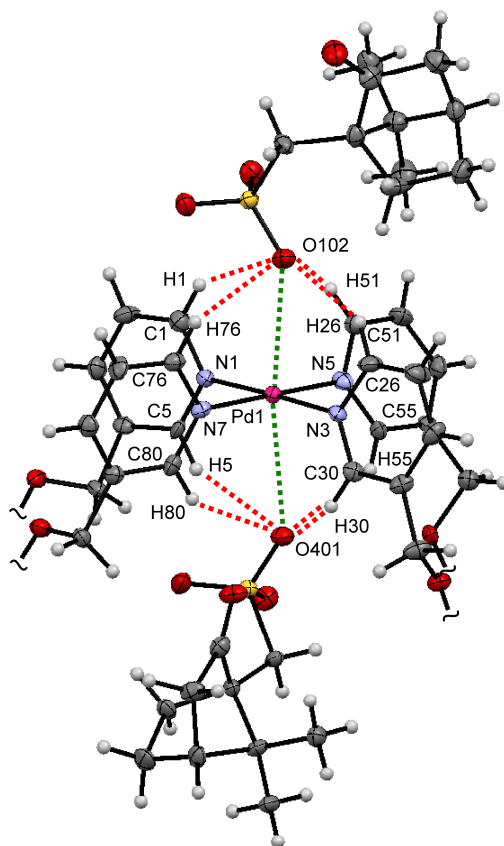
Pd1...O102 : 3.038 Å
 Pd1...O401 : 3.122 Å

Pd-N distance

Pd1-N1 : 2.023 Å
 Pd1-N3 : 2.003 Å
 Pd1-N5 : 2.023 Å
 Pd1-N7 : 2.027 Å

C-H...O hydrogen bonding

O102...H1 : 2.868 Å	O102...C1 : 3.614 Å
O102...H26 : 2.242 Å	O102...C26 : 3.075 Å
O102...H51 : 2.786 Å	O102...C51 : 3.469 Å
O102...H76 : 2.552 Å	O102...C76 : 3.364 Å
O401...H5 : 2.514 Å	O401...C5 : 3.374 Å
O401...H30 : 2.488 Å	O401...C30 : 3.264 Å
O401...H55 : 2.395 Å	O401...C55 : 3.174 Å
O401...H80 : 2.626 Å	O401...C80 : 3.463 Å



∠ O...Pd...O angle

∠ O102...Pd1...O401 : 171.36 °

∠ O...Pd-N angle

∠ O102...Pd1-N1 : 95.60 °
 ∠ O102...Pd1-N3 : 85.92 °
 ∠ O102...Pd1-N5 : 90.31 °
 ∠ O102...Pd1-N7 : 91.05 °
 ∠ O401...Pd1-N1 : 92.25 °
 ∠ O401...Pd1-N3 : 86.35 °
 ∠ O401...Pd1-N5 : 85.67 °
 ∠ O401...Pd1-N7 : 93.20 °

∠ C-H...O angle

∠ C1-H1...O102 : 136.18 °
 ∠ C26-H26...O102 : 145.78 °
 ∠ C51-H51...O102 : 129.55 °
 ∠ C76-H76...O102 : 143.79 °
 ∠ C5-H5...O401 : 150.64 °
 ∠ C30-H30...O401 : 138.79 °
 ∠ C55-H55...O401 : 139.06 °
 ∠ C80-H80...O401 : 147.17 °

Pd...O distance

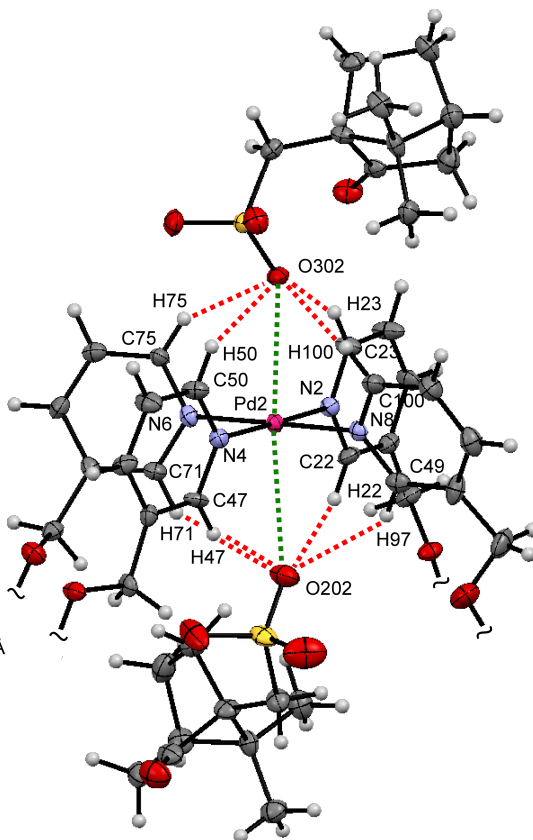
Pd2...O302 : 3.039 Å
 Pd2...O202 : 3.214 Å

Pd-N distance

Pd1-N2 : 2.034 Å
 Pd1-N4 : 2.020 Å
 Pd1-N6 : 2.030 Å
 Pd1-N8 : 2.027 Å

C-H...O hydrogen bonding

O302...H23 : 2.229 Å	O302...C23 : 3.100 Å
O302...H50 : 2.716 Å	O302...C50 : 3.483 Å
O302...H75 : 2.485 Å	O302...C75 : 3.301 Å
O302...H100 : 2.596 Å	O302...C100 : 3.328 Å
O202...H22 : 2.433 Å	O202...C22 : 3.274 Å
O202...H47 : 2.633 Å	O202...C47 : 3.500 Å
O202...H71 : 2.616 Å	O202...C71 : 3.451 Å
O202...H97 : 2.637 Å	O202...C97 : 3.438 Å



∠ O...Pd...O angle

∠ O202...Pd2...O120 : 173.08 °

∠ O...Pd-N angle

∠ O302...Pd2-N2 : 87.13 °
 ∠ O302...Pd2-N4 : 92.38 °
 ∠ O302...Pd2-N6 : 91.04 °
 ∠ O302...Pd2-N8 : 89.01 °
 ∠ O202...Pd2-N2 : 86.04 °
 ∠ O202...Pd2-N4 : 94.46 °
 ∠ O202...Pd2-N6 : 90.52 °
 ∠ O202...Pd2-N8 : 89.77 °

∠ C-H...O angle

∠ C23-H23...O302 : 152.29 °
 ∠ C50-H50...O302 : 138.21 °
 ∠ C75-H75...O302 : 143.97 °
 ∠ C100-H100...O302 : 133.99 °
 ∠ C22-H22...O202 : 147.48 °
 ∠ C47-H47...O202 : 151.92 °
 ∠ C71-H71...O202 : 146.89 °
 ∠ C97-H97...O202 : 142.33 °

Fig. S14 Coordination environments around the Pd²⁺ centres of 1D(*d*-camS)₂ with atomic numbering scheme. Red dotted lines denote C-H...O hydrogen bonding. Colour scheme: gray (carbon), white (hydrogen), light blue (nitrogen), red (oxygen), orange (sulphur), purple (palladium).

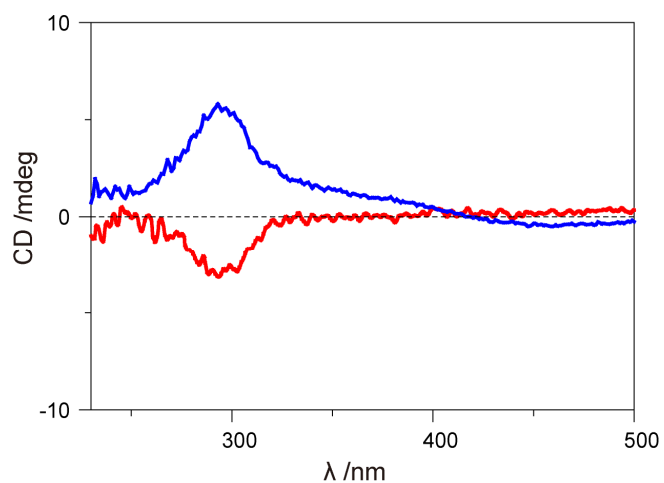


Fig. S15 Solid-state transmittance spectra (KBr disk) of **1**(*d*-camS)₄ (blue line) and **1**(*l*-camS)₄ (red line). Positive and negative CD originate from *d*-camS⁻ and *l*-camS⁻, respectively.

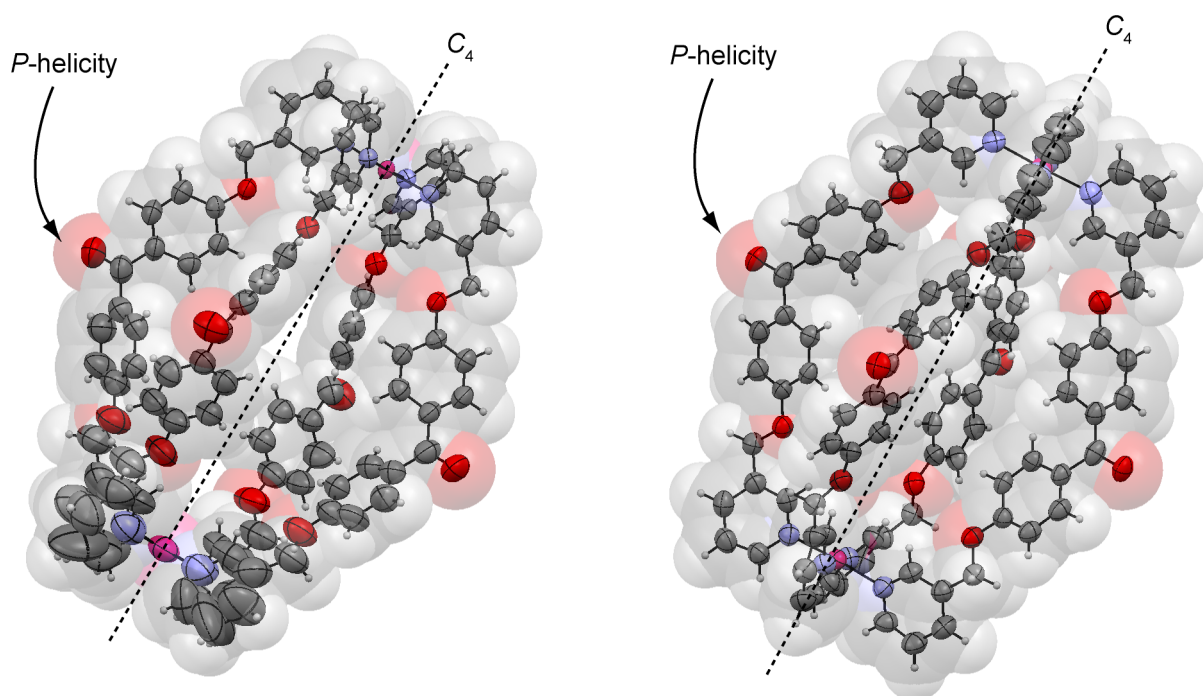


Fig. S16 ORTEP drawing (50 % probability ellipsoids) of the X-ray crystal structures of receptors **1** with *P*-form (both receptors are the components of an interlocked metallohelicate with *P*-form).⁶ The benzophenone cores possess *P*-helicity. Colour scheme: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen), purple (palladium).

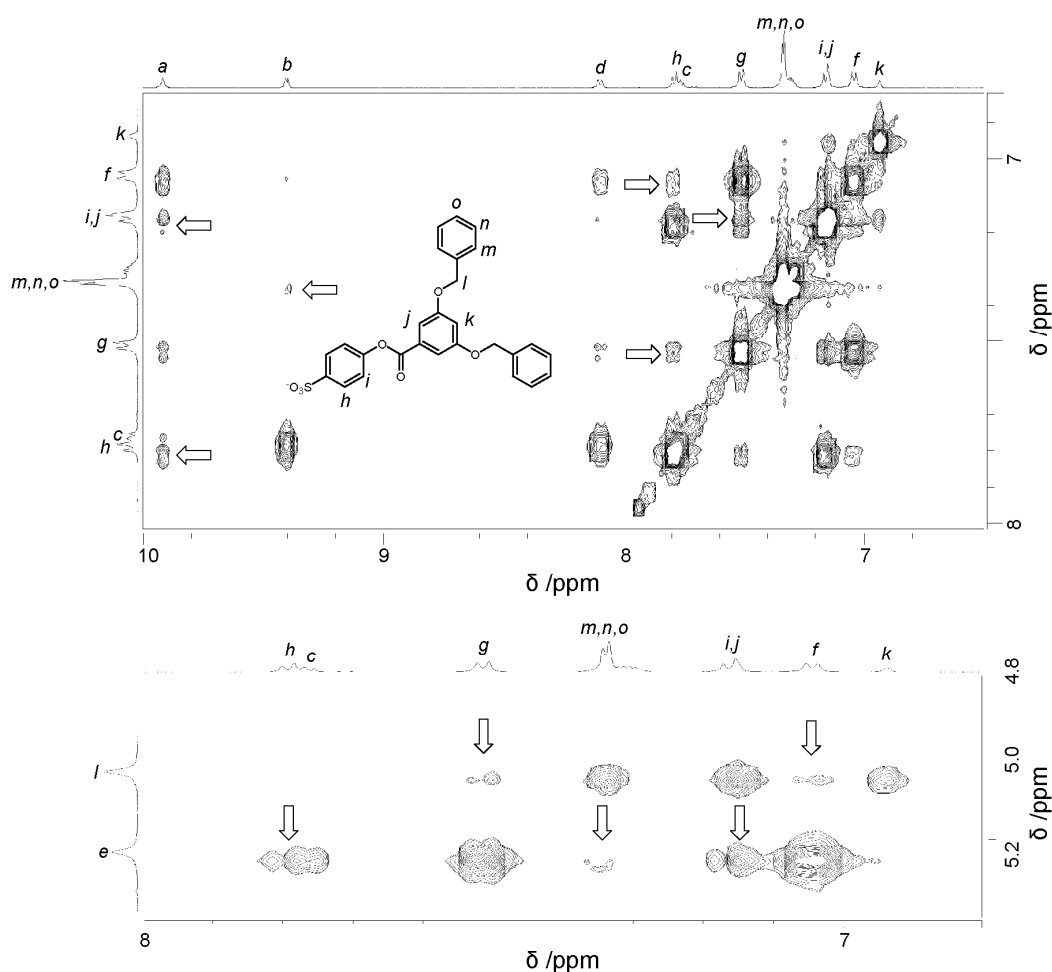


Fig. S17 Partial views of the 2D NOESY spectrum (500 MHz, DMSO- d_6 , rt) of **1** with 4 equiv DenS $^-$. ([**1**] = 2.5 mM and [DenS $^-$] = 10.0 mM). Mixing time = 1000 ms.

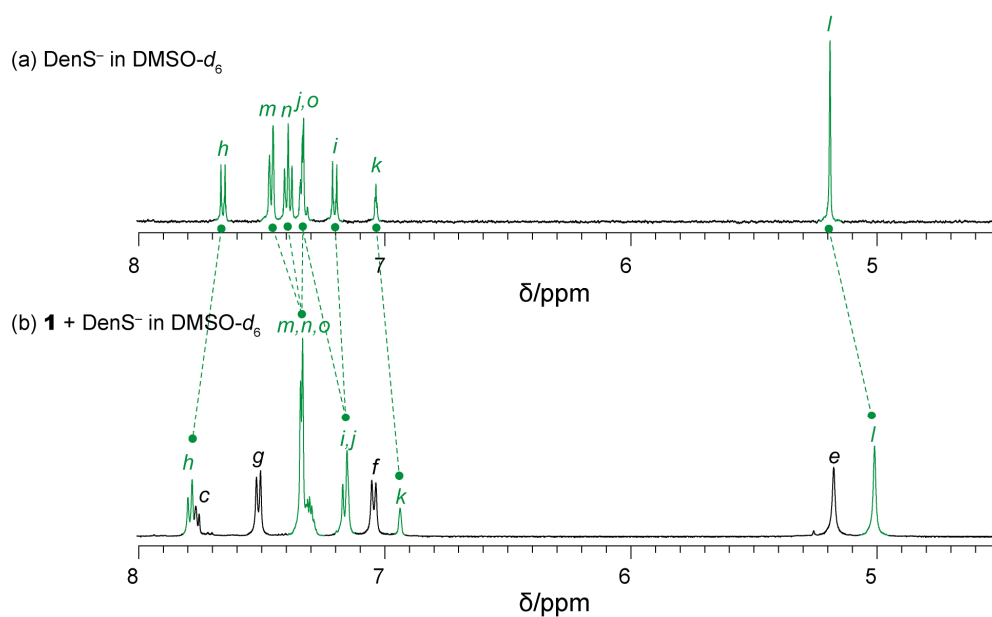


Fig. S18 Chemical shift change of the signals of *d*-camS $^-$ upon host-guest complexation. (a) DenS $^-$. (b) **1** + DenS $^-$ ([**1**] = 2.5 mM, [DenS $^-$] = 10.0 mM).

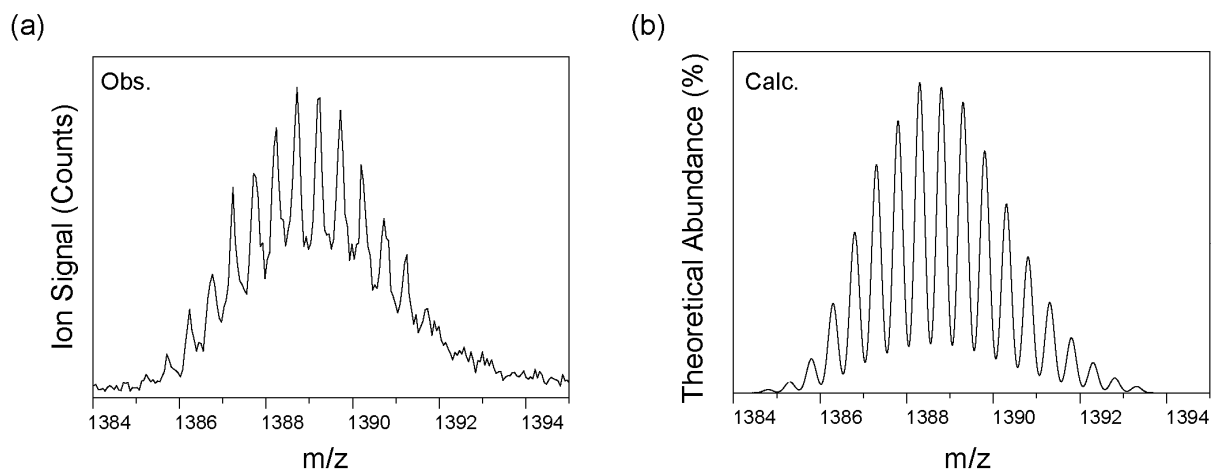


Fig. S19 (a) Observed and (b) calculated ion peaks of $[1+(\text{DenS})_2]^{2+}$.

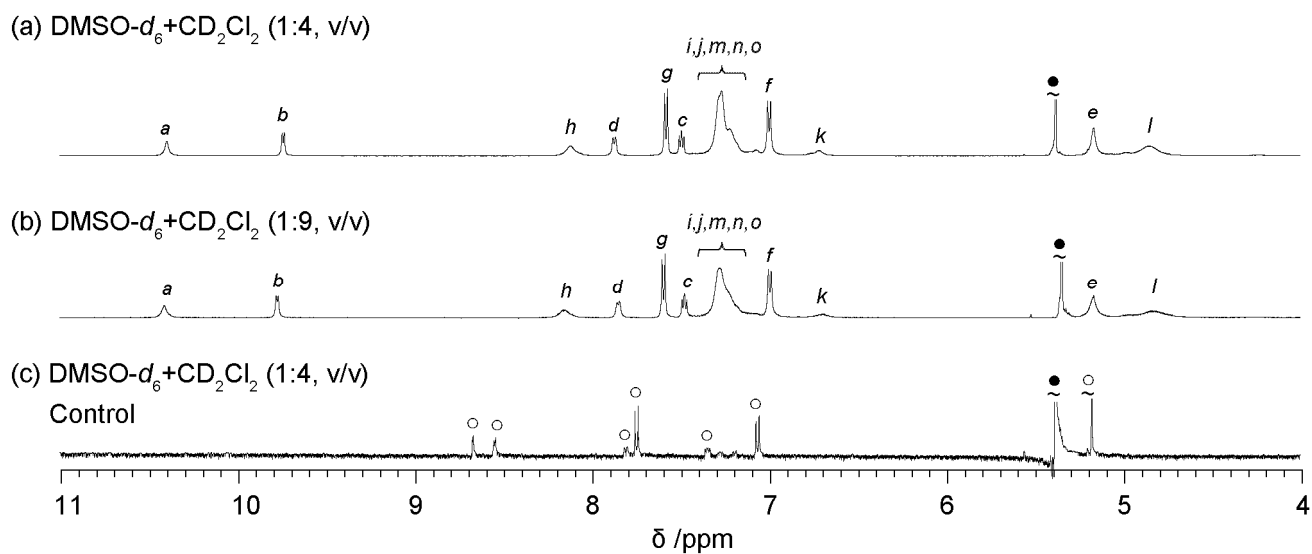


Fig. S20 (a), (b) ¹H NMR spectra (500 MHz, DMSO-*d*₆+CD₂Cl₂, rt) of **1** with 4 equiv DenS⁻. The chemical shifts are with respect to DMSO (δ = 2.48 ppm). (c) ¹H NMR spectrum (500 MHz, DMSO-*d*₆+CD₂Cl₂, rt) of the suspended solution of **1**(OTf)₄. Noise reduction was applied to the spectrum. (●) and (○) denote partially deuterated dichloromethane and free **L**, respectively.⁹

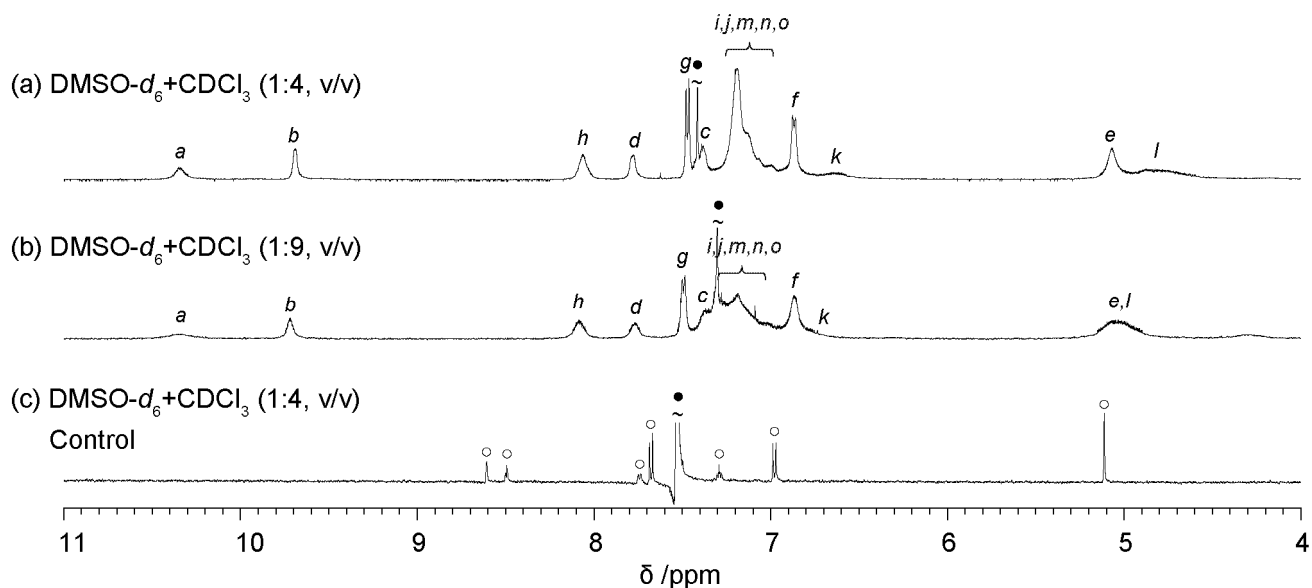


Fig. S21 (a), (b) ^1H NMR spectra (500 MHz, DMSO- d_6 +CDCl $_3$, rt) of **1** with 4 equiv DenS $^-$. The chemical shifts are with respect to DMSO ($\delta = 2.48$ ppm). (c) ^1H NMR spectrum (500 MHz, DMSO- d_6 +CDCl $_3$, rt) of the suspended solution of **1**(OTf) $_4$. Noise reduction was applied to the spectrum. (●) and (○) denote partially deuterated chloroform and free **L**, respectively.⁹

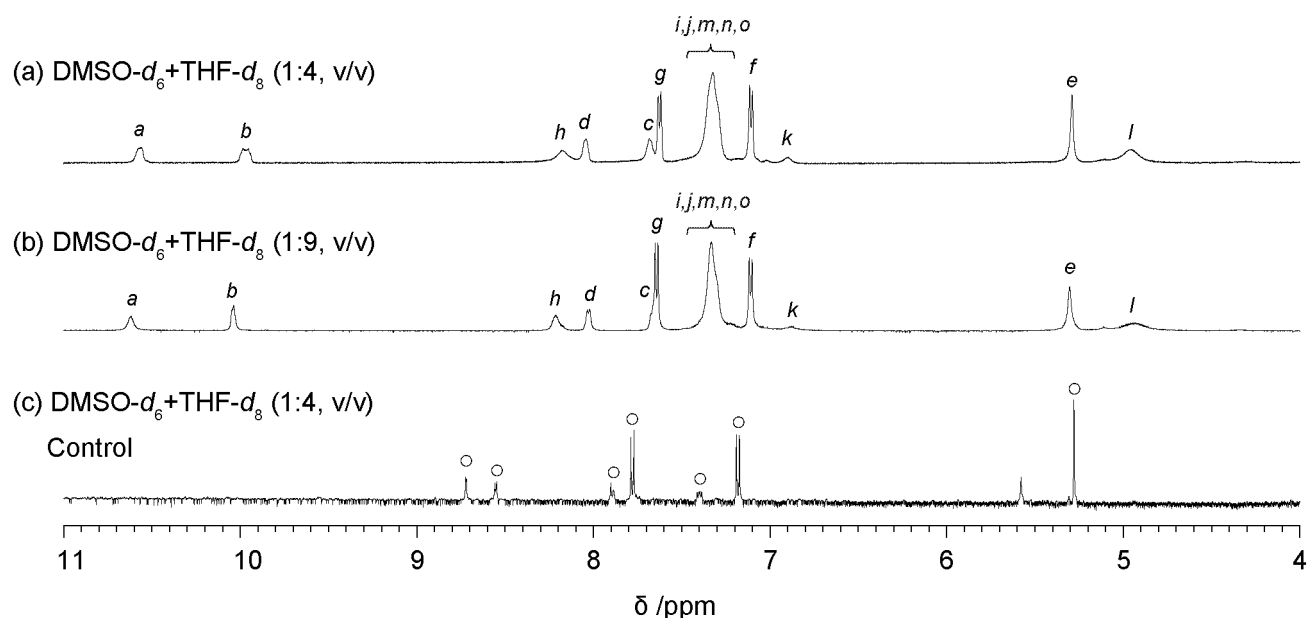


Fig. S22 (a), (b) ^1H NMR spectra (500 MHz, DMSO- d_6 +THF- d_8 , rt) of **1** with 4 equiv DenS $^-$. The chemical shifts are with respect to DMSO ($\delta = 2.48$ ppm). (c) ^1H NMR spectrum (500 MHz, DMSO- d_6 +THF- d_8 , rt) of the suspended solution of **1**(OTf) $_4$. Noise reduction was applied to the spectrum. (○) denotes free **L**.⁹

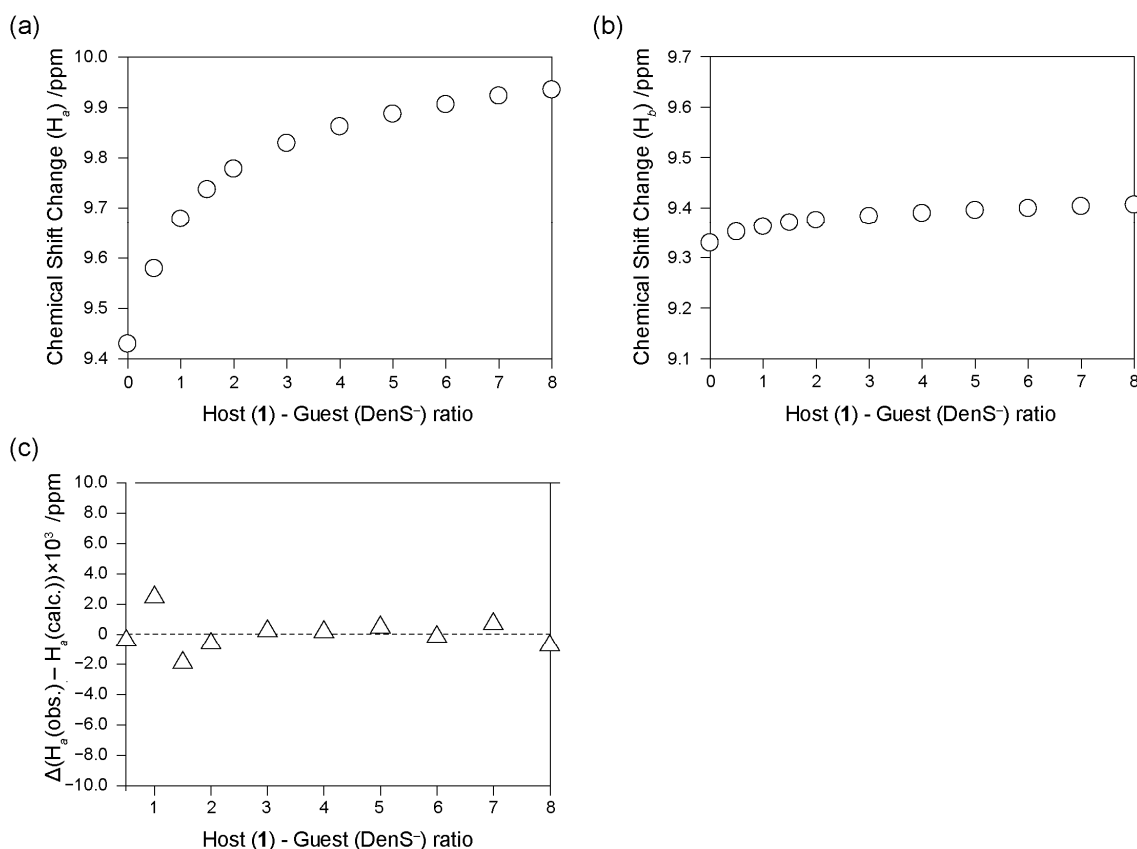


Fig. S23 ¹H NMR titration (DenS⁻) monitoring (a) H_a and (b) H_b . [**1**] = 1.0 mM. (c) $H_a(\text{obs.}) - H_a(\text{calc.})$. $H_a(\text{calc.})$ were calculated using WinEQNMR2 program⁵ (see also p. S22).

Table S2 Association constants $\log_{10}(K_{a1})$ and $\log_{10}(K_a)$ in DMSO-*d*₆.

Anion	$\log_{10}(K_{a1})$	$\log_{10}(K_a)$
OTs ⁻	2.9(3)	5.1(5)
ONs ⁻	3.01(10)	5.57(14)
DenS ⁻	3.7(2)	5.9(4)

$$K_{a1} = [\mathbf{1} \supset (\text{X})] / ([\mathbf{1}] \cdot [\text{X}]) \text{ and } K_a = [\mathbf{1} \supset (\text{X})_2] / ([\mathbf{1}] \cdot [\text{X}]^2)$$

Data fitting of the NMR titrations ($1 + OTs^-$)⁵

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 19:25:21 on 12/03/2010

Reactions: $M + L = ML$ ($\beta_1 = K_1$); $M + 2L = (ML)_2$ ($\beta_2 = K_1K_2$)

Data 2010 05 14

==== Anion Recognition ====

Equilibrium constants are \log_{10} values

NO. A PARAMETER DELTA ERROR CONDITION DESCRIPTION

1	1	2.93323E+00	1.000E-01	2.580E-01	2.496E+03	Stability constant(K1)
2	1	5.12105E+00	1.000E-01	5.104E-01	1.401E+04	Stability constant(K1K2)
3	1	9.44643E+00	1.000E-06	2.168E-03	5.890E+00	Shift of 1
4	1	9.89682E+00	1.000E-04	1.533E-01	1.823E+04	Shift of 1:1_complex
5	1	1.01493E+01	1.000E-04	1.872E-02	9.554E+01	Shift of 1:2_complex

ORMS ERROR = 1.65E-03 MAX ERROR = 1.95E-03 AT OBS.NO. 3

RESIDUALS SQUARED = 1.36E-05

RFACTOR = 0.0119 PERCENT

NO.	A	EXPT.	DEL	CALC.	DEL	RESIDUAL	% DEV	WEIGHT	Guest(OTs)	Host(1)	pH
1	1	9.5390E+00	9.5400E+00	-9.8324E-04	-1.0308E-02	1.0000E+00	5.0000E-04	1.0000E-03	0.0000E+00		
2	1	9.6170E+00	9.6170E+00	1.9073E-06	1.9833E-05	1.0000E+00	1.0000E-03	1.0000E-03	0.0000E+00		
3	1	9.6830E+00	9.6810E+00	1.9512E-03	2.0151E-02	1.0000E+00	1.5000E-03	1.0000E-03	0.0000E+00		
4	1	9.7330E+00	9.7322E+00	7.8106E-04	8.0249E-03	1.0000E+00	2.0000E-03	1.0000E-03	0.0000E+00		
5	1	9.8080E+00	9.8096E+00	-1.6432E-03	-1.6753E-02	1.0000E+00	3.0000E-03	1.0000E-03	0.0000E+00		
6	1	9.8650E+00	9.8644E+00	6.4468E-04	6.5351E-03	1.0000E+00	4.0000E-03	1.0000E-03	0.0000E+00		
7	1	9.9030E+00	9.9047E+00	-1.6518E-03	-1.6679E-02	1.0000E+00	5.0000E-03	1.0000E-03	0.0000E+00		
8	1	9.9350E+00	9.9354E+00	-3.5954E-04	-3.6189E-03	1.0000E+00	6.0000E-03	1.0000E-03	0.0000E+00		
9	1	9.9610E+00	9.9595E+00	1.4944E-03	1.5003E-02	1.0000E+00	7.0000E-03	1.0000E-03	0.0000E+00		
10	1	9.9790E+00	9.9789E+00	1.2302E-04	1.2328E-03	1.0000E+00	8.0000E-03	1.0000E-03	0.0000E+00		

TOLERANCE ON SUM OF SQUARES 0.0100

TOLERANCE ON EIGEN VALUES 0.0001

CONVERGANCE AFTER 7 ITERATIONS

Data fitting of the NMR titrations ($1 + \text{ONs}^-$)⁵

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 19:54:43 on 12/03/2010

Reactions: $M + L = ML$ ($\beta_1 = K_1$); $M + 2L = (ML)_2$ ($\beta_2 = K_1K_2$)

Data 2010 05 14

==== Anion Recognition ====

Equilibrium constants are \log_{10} values

NO. A PARAMETER DELTA ERROR CONDITION DESCRIPTION

1	1	3.00538E+00	1.000E-01	9.944E-02	7.556E+02	Stability constant(K1)
2	1	5.56744E+00	1.000E-01	1.441E-01	2.460E+03	Stability constant(K1K2)
3	1	9.43506E+00	1.000E-06	2.356E-03	8.241E+00	Shift of 1
4	1	1.00402E+01	1.000E-04	7.674E-02	4.693E+03	Shift of 1:1_complex
5	1	1.02835E+01	1.000E-04	1.367E-02	1.958E+02	Shift of 1:2_complex

ORMS ERROR = 1.30E-03 MAX ERROR = 1.40E-03 AT OBS.NO. 8

RESIDUALS SQUARED = 8.42E-06

RFACTOR = 0.0092 PERCENT

NO.	A	EXPT.	DEL	CALC.	DEL	RESIDUAL	% DEV	WEIGHT	Guest(ONs)	Host(1)	pH
1	1	9.5730E+00	9.5736E+00	-6.4945E-04	-6.7842E-03	1.0000E+00	5.0000E-04	1.0000E-03	0.0000E+00		
2	1	9.6890E+00	9.6892E+00	-1.9264E-04	-1.9883E-03	1.0000E+00	1.0000E-03	1.0000E-03	0.0000E+00		
3	1	9.7870E+00	9.7863E+00	7.3624E-04	7.5226E-03	1.0000E+00	1.5000E-03	1.0000E-03	0.0000E+00		
4	1	9.8630E+00	9.8638E+00	-7.5817E-04	-7.6870E-03	1.0000E+00	2.0000E-03	1.0000E-03	0.0000E+00		
5	1	9.9780E+00	9.9772E+00	8.3923E-04	8.4108E-03	1.0000E+00	3.0000E-03	1.0000E-03	0.0000E+00		
6	1	1.0052E+01	1.0051E+01	8.6975E-04	8.6525E-03	1.0000E+00	4.0000E-03	1.0000E-03	0.0000E+00		
7	1	1.0099E+01	1.0100E+01	-1.3247E-03	-1.3117E-02	1.0000E+00	5.0000E-03	1.0000E-03	0.0000E+00		
8	1	1.0133E+01	1.0134E+01	-1.3952E-03	-1.3769E-02	1.0000E+00	6.0000E-03	1.0000E-03	0.0000E+00		
9	1	1.0160E+01	1.0159E+01	1.2846E-03	1.2644E-02	1.0000E+00	7.0000E-03	1.0000E-03	0.0000E+00		
10	1	1.0177E+01	1.0177E+01	1.8406E-04	1.8086E-03	1.0000E+00	8.0000E-03	1.0000E-03	0.0000E+00		

TOLERANCE ON SUM OF SQUARES 0.0100

TOLERANCE ON EIGEN VALUES 0.0001

CONVERGANCE AFTER 8 ITERATIONS

Data fitting of the NMR titrations ($1 + \text{DenS}^-$)⁵

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 19:33:52 on 12/07/2010

Reactions: $M + L = ML$ ($\beta_1 = K_1$); $M + 2L = (ML)_2$ ($\beta_2 = K_1K_2$)

Data 2010 05 14

==== Anion Recognition ====

Equilibrium constants are \log_{10} values

NO. A PARAMETER DELTA ERROR CONDITION DESCRIPTION

1	1	3.68282E+00	1.000E-01	1.785E-01	1.444E+03	Stability constant(K1)
2	1	5.86840E+00	1.000E-01	3.552E-01	7.728E+03	Stability constant(K1K2)
3	1	9.44991E+00	1.000E-06	2.259E-03	1.498E+00	Shift of 1
4	1	9.79416E+00	1.000E-02	3.263E-02	1.703E+03	Shift of 1:1_complex
5	1	1.00910E+01	1.000E-02	3.728E-02	5.218E+02	Shift of 1:2_complex

ORMS ERROR = 1.52E-03 MAX ERROR = 2.45E-03 AT OBS.NO. 2

RESIDUALS SQUARED = 1.16E-05

RFACTOR = 0.0110 PERCENT

NO.	A	EXPT.	DEL	CALC.	DEL	RESIDUAL	% DEV	WEIGHT	Guest(DenS)	Host(1)	pH
1	1	9.5790E+00	9.5794E+00	-4.2248E-04	-4.4105E-03	1.0000E+00	5.0000E-04	1.0000E-03	0.0000E+00		
2	1	9.6780E+00	9.6756E+00	2.4452E-03	2.5266E-02	1.0000E+00	1.0000E-03	1.0000E-03	0.0000E+00		
3	1	9.7370E+00	9.7389E+00	-1.9217E-03	-1.9736E-02	1.0000E+00	1.5000E-03	1.0000E-03	0.0000E+00		
4	1	9.7780E+00	9.7786E+00	-6.2180E-04	-6.3591E-03	1.0000E+00	2.0000E-03	1.0000E-03	0.0000E+00		
5	1	9.8290E+00	9.8288E+00	2.2316E-04	2.2704E-03	1.0000E+00	3.0000E-03	1.0000E-03	0.0000E+00		
6	1	9.8620E+00	9.8618E+00	1.6499E-04	1.6729E-03	1.0000E+00	4.0000E-03	1.0000E-03	0.0000E+00		
7	1	9.8870E+00	9.8865E+00	4.7398E-04	4.7939E-03	1.0000E+00	5.0000E-03	1.0000E-03	0.0000E+00		
8	1	9.9060E+00	9.9062E+00	-1.6022E-04	-1.6174E-03	1.0000E+00	6.0000E-03	1.0000E-03	0.0000E+00		
9	1	9.9230E+00	9.9223E+00	6.9237E-04	6.9774E-03	1.0000E+00	7.0000E-03	1.0000E-03	0.0000E+00		
10	1	9.9350E+00	9.9358E+00	-7.6008E-04	-7.6505E-03	1.0000E+00	8.0000E-03	1.0000E-03	0.0000E+00		

TOLERANCE ON SUM OF SQUARES 0.0100

TOLERANCE ON EIGEN VALUES 0.0001

CONVERGANCE AFTER 7 ITERATIONS

References

- (1) R. Kuroda, T. Harada and Y. Shindo, *Rev. Sci. Instrum.*, 2001, **72**, 3802.
- (2) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- (3) A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148.
- (4) See: <http://www.ccdc.cam.ac.uk/products/mercury/>
- (5) WinEQNMR2, see: M. J. Hynes, *J. Chem. Soc. Dalton Trans.*, 1993, 311.
- (6) M. Fukuda, R. Sekiya and R. Kuroda, *Angew. Chem. Int. Ed.*, 2008, **47**, 706.
- (7) D. Xie, M. Jiang, G. Zhang and D. Chen, *Chem. Eur. J.*, 2007, **13**, 3346.
- (8) A. K. Rappe', K. S. Colwell and C. J. Casewit, *Inorg. Chem.*, 1993, **32**, 3438.
- (9) Since bridging ligand **L** is slightly soluble in CH₂Cl₂, CHCl₃, and THF, small amount of **1** was decomposed and free **L** dissolved in the mixed solvent solutions.