Supplementary Information

Syntheses and Structures of Mono-, Di- and Tetranuclear Rhodium or Iridium Complexes of Thiacalix[4]arene Derivatives†

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General procedure. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. TC4A(OH)$_4$ (**1**)[1], TC4A(SH)$_4$ (**2**)[2], [Cp*IrCl$_2$]$_2$[3] and [Cp*RhCl$_2$]$_2$[3] were synthesized as described in the literature. Acetone, THF, CH_2Cl_2 and hexane were distilled under nitrogen over appropriate drying reagents ($CaSO_4$, sodium benzophenone ketyl or P_2O_5). Potassium carbonate, methyl iodide, *N,N*-dimethylthiocarbamoyl chloride, lithium aluminum hydride and boron tribromide (1 M solution in CH_2Cl_2) were obtained commercially and used without further purification. NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were recorded using a Shimadzu FTIR-8300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS analyzer.

Synthesis of TC4A(OMe)$_2$(OH)$_2$ (4).[4] To a suspension of TC4A(OH)$_4$ (**1**) (6.00 g, 8.32 mmol) and K_2CO_3 (1.15 g, 8.32 mmol) in acetone (50 mL) was added methyl iodide (5.2 mL, 84 mmol), and the mixture was stirred at reflux for 42 h. After addition of dilute hydrochloric acid, the resulting mixture was extracted with chloroform. The solvent was evaporated, and the residue was washed with acetone to give a white solid of **4**. Yield, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H, OH), 7.61 (s, 4H, C_6H_2), 7.16 (s, 4H, C_6H_2), 4.01 (s, 6H, CH_3), 1.32 (s, 18H, Bu^t), 0.95 (s, 18H, Bu^t).

Synthesis of TC4A(OMe)$_2$(OC(=S)NMe$_2$)$_2$ (5). A suspension of **4** (5.54 g, 7.40 mmol), K_2CO_3 (10.2 g, 74.0 mmol) and *N,N*-dimethylthiocarbamoyl chloride (9.14 g, 74.0 mmol) in acetone (100 mL) was stirred at reflux for 42 h. After the solvent was evaporated, the residue was extracted with $CHCl_3$. The solvent was evaporated, and the residue was washed with acetone to give a white solid of **5**. This product was used directly for the next step without further purification. Yield, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7–7.2 (m, 8H, C_6H_2), 3.41 (s, 12H, NCH_3), 3.23 (s, 6H, OCH_3), 1.4–1.2 (m, 36H, Bu^t). IR spectrum (KBr): 1533 cm^{-1}.

Synthesis of TC4A(OMe)$_2$(SC(=O)NMe$_2$)$_2$ (6). Compound **5** (5.64 g, 6.11 mmol) was heated in vacuo at 260 ^{o}C until the IR frequency of compound **5** disappeared. The resulting solid was washed with acetone to give a white solid of **6**. This product was used directly for the next step without further purification. Yield, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6–7.4 (m, 8H, C_6H_2), 3.20 (s, 6H, OCH_3), 2.98 (s, 12H, NCH_3), 1.4–1.1 (m, 36H, Bu^t). IR spectrum (KBr): 1674 cm^{-1}.

Synthesis of TC4A(OMe)$_2$(SH)$_2$ (7). To a solution of **6** (5.40 g, 5.85 mmol) in THF (20 mL) was added lithium aluminum hydride (1.11 g, 29.2 mmol) in portions at room temperature, and the reaction mixture was stirred for 9 h. Excess lithium aluminum hydride was quenched by careful addition of H_2O at 0 ^oC. After THF was evaporated, the solution was neutralized by addition of dilute hydrochloric acid and extracted with chloroform. The solvent was evaporated, and the residue was washed with acetone to give a white solid of **7**. Yield, 45%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 4H, C_6H_2), 7.43 (s, 4H, C_6H_2), 4.99 (br, 2H, SH), 3.77 (s, 6H, OCH_3), 1.28 (s, 18H, Bu^t), 1.18 (s, 18H, Bu^t). IR spectrum (KBr): 2529 cm^{-1}.

Synthesis of TC4A(OH)$_2$(SH)$_2$ (3). To a suspension of **7** (2.07 g, 2.65 mmol) in CH_2Cl_2 (40 mL) was added 1 M BBr_3 solution in CH_2Cl_2 (6.6 mL). After stirring for 1 h, the reaction mixture was poured into 300 mL of H_2O. The mixture was extracted with Et_2O and the organic phase was dried over Na_2SO_4. After the solvent was evaporated, the residue was washed with MeOH to give a white solid of **3**. Yield, 89%. Anal. Calcd for $C_{40}H_{48}O_2S_6$: C, 63.78; H, 6.42; S, 25.54. Found: C, 63.08; H, 6.58; S, 25.54. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 4H, C_6H_2), 7.18 (s, 2H, OH), 7.14 (s, 4H, C_6H_2,), 6.40 (s, 2H, SH), 1.33 (s, 18H, Bu^t), 0.88 (s, 18H, Bu^t). IR spectrum (KBr): 3213, 2509 cm^{-1}.

Synthesis of (Cp*Rh){η^3-TC4A(OH)$_2$(O)$_2$} (8a). A supension of [Cp*$RhCl_2$]$_2$ (30.9 mg, 0.050 mmol), **1** (72.1 mg, 0.10 mmol) and K_2CO_3 (28 mg, 0.20 mmol) in THF (4.0 mL) was stirred overnight at room temperature. The reaction mixture was filtered and the filtrate was dried up in vacuo. Recrystallization from CH_2Cl_2-hexane gave complex **8a**·2CH_2Cl_2 as red crystals. Yield, 98%. Anal. Calcd for $C_{50}H_{61}O_4RhS_4 \cdot 2CH_2Cl_2$: C, 55.41; H, 5.81; S, 11.38. Found: C, 55.74; H, 5.65; S, 11.77. ^1H NMR ($CDCl_3$): δ 10.98 (s, 2H, OH), 7.67 (d, 2H, C_6H_2, J = 2.4 Hz), 7.51 (d, 2H, C_6H_2, J = 2.4 Hz), 7.45 (d, 2H, C_6H_2, J = 2.4 Hz), 7.36 (d, 2H, C_6H_2, J = 2.4 Hz), 1.98 (s, 15H, Cp*), 1.20 (s, 18H, *t*-Bu), 1.17 (s, 18H, *t*-Bu).

Synthesis of (Cp*Ir){η^3-TC4A(OH)$_2$(O)$_2$} (8b). A suspension of [Cp*$IrCl_2$]$_2$ (39.8 mg, 0.050 mmol), **1** (72.1 mg, 0.10 mmol) and K_2CO_3 (28 mg, 0.20 mmol) in THF (4.0 mL) was stirred overnight at room temperature. The reaction mixture was filtered and the filtrate was dried up in vacuo. Recrystallization from CH_2Cl_2-hexane gave complex **8b**·2CH_2Cl_2 as orange crystals. Yield, 97%. Anal. Calcd for $C_{50}H_{61}IrO_4S_4 \cdot 2CH_2Cl_2$: C, 51.34; H, 5.39; S, 10.54. Found: C, 51.65; H, 5.52; S, 10.68. ^1H NMR ($CDCl_3$): δ 10.57 (s, 2H, OH), 7.68 (br, 2H, C_6H_2), 7.46 (d, 2H, C_6H_2, J = 2.4 Hz), 7.45 (d, 2H, C_6H_2, J = 2.4 Hz), 7.42 (d, 2H, C_6H_2, J = 2.4 Hz), 1.99 (s, 15H, Cp*), 1.21 (s, 18H, *t*-Bu), 1.17 (s, 18H, *t*-Bu).

Synthesis of (Cp*Rh)$_2${η^3:η^3-TC4A(S)$_4$} (9a). A solution of [Cp*$RhCl_2$]$_2$ (30.9 mg, 0.050 mmol) and **2** (78.5 mg, 0.10 mmol) in THF (4.0 mL) was stirred overnight at room temperature. After the reaction mixture was dried up in vacuo, the residue was recrystallized from THF-hexane to give complex **9a**·2THF as red crystals. Otherwise, recrystallization from CH_2Cl_2–hexane to give complex **9a** as red crystals. Yield, 61%. Anal. Calcd for $C_{60}H_{74}Rh_2S_8{\cdot}2C_4H_8O$: C, 58.26; H, 6.47, S: 18.30. Found: C, 57.78; H, 6.78, S: 18.44. ^{1}H NMR ($CDCl_3$): δ 7.20 (d, 4H, C_6H_2, J = 2.0 Hz), 6.94 (d, 4H, C_6H_2, J = 2.0 Hz), 1.82 (s, 30H, Cp*), 1.05 (s, 36H, *t*-Bu).

Synthesis of (Cp*Ir)$_2${η^3:η^3-TC4A(S)$_4$} (9b). A solution of [Cp*IrCl$_2$]$_2$ (39.8 mg, 0.10 mmol) and **2** (78.5 mg, 0.10 mmol) in THF (4.0 mL) was stirred overnight at room temperature. After the reaction mixture was dried up in vacuo, the residue was recrystallized from THF-hexane to give complex **9b**·2THF as orange crystals. Yield, 68%. Otherwise, recrystallization from CH_2Cl_2–hexane to give complex **9b** as orange crystals. Anal. Calcd for $C_{60}H_{74}Ir_2S_8{\cdot}2C_4H_8O$: C, 51.68; H, 5.74; S, 16.23. Found: C, 51.19; H, 5.97; S, 16.35. ^{1}H NMR ($CDCl_3$): δ 7.17 (d, 4H, C_6H_2, J = 2.0 Hz), 7.01 (d, 4H, C_6H_2, J = 2.0 Hz), 1.91 (s, 30H, Cp*), 1.07 (s, 36H, *t*-Bu).

Synthesis of (Cp*Rh)$_2$(Cp*RhCl)$_2${η^3:η^3:η^1:η^1-TC4A(O)$_2$(S)$_2$} (10a). To a solution of [Cp*RhCl$_2$]$_2$ (61.5 mg, 0.0996 mmol) and **3** (37.5 mg, 0.0498 mmol) in THF (5.0 mL) was added 4 equiv of NEt_3 (28 μL, 0.20 mmol), and the mixture was stirred overnight at room temperature. The reaction mixture was filtered, and the filtrate was dried up in vacuo. Recrystallization from CH_2Cl_2–hexane gave red crystals of **10a**·4CH_2Cl_2. Yield, 70%. As confirmed by the X-ray analysis, the crystals of **10a**·4CH_2Cl_2 obtained here contain four solvating CH_2Cl_2 molecules. However, the crystals lose three of the solvating CH_2Cl_2 molecules when they are thoroughly dried in vacuo. This has been confirmed by the ^{1}H NMR of the dried sample of **10a**·4CH_2Cl_2, and therefore the calculated values in elemental analysis are based on the formula with one solvating CH_2Cl_2. Anal. Calcd for $C_{80}H_{104}Cl_4O_2Rh_4S_6{\cdot}CH_2Cl_2$: C, 50.45; H, 5.54; S, 9.98. Found: C, 50.05; H, 5.69; S, 10.26. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.6–7.4 (br, 2H, C_6H_2), 7.35–7.25 (br, 2H), 7.25 (d, 2H, C_6H_2, J = 2.2 Hz), 7.00 (d, 2H, C_6H_2, J = 2.2 Hz), 1.86 (s, 30H, Cp*), 1.55 (s, 30H, Cp*), 1.21 (s, 18H, Bu^t), 1.08 (s, 18H, Bu^t). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ 7.48 (s, 2H, C_6H_2), 7.25 (br, 4H, C_6H_2), 7.00 (d, 2H, C_6H_2, J = 2.2 Hz), 1.86 (s, 30H, Cp*), 1.55 (s, 30H, Cp*), 1.21 (s, 18H, Bu^t), 1.08 (s, 18H, Bu^t).

Synthesis of (Cp*Ir)$_2$(Cp*IrCl)$_2${η^3:η^3:η^1:η^1-TC4A(O)$_2$(S)$_2$} (10b). To a solution of [Cp*IrCl$_2$]$_2$ (76.2 mg, 0.956 mmol) and **3** (36.0 mg, 0.0478 mmol) in THF (5.0 mL) was added 4 equiv of NEt_3 (27 μL, 0.19 mmol), and the mixture was stirred overnight at room temperature. The reaction mixture was filtered, and the filtrate was dried up in vacuo. Recrystallization from CH_2Cl_2–hexane gave orange crystals of **10b**·4CH_2Cl_2. Yield, 63%. As confirmed by the X-ray analysis, the crystals of **10b**·4CH_2Cl_2 obtained here contain four solvating CH_2Cl_2 molecules. However, the crystals lose three of the solvating CH_2Cl_2 molecules when they are thoroughly dried in vacuo. This has been confirmed by the ^{1}H NMR of the dried sample of **10b**·4CH_2Cl_2, and therefore the calculated values in elemental analysis are based on the formula with one solvating CH_2Cl_2. Anal. Calcd for

$C_{80}H_{104}Cl_4Ir_4O_2S_6·CH_2Cl_2$: C, 42.56; H, 4.67; S, 8.42. Found: C, 42.75; H, 4.79; S, 8.61. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.7–8.45 (br, 2H, C_6H_2), 8.20–7.9 (br, 2H, C_6H_2), 7.34 (d, 2H, C_6H_2, J = 2.2 Hz), 7.02 (d, 2H, C_6H_2, J = 2.2 Hz), 1.92 (s, 30H, Cp*), 1.54 (s, 30H, Cp*), 1.23 (s, 18H, Bu^t), 1.10 (s, 18H, Bu^t). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ 8.63 (br s, 2H, C_6H_2), 8.10 (br s, 2H, C_6H_2), 7.34 (d, 2H, C_6H_2, J = 2.2 Hz), 7.02 (d, 2H, C_6H_2, J = 2.2 Hz), 1.92 (s, 30H, Cp*), 1.54 (s, 30H, Cp*), 1.23 (s, 18H, Bu^t), 1.10 (s, 18H, Bu^t).

Synthesis of (Cp*RhCl)$_2${η^2-TC4A(OH)$_2$(S)$_2$} (11a). A solution of $[Cp*RhCl_2]_2$ (28.8 mg, 0.0466 mmol) and **3** (35.1 mg, 0.0466 mmol) in THF (5.0 mL) was stirred overnight at room temperature. The solution was dried up in vacuo to give a red solid. Recrystallization from CH_2Cl_2–hexane afforded red crystals of **11a**·CH_2Cl_2. Yield, 77%. Anal. Calcd for $C_{60}H_{76}Cl_2O_2Rh_2S_6·CH_2Cl_2$: C, 52.96; H, 5.68; S, 13.91. Found: C, 52.59; H, 6.02; S, 13.80. ^{1}H NMR (400 MHz, C_4D_8O) δ 7.85 (d, 2H, C_6H_2, J = 2.4 Hz), 7.74 (d, 2H, C_6H_2, J = 2.4 Hz), 7.33 (s, 2H, OH), 6.94 (d, 2H, C_6H_2, J = 2.0 Hz), 6.89 (d, 2H, C_6H_2, J = 2.0 Hz), 1.60 (s, 30H, Cp*), 1.40 (s, 18H, Bu^t), 0.87 (s, 18H, Bu^t).

Synthesis of [(Cp*IrCl)$_2${η^2-TC4A(OH)$_2$(S)$_2$}] (11b). A solution of $[Cp*IrCl_2]_2$ (36.9 mg, 0.0463 mmol) and **3** (34.9 mg, 0.0463 mmol) in THF (5.0 mL) was stirred overnight at room temperature. The solution was dried up in vacuo to give an orange solid. Recrystallization from CH_2Cl_2–hexane afforded orange crystals of **11b**·CH_2Cl_2. Yield, 73%. Anal. Calcd for $C_{60}H_{76}Cl_2Ir_2O_2S_6·CH_2Cl_2$: C, 46.91; H, 5.03; S, 12.32. Found: C, 47.03; H, 5.21; S, 11.70. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2H, C_6H_2, J = 2.9 Hz), 7.70 (d, 2H, C_6H_2, J = 2.9 Hz), 6.95 (d, 2H, C_6H_2, J = 2.2 Hz), 6.86 (d, 2H, C_6H_2, J = 2.2 Hz), 6.67 (s, 2H, OH), 1.65 (s, 30H, Cp*), 1.37 (s, 18H, Bu^t), 0.86 (s, 18H, Bu^t).

Synthesis of [(Cp*Rh)$_2${η^3:η^3-TC4A(O)$_2$(S)$_2$}] (12a). To a solution of Complex **11a** (46.2 mg, 0.0334 mmol) in THF (5.0 mL) was added 2 equiv of NEt_3 (9.3 μL, 0.067 mmol) at room temperature and the mixture was stirred overnight. The reaction mixture was dried up in vacuo, and the residue was extracted with hexane. The solution was concentrated and cooled in refrigerator overnight to give red crystals of **12a**. Yield, 98%. Anal. Calcd for $C_{60}H_{74}O_2Rh_2S_6$: C, 58.81; H, 6.09; S, 15.70. Found: C, 59.16; H, 6.52; S, 15.06. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, C_6H_2, J = 2.0 Hz), 7.26 (d, 4H, C_6H_2, J = 2.0 Hz), 6.98 (d, 2H, C_6H_2, J = 2.4 Hz), 6.69 (d, 2H, C_6H_2, J = 2.4 Hz), 1.85 (s, 30H, Cp*), 1.26 (s, 18H, Bu^t), 0.88 (s, 18H, Bu^t).

Synthesis of [(Cp*Ir)$_2${η^3:η^3-TC4A(O)$_2$(S)$_2$}] (12b). To a solution of Complex **11b** (48.9 mg, 0.0313 mmol) in THF (5.0 mL) was added 2 equiv of NEt_3 (8.7 μL, 0.063 mmol) at room temperature and the mixture was stirred overnight. The reaction mixture was dried up in vacuo, and the residue was extracted with hexane. The solution was concentrated and cooled in refrigerator overnight to give orange crystals of **12b**. Yield, 93%. Anal. Calcd for $C_{60}H_{74}Ir_2O_2S_6$: C, 51.33; H, 5.31; S, 13.70. Found: C, 51.54; H, 5.52; S, 13.14. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, C_6H_2, J = 2.0 Hz), 7.33 (d, 2H, C_6H_2, J = 2.0 Hz), 6.97 (d, 2H, C_6H_2, J = 2.2 Hz), 6.77 (d, 2H, C_6H_2, J = 2.2 Hz), 1.92 (s, 30H, Cp*), 1.27 (s, 18H, Bu^t), 0.91 (s, 18H, Bu^t).

Reaction of 12a and [Cp*RhCl$_2$]$_2$. A solution of **12a** (95.5 mg, 0.0799 mmol) and [Cp*RhCl$_2$]$_2$ (48.2 mg, 0.0799 mmol) in THF (5.0 mL) was stirred overnight. The solution was dried up in vacuo to give a red solid. Recrystallization from CH_2Cl_2–hexane afforded red crystals of **10a**·4CH_2Cl_2. Yield, 70%.

Reaction of 12b and [Cp*IrCl$_2$]$_2$. A solution of **12b** (97.7 mg, 0.0696 mmol) and [Cp*IrCl$_2$]$_2$ (55.4 mg, 0.0696 mmol) in THF (5.0 mL) was stirred overnight. The solution was dried up in vacuo to give an orange solid. Recrystallization from CH_2Cl_2–hexane afforded orange crystals of **10b**·4CH_2Cl_2. Yield, 62%.

X-ray Crystal Structure Determination of 8b, 9a, 9b and 10b. Single crystals suitable for X-ray diffraction study were mounted on a glass fiber for **8b, 9a** and **9b** or sealed in a glass capillary for **10b** and used for data collection. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation. Empirical absorption correction and Lorentz-polarization corrections were applied. The structures were solved by direct methods (SIR92)[5], expanded using Fourier techniques[6] and refined by full-matrix least-squares method on F_2 (SHELXL97)[7]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model. ORTEP diagrams of **8b, 9a** and **9b** are shown in Figure S1-S3.

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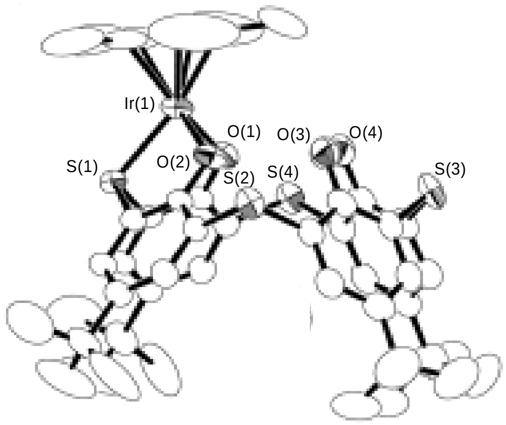

Fig. S1 ORTEP drawing of **8b** with the hydrogen atoms and the solvents omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)–S(1) = 2.358(2), Ir(1)–O(1) = 2.078(5), Ir(1)–O(2) = 2.088(5).

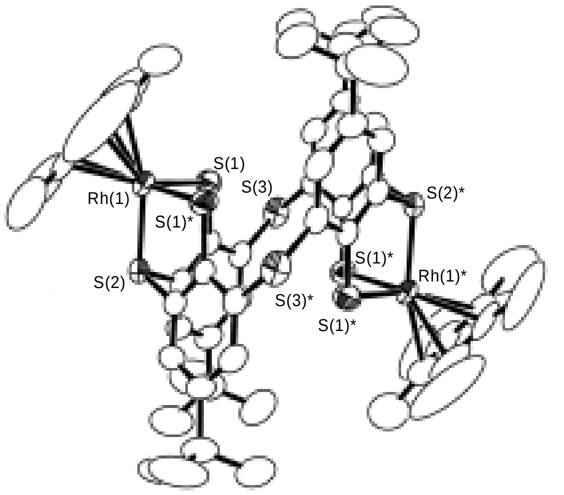

Fig. S2 ORTEP drawing of **9a** with the hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Rh(1)–S(1) = 2.337(2), Rh(1)–S(2) = 2.284(2).

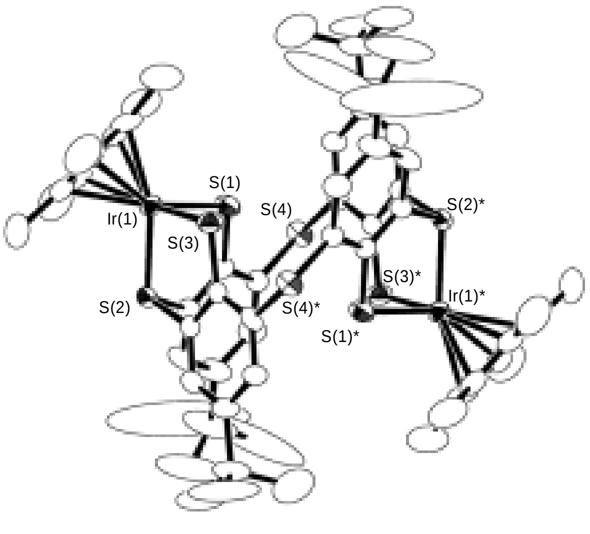

Fig. S3 ORTEP drawing of **9b** with the hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)–S(1) = 2.343(2), Ir(1)–S(2) = 2.291(1), Ir(1)–S(3) = 2.349(2).