Supporting Information

Switching of Charge Transport Pathways via Delocalization Changes in Single-molecule Metallacycles Junctions

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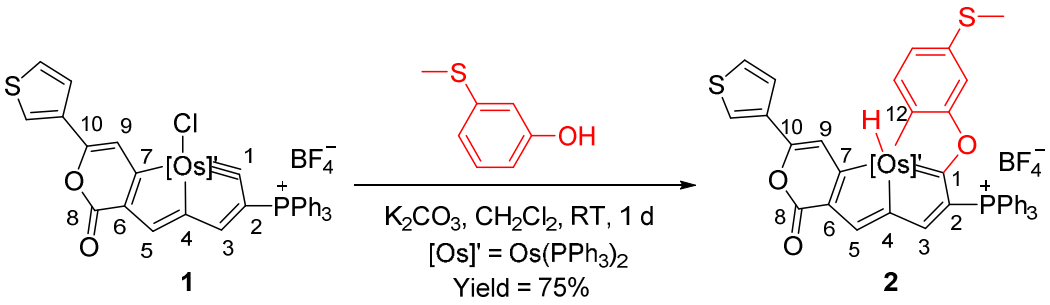
Contents

1. Compounds Syntheses Procedures

General information

All syntheses were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane) prior to use. The lactone-fused osmapentalyne **1** was synthesized according to the published literature[1]. The other reagents and solvents were used as purchased from commercial sources without further purification. Column chromatography was performed on silica gel (200–300 mesh) in air. NMR spectra was collected on a Brucker AV-600 spectrometer (600 MHz). ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ) are relative to tetramethylsilane, and $^{31}P\{^{1}H\}$ NMR chemical shifts are relative to 85% H_3PO_4. Two-dimensional and one-dimensional NMR spectra are abbreviated as HSQC (heteronuclear single quantum coherence), HMBC (heteronuclear multiple bond coherence) and DEPT (distortionless enhancement by polarization transfer). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Elemental analysis (EA) data were collected on a Vario EL III elemental analyzer. The high-resolution mass spectra (HRMS) experiments were performed on a Bruker En Apex Ultra 7.0T FT-MS. Absorption spectra were recorded on a Shimadzu UV2550 UV–vis spectrophotometer.

Preparation and characterization of 2



A mixture of compound **1** (100 mg, 0.075 mmol), 3-(Methylsulfanyl)benzenol (53 mg, 0.38 mmol) and K_2CO_3 (52 mg, 0.38 mmol) in 10 mL dichloromethane was stirred at RT for 1 d to give a violet solution, and then the solid suspension was removed by filtration. The volume of the filtrate was reduced under vacuum to approximately 2 mL, and then loaded on silica gel column eluted by dichloromethane/methanol (10/1). The violet band was collected, and the solvent was evaporated to dryness under vacuum to give a violet solid. Yield, 81 mg, 75%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 9.00 (s, 1H, H5), 8.81 (s, 1H, H3), 6.03 (s, 1H, H9), 2.32 (s, 3H, SC*H*$_3$), -2.89 (t, $J_{P\text{-}H}$ = 14.6 Hz, 1H, Os*H*), 7.90–6.56 ppm (51H, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 9.23 (s, C*P*Ph$_3$), -3.28 ppm (s, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 255.3 (td, J_{PC} = 5.4 Hz, J_{PC} = 5.4 Hz, C1), 201.4 (t, J_{PC} = 10.0 Hz, C7), 191.7 (dt, J_{PC} = 27.2 Hz, J_{PC} = 3.6 Hz, C4), 169.8 (d, J_{PC} = 14.8 Hz, C3), 169.3 (s, C10), 160.9 (s, C5), 158.1 (s, C8), 147.7 (s, C6), 132.1 (t, J_{PC} = 9.1 Hz, C12), 121.7 (d, J_{PC} = 73.7 Hz, C2), 110.4 (s, C9), 16.5 (s, S*C*H$_3$), 148.6–120.1 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{75}H_{58}BF_4O_3OsP_3S_2$: C 62.50, H 4.06; found: C 62.15, H 4.35. HRMS (ESI): *m/z* calcd for $[C_{75}H_{58}O_3OsP_3S_2]^+$, 1355.2653; found, 1355.2662.

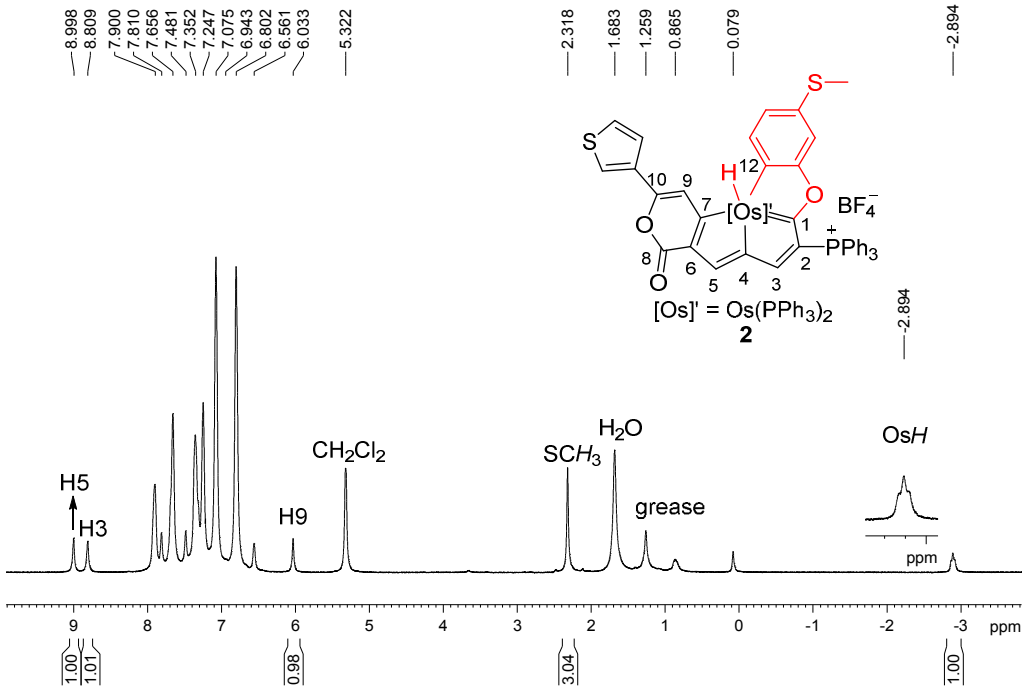


Figure S1. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2.**

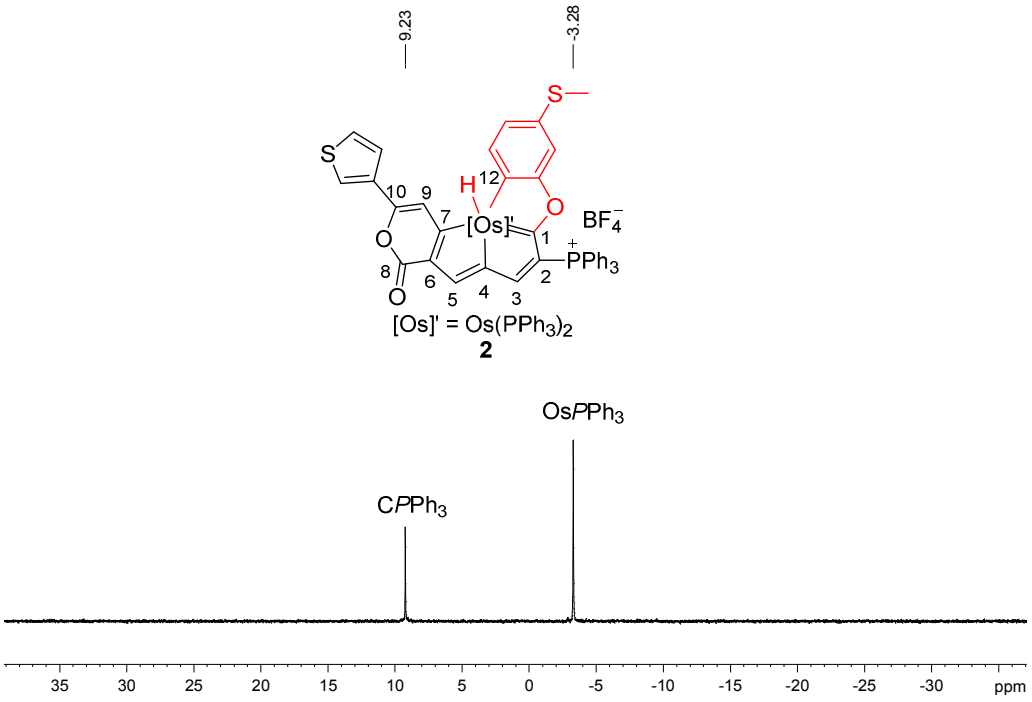


Figure S2. The ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2.**

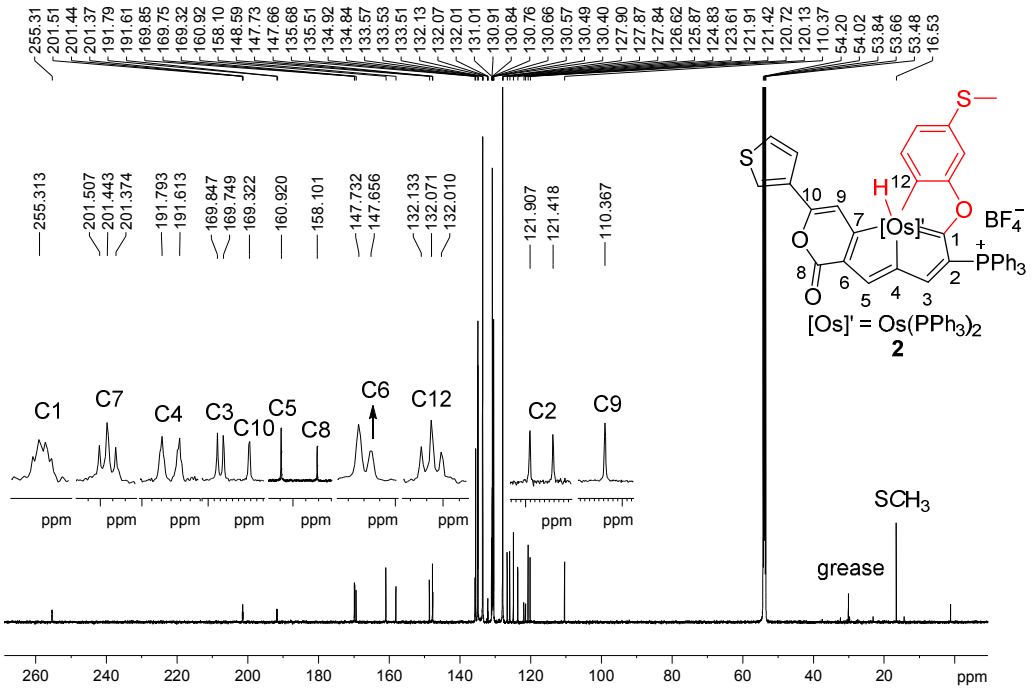


Figure S3. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2.**

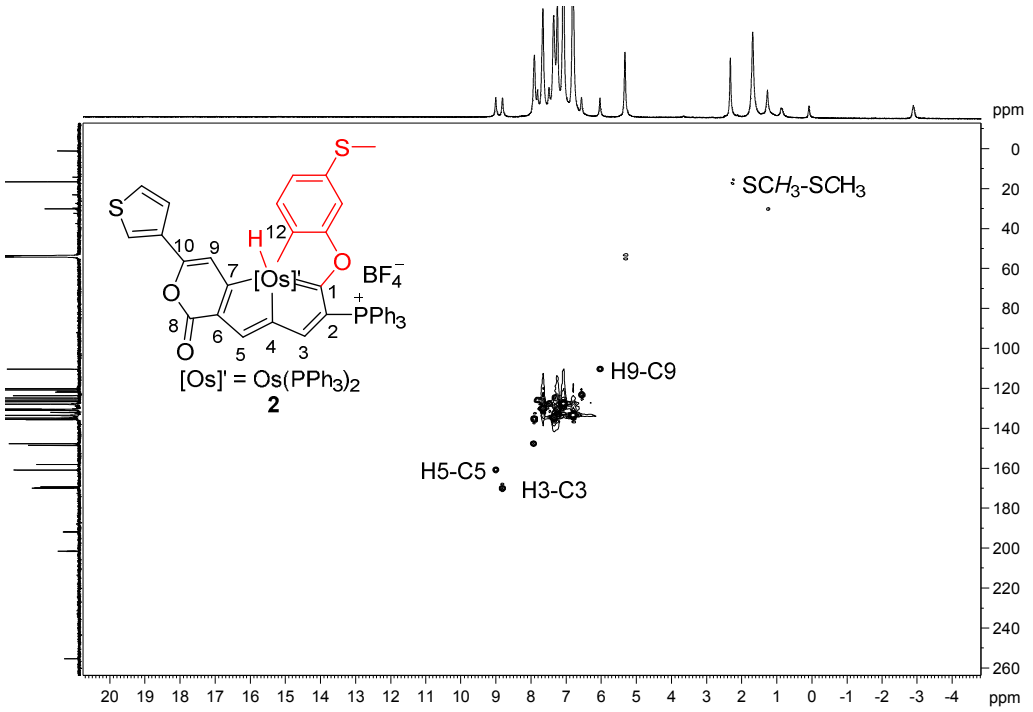


Figure S4. Two-dimensional ^{1}H-^{13}C HSQC spectrum of complex **2** in CD_2Cl_2.

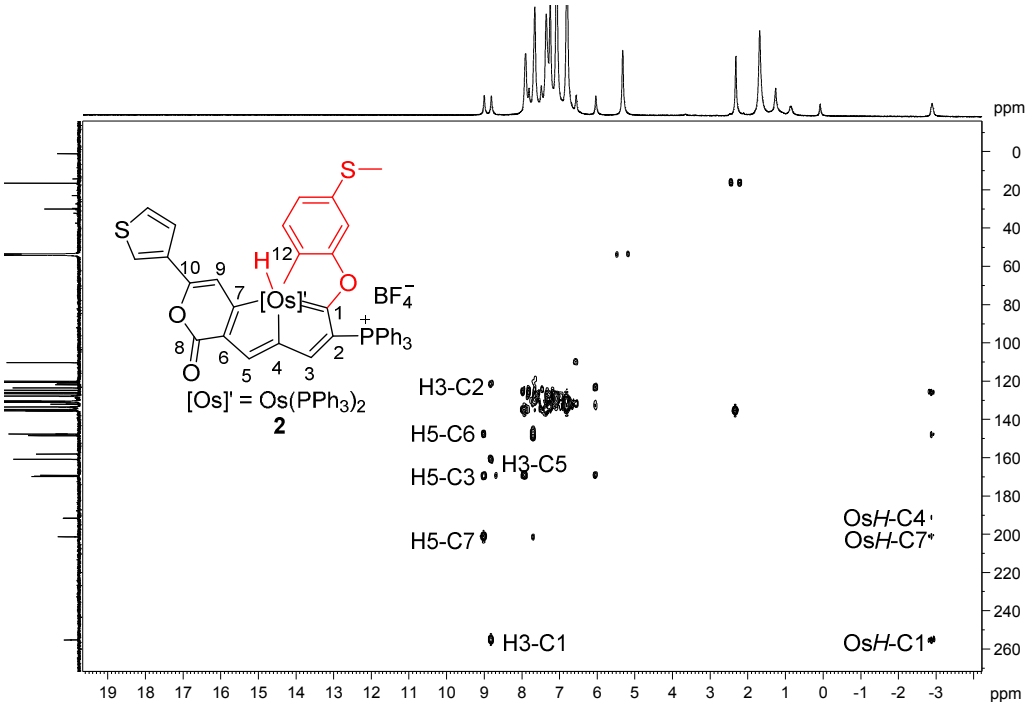


Figure S5. Two-dimensional ^{1}H-^{13}C HMBC spectrum of complex **2** in CD_2Cl_2.

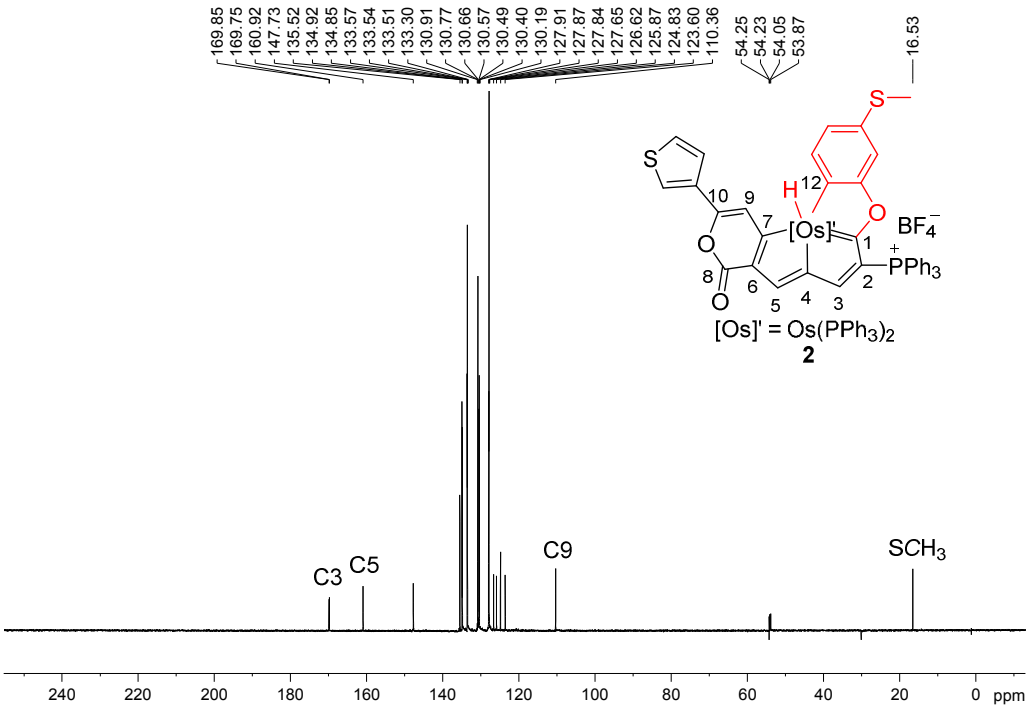


Figure S6. DEPT-135 spectrum (150.9 MHz, CD_2Cl_2) of complex **2** in CD_2Cl_2.

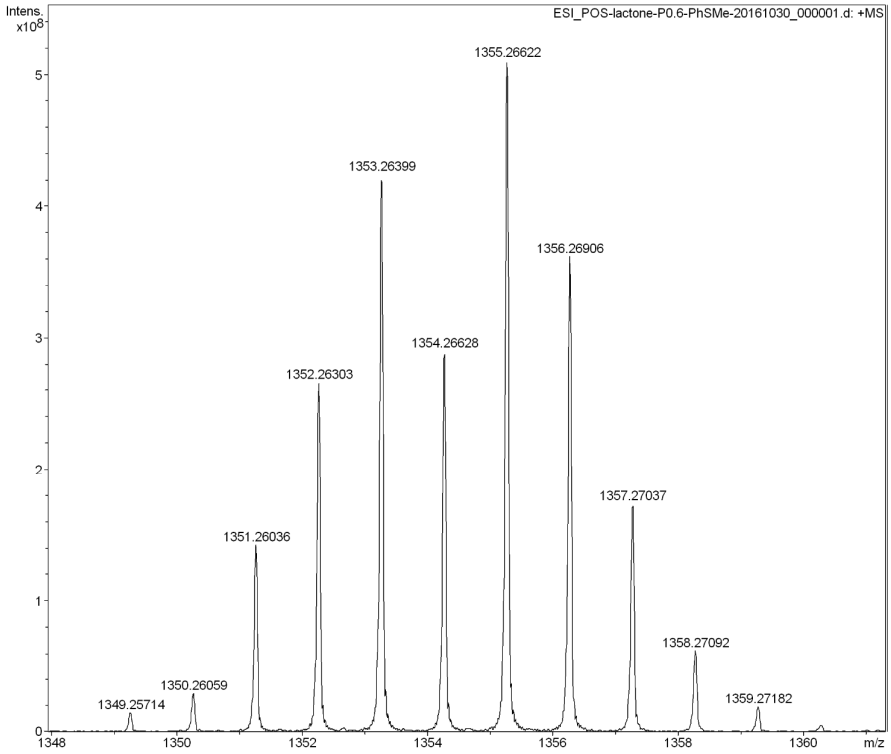
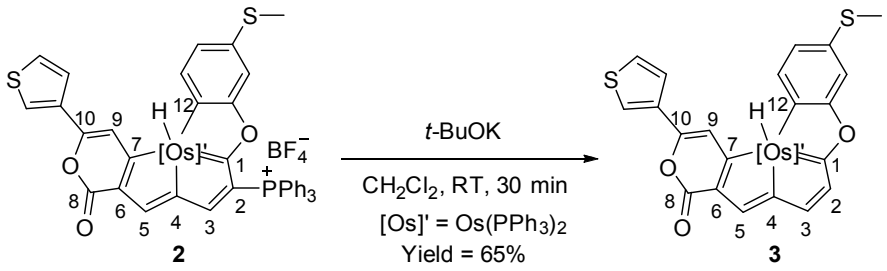


Figure S7. Positive-ion ESI-MS spectrum of $[\mathbf{2}]^+$ measured in dichloromethane.

Preparation and characterization of 3



A mixture of compound **2** (80 mg, 0.056 mmol), and *t*-BuOK (19 mg, 0.17 mmol) in 5 mL dichloromethane was stirred at RT for 30 min to give a red solution, and then the solid suspension was removed by filtration. The volume of the filtrate was reduced under vacuum to approximately 2 mL, and then loaded on silica gel column eluted by dichloromethane/acetone (20/1). The red band was collected, and the solvent was evaporated to dryness under vacuum to give a violet solid. Yield, 39 mg, 65%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 8.72 (s, 1H, H3), 8.32 (s, 1H, H5), 7.01 (s, 1H, H2), 6.54 (s, 1H, H9), 2.35 (s, 3H, SCH_3), -3.04 (t, J_{PH} = 15.3 Hz,

1H, Os*H*), 8.19–6.61 ppm (51H, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = -1.32 ppm (s, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 260.7 (t, J_{PC} = 6.4 Hz, C1), 194.9 (s, C4), 187.8 (t, J_{PC} = 10.9 Hz, C7), 169.5 (s, C10), 167.0 (s, C3), 158.9 (s, C8), 149.3 (s, C5), 147.2 (s, C6), 142.9 (s, C2), 133.5 (s, C12), 111.2 (s, C9), 17.3 (s, S*C*H$_3$), 148.2–122.8 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{57}H_{44}O_3OsP_2S_2$: C 62.62, H 4.06; found: C 62.60, H 4.37. HRMS (ESI): *m/z* calcd for $[C_{57}H_{44}O_3OsP_2S_2]^+$, 1094.1817; found, 1094.1816.

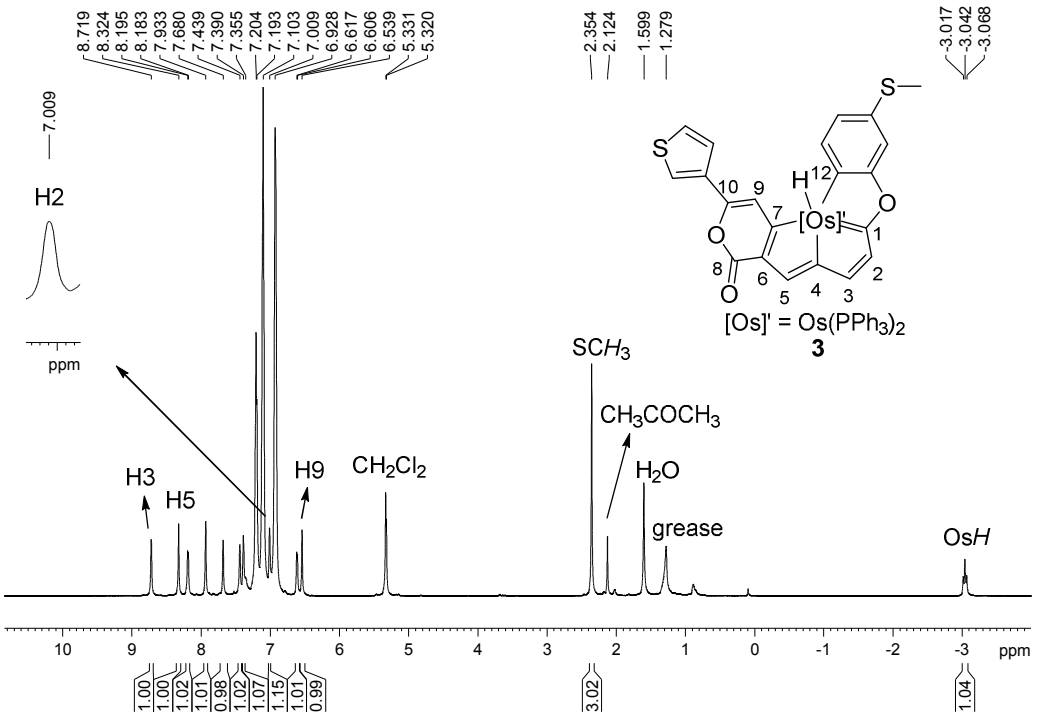


Figure S8. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **3**.

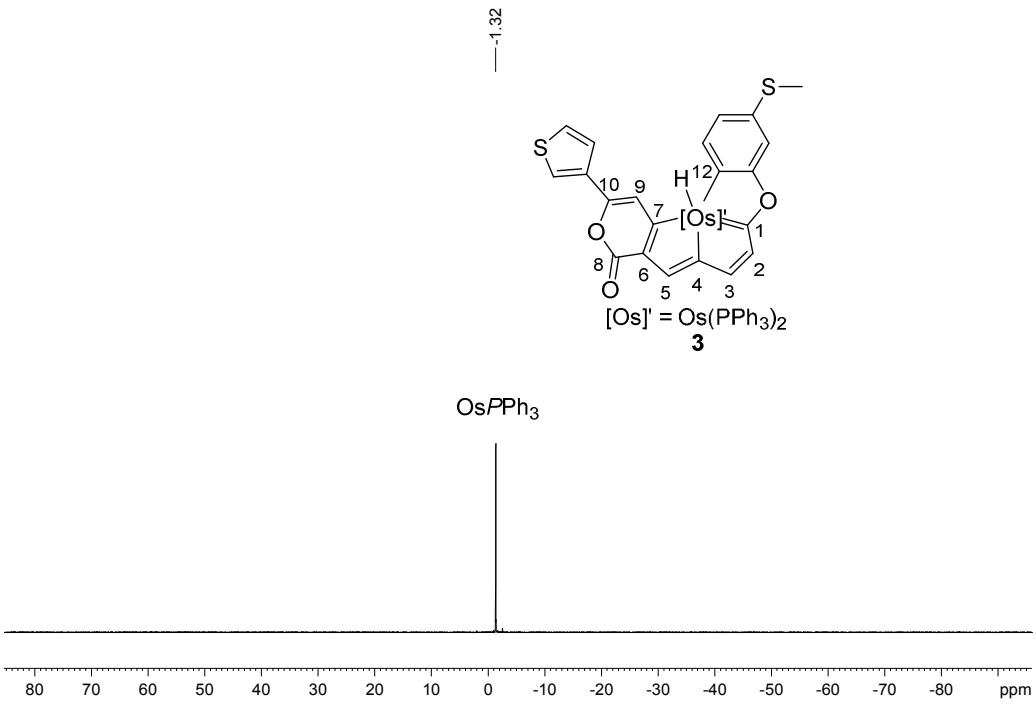


Figure S9. The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **3**.

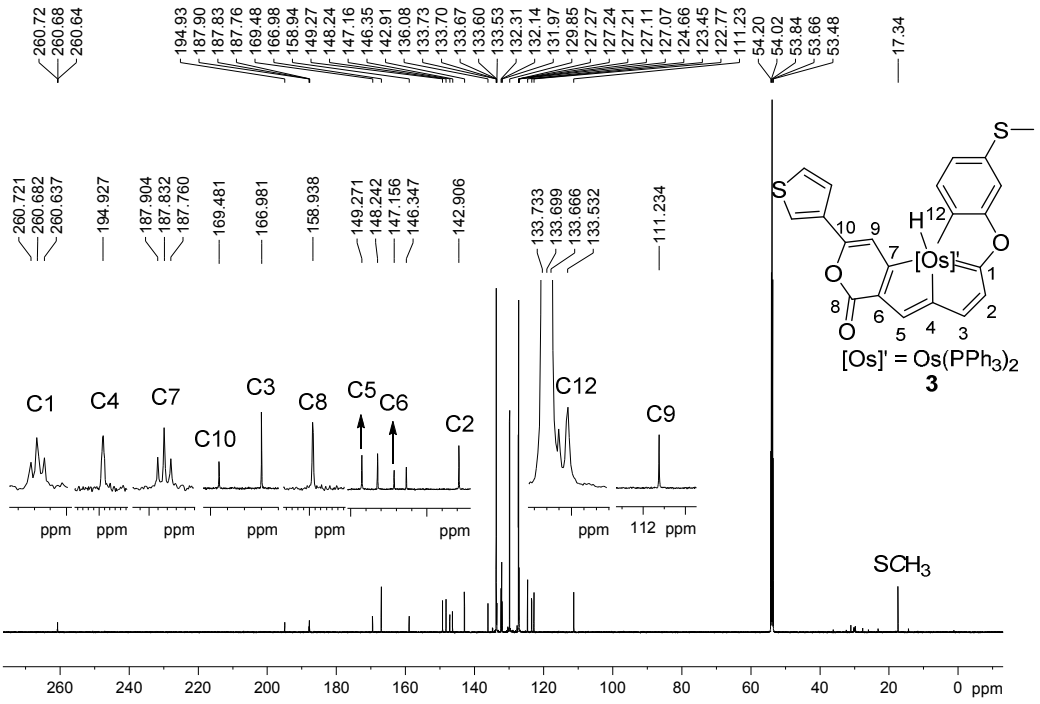


Figure S10. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **3**.

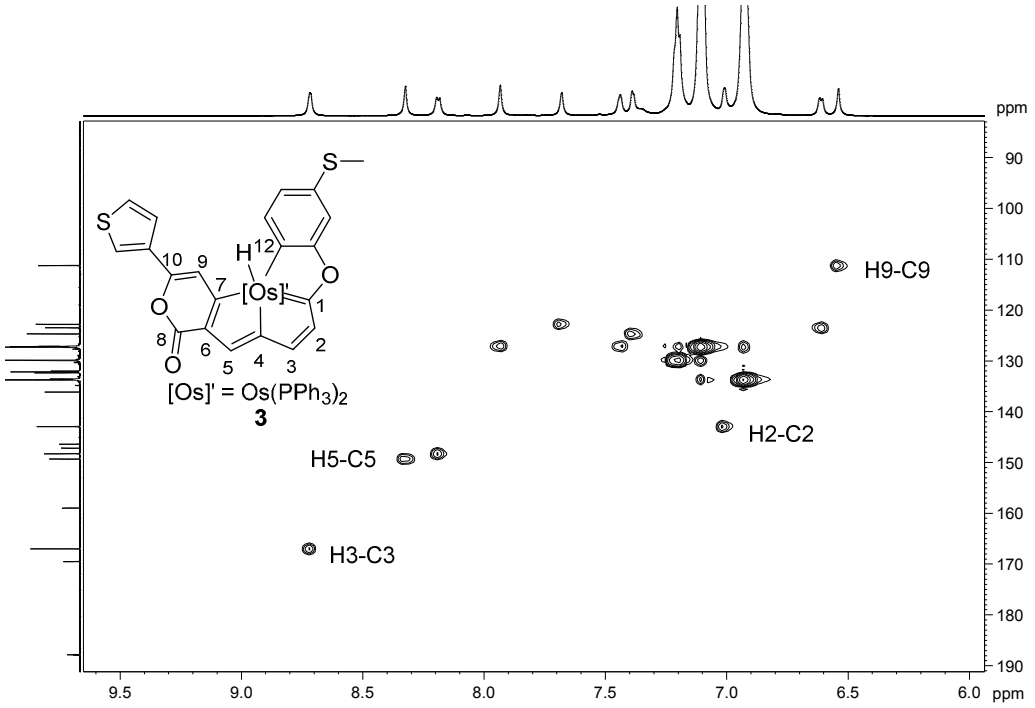


Figure S11. Two-dimensional ^{1}H-^{13}C HSQC spectrum of complex **3** in CD_2Cl_2.

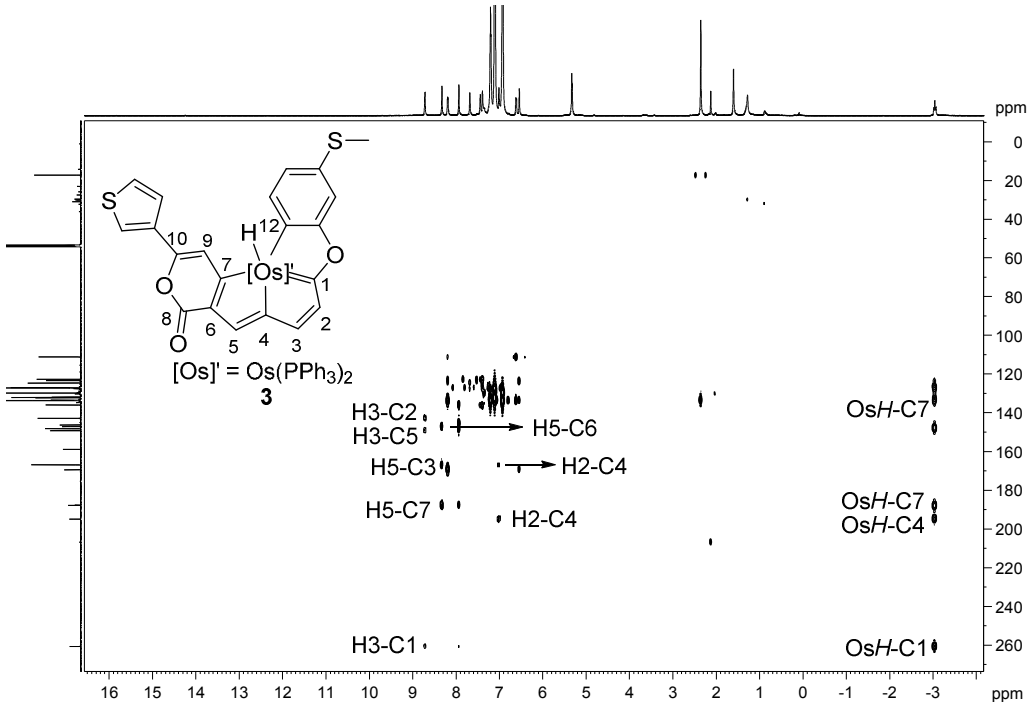


Figure S12. Two-dimensional ^{1}H-^{13}C HMBC spectrum of complex **3** in CD_2Cl_2.

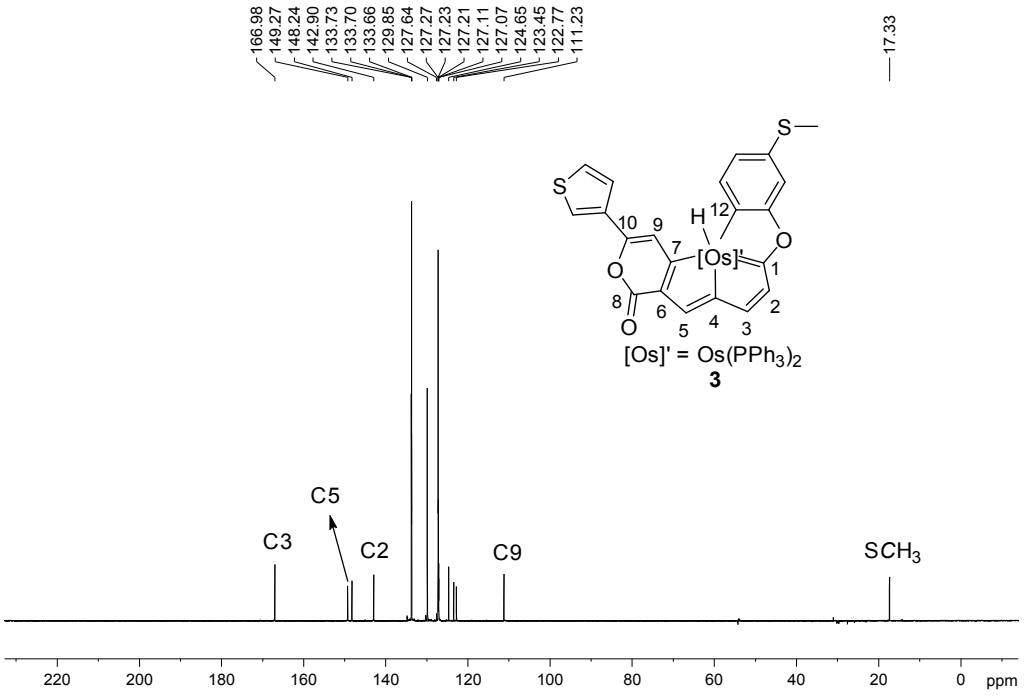


Figure S13. DEPT-135 spectrum (150.9 MHz) of complex **3** in CD_2Cl_2.

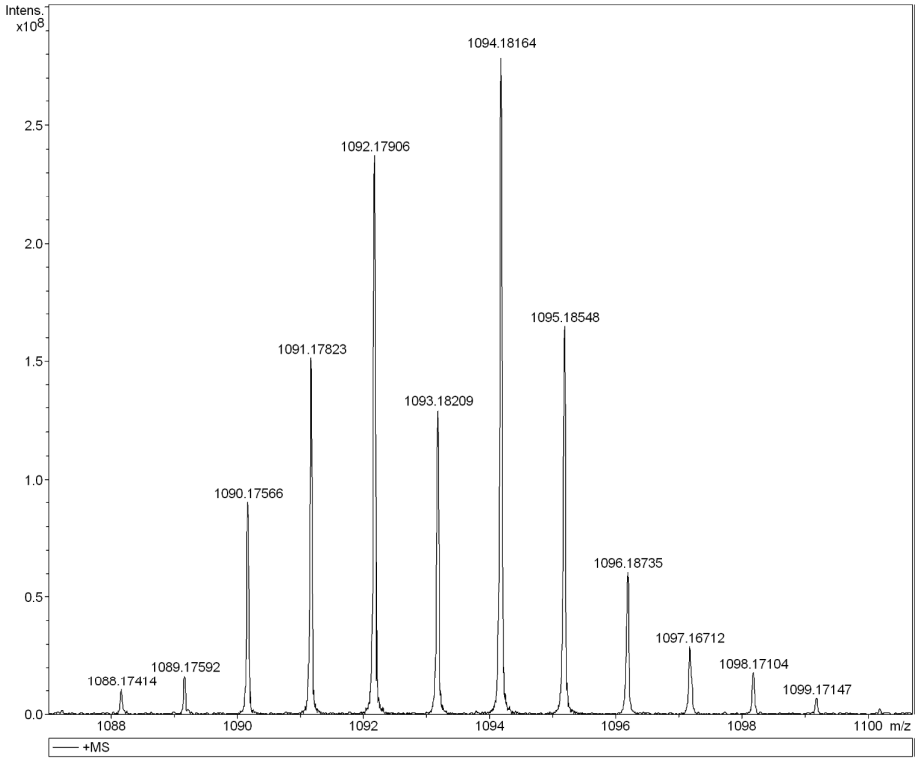
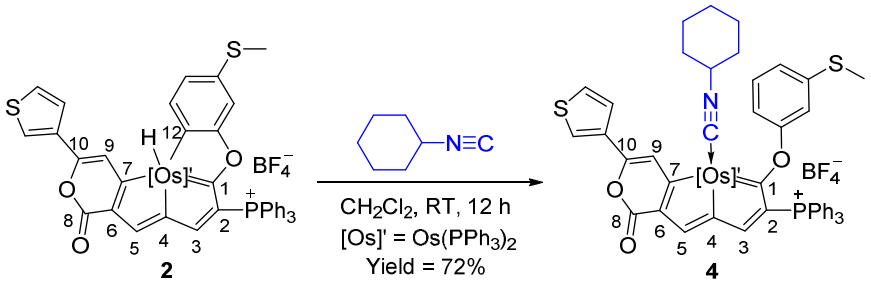


Figure S14. Positive-ion ESI-MS spectrum of $[\mathbf{3}]^+$ measured in dichloromethane.

Preparation and characterization of 4



Cyclohexyl isocyanide (42.9 μL, 0.345 mmol) was added to a solution of compound **2** (100 mg 0.069 mmol) in 5 mL dichloromethane. The mixture was stirred at RT for 12 h to give a red solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then loaded on silica gel column eluted by dichloromethane/methanol (50/1). The red band was collected, and the solvent was evaporated to dryness under vacuum to give a red solid. Yield, 77 mg, 72%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 9.19 (s, 1H, H5), 8.70 (d, J_{PH} = 6.3 Hz 1H, H3), 6.68 (s, 1H, H9), 3.54 (br, 1H, Cy), 2.30 (s, 3H, SCH_3), 1.67–1.50 (br, 4H, Cy), 1.20–1.06 (br, 6H, Cy), 7.73–6.56 ppm (52H, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 12.15 (s, C*P*Ph$_3$), -3.00 ppm (s, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 239.1 (td, J_{PC} = 9.2 Hz, J_{PC} = 3.6 Hz, C1), 209.9 (t, J_{PC} = 12.7 Hz, C7), 190.4 (dt, J_{PC} = 29.0, J_{PC} = 5.4 Hz, C4), 165.5 (d, J_{PC} = 18.2 Hz, C3), 159.6 (s, C5), 150.3 (s, C6), 146.4 (s, C8), 144.6 (t, J_{PC} = 12.7 Hz, Os*C*NCy), 136.7 (d, J_{PC} = 65.4 Hz, C2), 136.2 (s, C10) 122.9 (s, C9), 55.4 (s, Cy), 33.8 (s, Cy), 25.2 (s, Cy), 24.4 (s, Cy), 15.7 (s, S*C*H$_3$), 159.0–116.1 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{82}H_{69}BF_4NO_3OsP_3S_2$: C 63.52, H 4.49, N 0.90; found: C 63.69, H 4.68, N 1.02. HRMS (ESI): *m/z* calcd for $[C_{82}H_{69}NO_3OsP_3S_2]^+$, 1464.3546; found, 1464.3543.

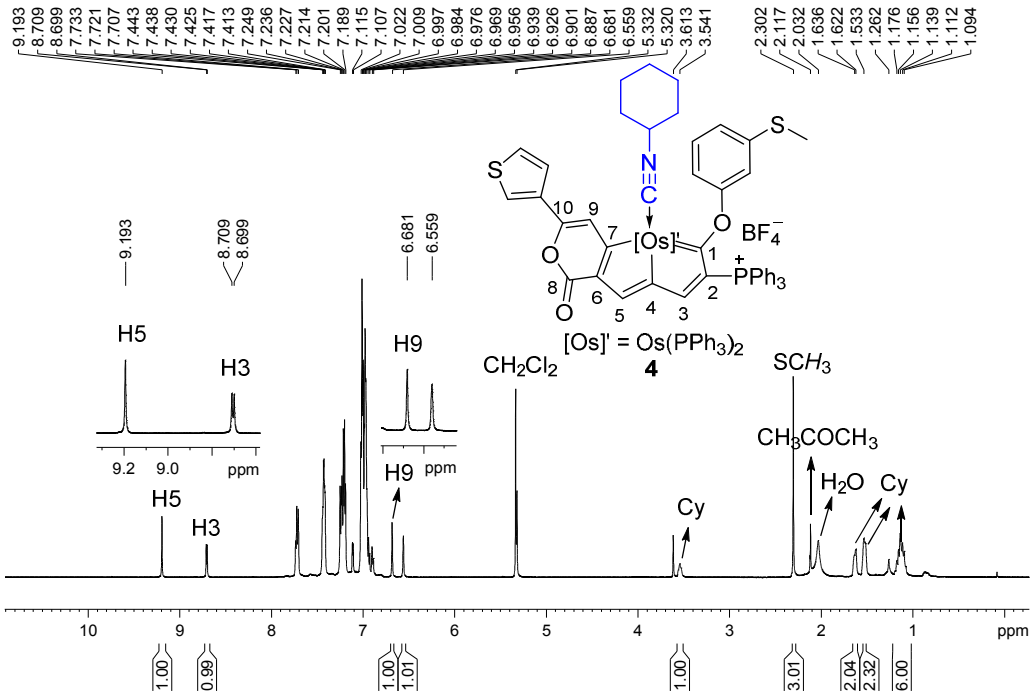


Figure S15. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **4**.

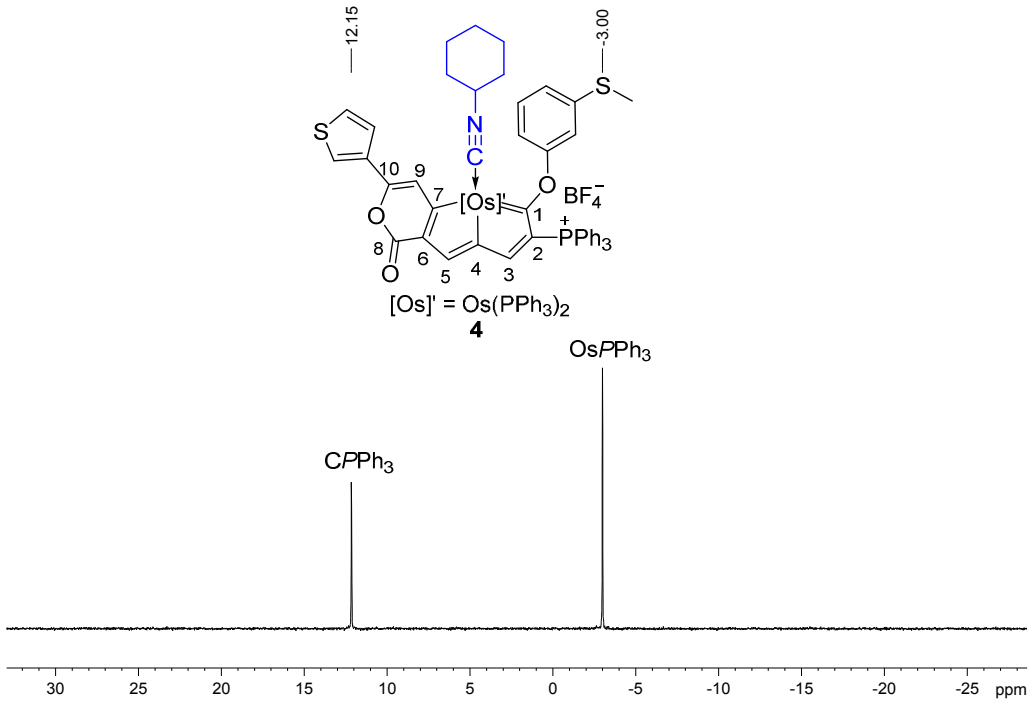


Figure S16. The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **4**.

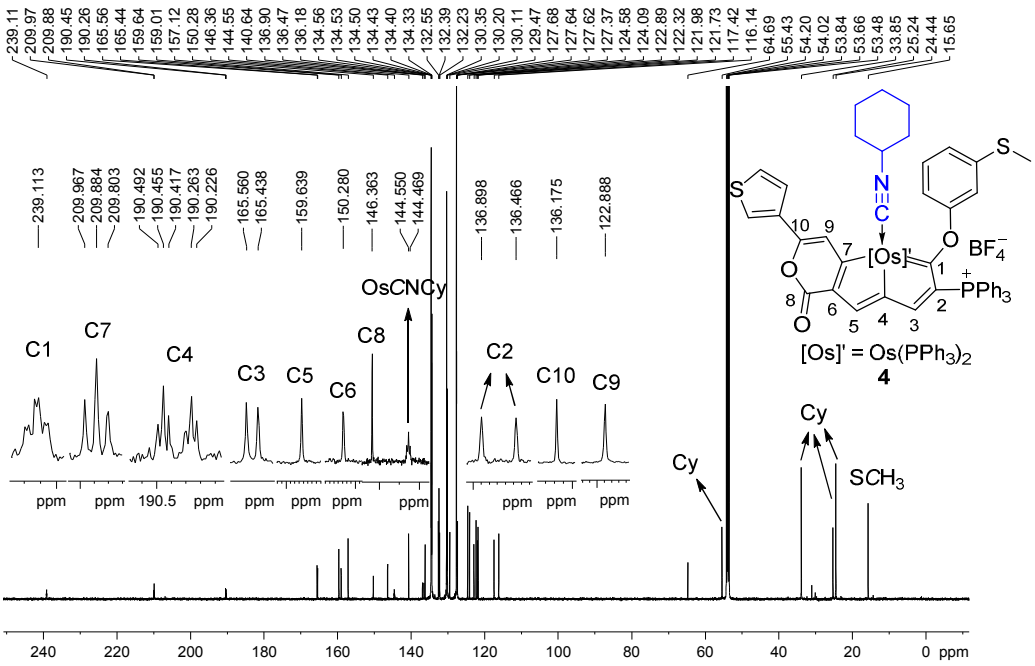


Figure S17. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **4**.

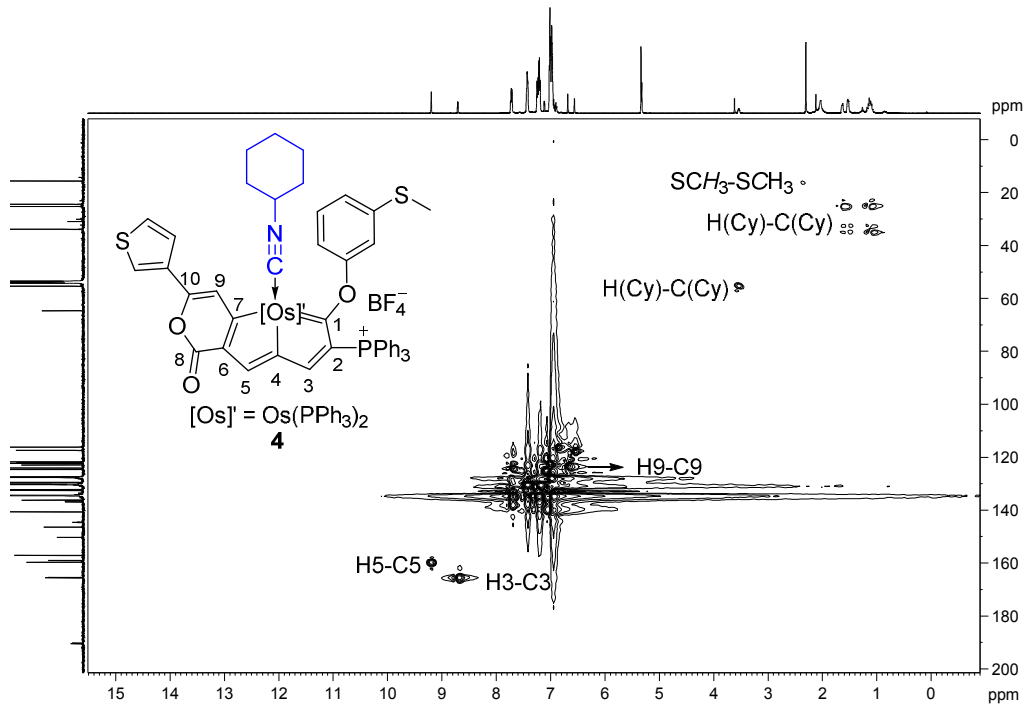


Figure S18. Two-dimensional ^{1}H-^{13}C HSQC spectrum of complex **4** in CD_2Cl_2.

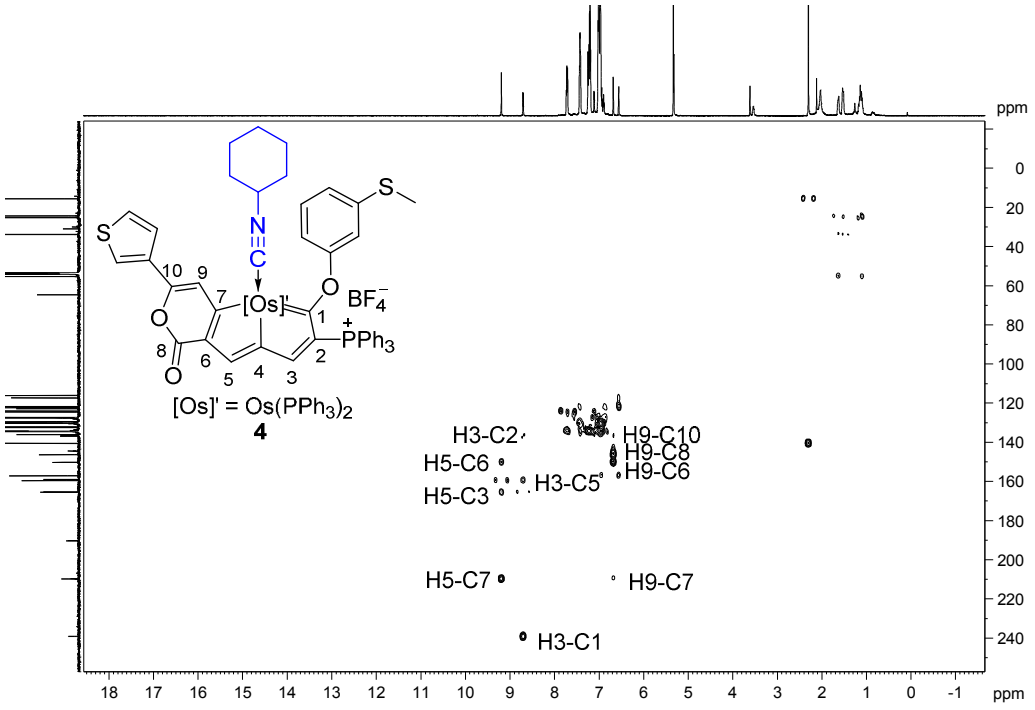


Figure S19. Two-dimensional ^{1}H-^{13}C HMBC spectrum of complex **4** in CD_2Cl_2.

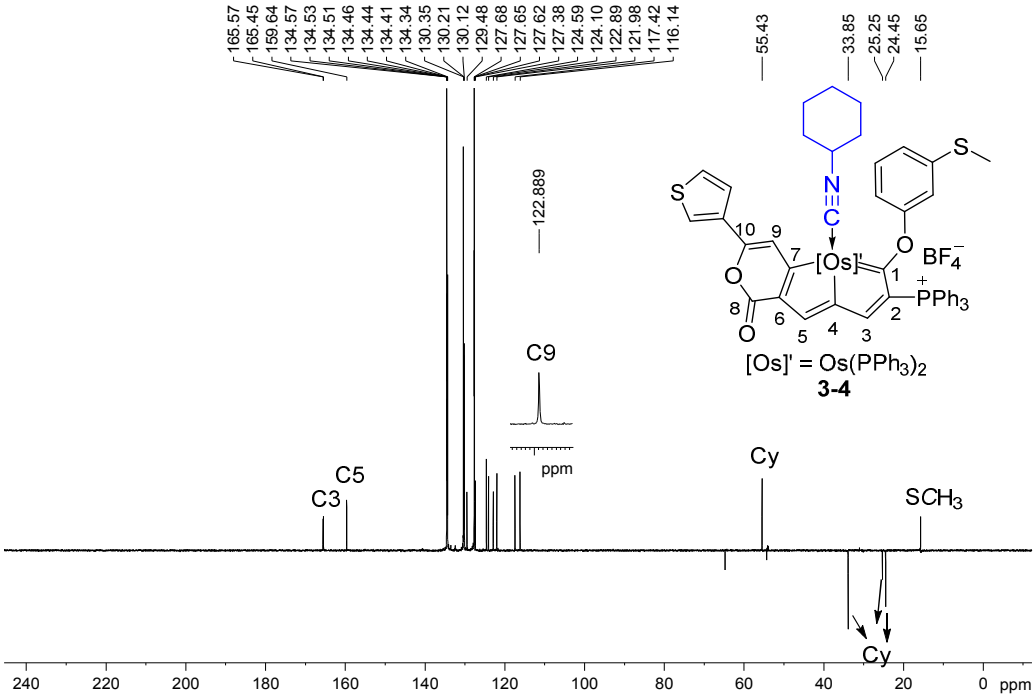


Figure S20. DEPT-135 spectrum (150.9 MHz) of complex **4** in CD_2Cl_2.

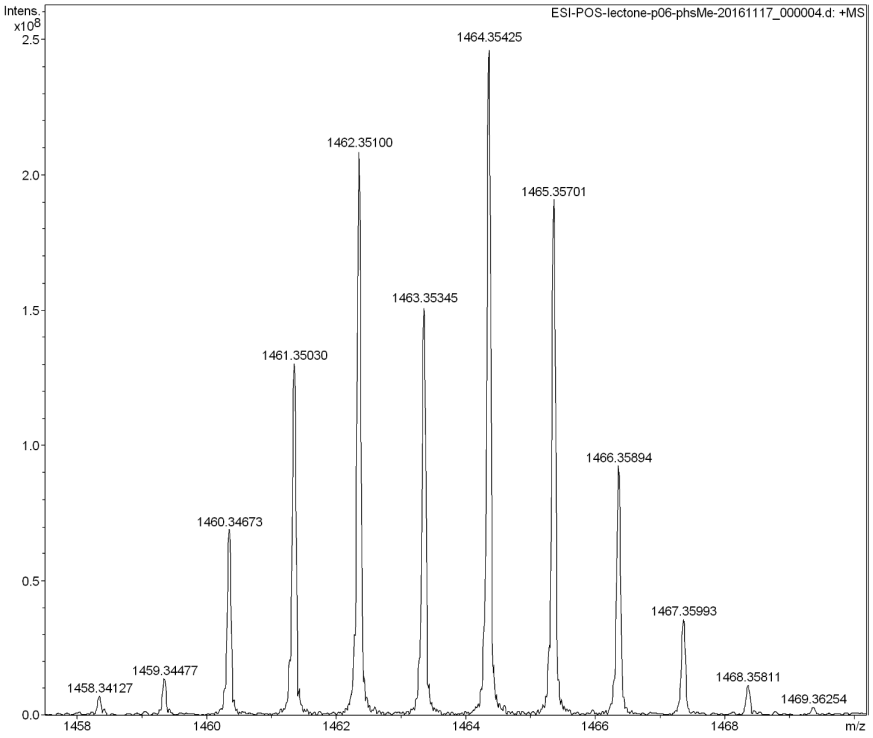


Figure S21. Positive-ion ESI-MS spectrum of $[\mathbf{4}]^+$ measured in dichloromethane.

2. X-ray Crystallographic Analysis

All single crystals suitable for X-ray diffraction were grown from dichloromethane solution layered with hexane. Single-Crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector for **2**, and **4** with a Cu Kα radiation (λ = 1.54184 Å). Single-Crystal X-ray diffraction data was collected on an Aglient supernova diffractometer with a Cu Kα radiation (λ = 1.54184 Å) for **3**. Multi-scan absorption corrections were applied for **2**, **3**, and **4**. Using Olex2[2], the structure of **2**, **3**, and **4** were solved with ShelXT[3] structure solution program using Direct methods and refined with the ShelXL[4] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Some of the solvent molecules and phenyl groups were disordered and refined with suitable restrains. CCDC-1554106 (**2**), CCDC-1554107 (**3**), and CCDC-1554108 (**4**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal Data for 2: $C_{77}H_{62}BCl_2F_4O_4OsP_3S_2$ $[C_{75}H_{58}O_3OsP_3S_2]BF_4 \cdot CH_2Cl_2 \cdot H_2O$ (*Mr* =1544.19 g/mol): monoclinic, crystal dimension 0.20 × 0.20 × 0.20 mm, space group $P2_1/n$ (no. 14), a = 11.65604(17) Å, b = 24.1742(4) Å, c = 24.0038(4) Å, α = 90°, β = 100.4787(15)°, γ = 90°, V = 6650.88(18) Å^3, Z = 4, T = 197.7(6) K, μ(CuKα) = 6.146 mm^{-1}, *Dcalc* = 1.543 g/cm^3, 22601 reflections measured (7.314° ≤ 2Θ ≤ 124.272°), 10407 unique (R_{int} = 0.0358, R_{sigma} = 0.0505) which were used in all calculations. The final R_1 was 0.0309 (I > 2σ(I)) and wR_2 was 0.0758 (all data). GOF = 1.045. Residual electron density (e. Å^{-3}) max/min: 0.84/-0.66.

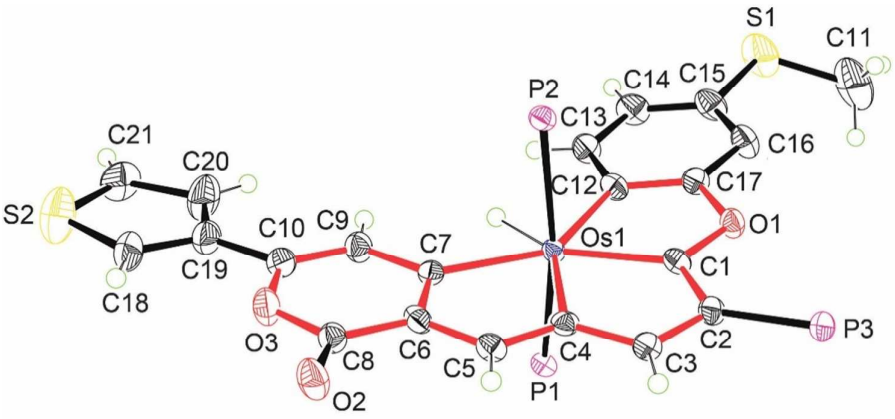


Figure S22. X-ray molecular structure for the cation of complex **2** drawn with 50% probability level. The phenyl groups in PPh_3 groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C12 2.152(3), Os1–C1 2.056(3), Os1–C4 2.115(3), Os1–C7 2.121(3), C12–C17 1.388(5), C17–O1 1.398(4), O1–C1 1.340(4), C1–C2 1.426(5), C2–C3 1.392(4), C3–C4 1.401(5), C4–C5 1.383(5), C5–C6 1.383(5), C6–C7 1.411(5), C7–C9 1.420(5), C9–C10 1.357(5), C10–O3 1.365(5), O3–C8 1.378(4), C8–C6 1.451(5), C8–O2 1.212(5); Os1–C12–C17 115.2(2), C12–C17–O1 116.3(3), C17–O1–C1 111.6(3), O1–C1–Os1 123.4(2), C1–Os1–C12 73.14(13), Os1–C1–C2 122.2(2), C1–C2–C3 110.9(3), C2–C3–C4 114.7(3), C3–C4–Os1 118.9(2), C4–Os1–C1 73.14(12), Os1–C4–C5 119.2(2), C4–C5–C6 113.7(3), C5–C6–C7 116.2(3), C6–C7–Os1 116.3(2), C7–Os1–C4 74.51(12), C6–C7–C9 114.7(3), C7–C9–C10 122.7(3), C9–C10–O3 121.3(3), C10–O3–C8 121.9(3), O3–C8–C6 116.4(3), C8–C6–C7 123.0(3).

Crystal Data for 3: $C_{77}H_{84}O_{13}OsP_2S_2$ $[C_{57}H_{44}O_3OsP_2S_2]\cdot 5C_4H_8O_2$ (*Mr* =1533.70 g/mol): monoclinic, crystal dimension 0.40 × 0.30 × 0.25 mm space group $P2_1/n$ (no. 14), a = 15.7051(2) Å, b = 18.7402(2) Å, c = 24.2360(3) Å, α = 90°, β = 103.7050(10)°, γ = 90°, V = 6929.97(15) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 5.000 mm^{-1}, *Dcalc* = 1.470 g/cm^3, 26083 reflections measured (7.472° ≤ 2Θ ≤ 130°), 11776 unique (R_{int} = 0.0387 R_{sigma} = 0.0398) which were used in all calculations. The final R_1 was 0.0435 (I > 2σ(I)) and wR_2 was 0.1165 (all data). GOF = 1.024. Residual electron density (e. Å^{-3}) max/min: 1.94/-1.62.

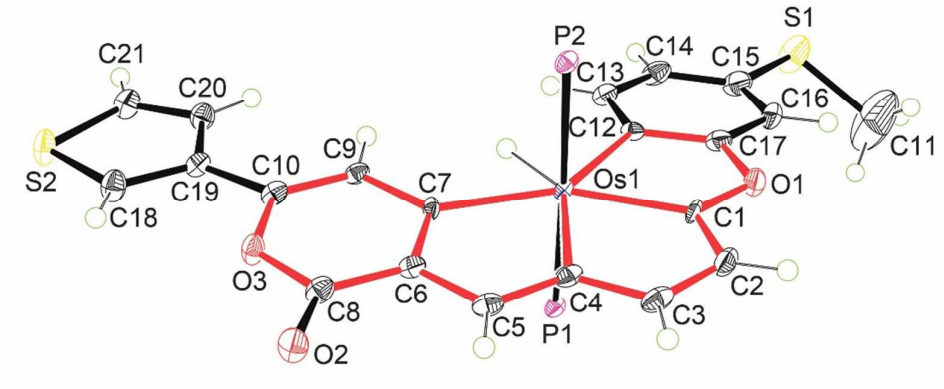


Figure S23. X-ray molecular structure for the cation of complex **3** drawn with 50% probability level. The phenyl groups in PPh_3 groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C12 2.161(3), Os1–C1 2.059(3), Os1–C4 2.131(4), Os1–C7 2.121(3), C12–C17 1.395(5), C17–O1 1.355(5), O1–C1 1.343(5), C1–C2 1.410(5), C2–C3 1.363(6), C3–C4 1.427(5), C4–C5 1.375(6), C5–C6 1.412(5), C6–C7 1.402(5), C7–C9 1.441(5), C9–C10 1.343(5), C10–O3 1.373(4), O3–C8 1.386(5), C8–C6 1.444(5), C8–O2 1.214(5); Os1–C12–C17 114.6(3), C12–C17–O1 116.7(3), C17–O1–C1 112.3(3), O1–C1–Os1 122.9(3), C1–Os1–C12 73.43(15), Os1–C1–C2 121.7(3), C1–C2–C3 112.8(3), C2–C3–C4 114.7(4), C3–C4–Os1 117.3(3), C4–Os1–C1 73.36(14), Os1–C4–C5 119.1(3), C4–C5–C6 113.3(3), C5–C6–C7 116.3(3), C6–C7–Os1 116.7(3), C7–Os1–C4 74.54(14), C6–C7–C9 115.1(3), C7–C9–C10 122.4(3), C9–C10–O3 121.4(3), C10–O3–C8 121.5(3), O3–C8–C6 116.8(3), C8–C6–C7 122.9(3).

Crystal Data for 4: $C_{83}H_{71}BCl_2F_4NO_3OsP_3S_2$ $[C_{82}H_{69}NO_3OsP_3S_2]BF_4 \cdot CH_2Cl_2$ (*Mr* =1635.34 g/mol): monoclinic, crystal dimension 0.20 × 0.08 × 0.05 mm, space group Cc (no. 9), a = 26.5713(18) Å, b = 12.6213(5) Å, c = 23.1715(17) Å, α = 90°, β = 109.741(8)°, γ = 90°, V = 7314.2(9) Å^3, Z = 4, T = 180.00(14) K, μ(CuKα) = 5.616 mm^{-1}, *Dcalc* = 1.485 g/cm^3, 11173 reflections measured (7.07° ≤ 2Θ ≤ 123.638°), 7218 unique (R_{int} = 0.0555, R_{sigma} = 0.0818) which were used in all calculations. The final R_1 was 0.0414 (I > 2σ(I)) and wR_2 was 0.1026 (all data). GOF = 1.053. Residual electron density (e. Å^{-3}) max/min: 1.28/-1.33.

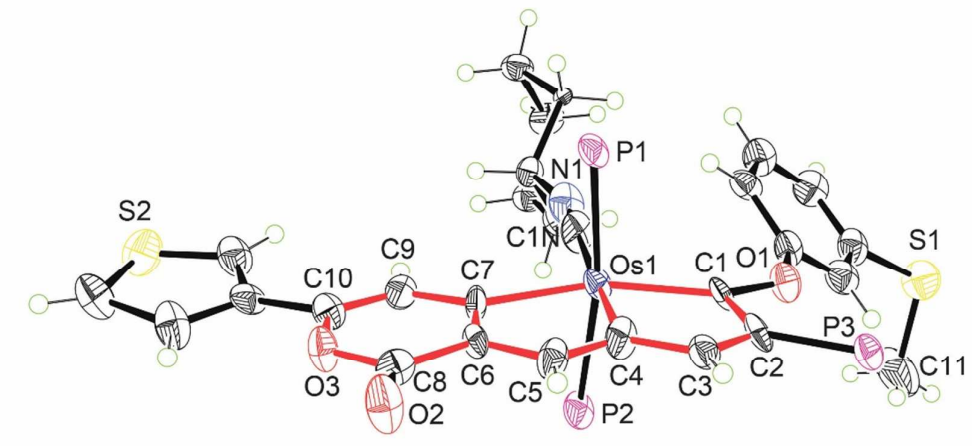


Figure S24. X-ray molecular structure for the cation of complex **4** drawn with 50% probability level. The phenyl groups in PPh_3 groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1N 2.007(14), Os1–C1 2.074(10), Os1–C4 2.091(14), Os1–C7 2.160(12), C1–C2 1.435(16), C2–C3 1.391(17), C3–C4 1.382(16), C4–C5 1.383(19), C5–C6 1.426(16), C6–C7 1.403(18), C7–C9 1.402(16), C9–C10 1.364(18), C10–O3 1.364(14), O3–C8 1.391(13), C8–C6 1.471(17), C8–O2 1.196(16); Os1–C1–C2 114.9(8), C1–C2–C3 116.4(10), C2–C3–C4 113.5(12), C3–C4–Os1 118.0(10), C4–Os1–C1 76.7(5), Os1–C4–C5 119.0(8), C4–C5–C6 111.6(12), C5–C6–C7 121.0(11), C6–C7–Os1 110.9(8), C7–Os1–C4 77.4(5), C6–C7–C9 116.7(11), C7–C9–C10 121.5(12), C9–C10–O3 121.7(10), C10–O3–C8 122.5(9), O3–C8–C6 114.8(10), C8–C6–C7 122.7(10).

3. UV-vis Absorption Spectra

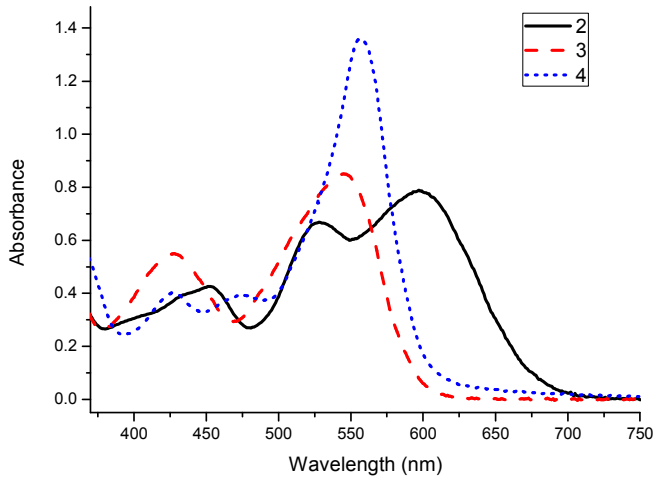


Figure S25. UV-Vis absorption of complex **2**, **3**, and **4** (5.0×10^{-5} mol/L) measured in CH_2Cl_2 solution at room temperature.

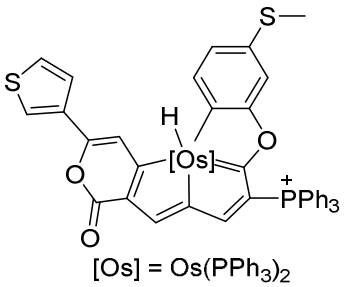
The absorption band detected at λ = 597 nm, 528 nm, and 453 nm of complex **2** can be assigned to the electronic transitions HOMO→LUMO, HOMO-1→LUMO, and HOMO→LUMO+1. And the absorption bands of complex **3** at λ = 545 nm, 427 nm and complex **4** at λ = 557 nm, 474 nm, 427 nm can be also ascribed to HOMO→ LUMO, HOMO-1→LUMO for **3** and HOMO→LUMO, HOMO-3→LUMO, HOMO →LUMO+1 for **4**.

4. Computational calculations

All the calculations were performed with the Gaussian 09 software package.[5] The B3LYP/6-31G* level[6-8] of density functional theory was used to optimize all of the structures studied in this work. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double−ζ valence basis set (LanL2DZ) were used to describe Os, S, and P atom, whereas the standard 6-31G* basis set was used for C, O, N, and H.[9] Polarization functions were added for Os (ζ(f) = 0.886), S

(ζ(d) = 0.421), and P (ζ(d) = 0.340).[10] We calculated the UV-vis absorption spectra of the cationic part of **2**, **3**, and **4** using the PCM model with dichloromethane as the solvent.

Cartesian coordinates for the species in this study:



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P	-0.87244800	2.41029700	0.69000100
S	2.10106100	-1.25946800	6.23843100
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O	-3.54532400	1.18452100	-4.33372700
C	-0.09093300	0.50932700	-1.87380700
C	-2.38275500	0.59729500	-2.32019000
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C	-2.47783500	0.17464600	-0.96507000
C	0.04218100	-0.35841800	2.13824900
C	-1.07791600	0.77754400	-2.81129400
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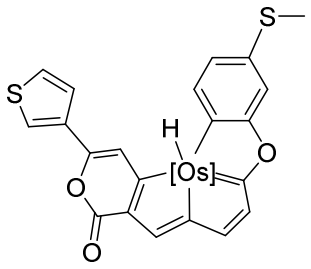

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C	1.03955300	-4.66273000	3.36557600
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C	-2.41799700	5.23055400	-2.42279000
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C	3.82696800	4.06406800	-2.46882100
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C	-7.36825900	-0.06798000	2.02419400
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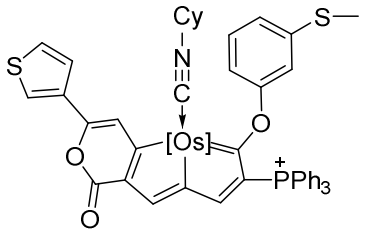

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S	-8.47814400	-0.06650300	-0.89558400
H	-6.18571500	0.82620700	-0.76829200
H	-9.52914100	-2.31288200	-0.88206100

5. Mechanically Controllable Break Junction

Mechanically controllable break junction (MCBJ) technique was used to measure the current through a molecule trapped between two gold electrodes. Fig. S26 gives photos of our MCBJ setup. During the MCBJ measurement, a flexible substrate was pressed by two supports on both ends. A notched gold wire, as well as a liquid cell containing target molecules, were fixed onto the substrate. The solvent for the measurement requires proper polarity and ion concertation to avoid the leakage current through solvent, thus the chemical reaction to in-situ convert the compounds **2** to **3** and **4** remains challenging. Then a pushing road was employed to bend/release the substrate, resulting in the repeating breaking/re-connecting of gold wire. To have a precise control, a piezo actuator was used as the pushing road. During the repeating breaking/re-connecting operation, the evolution of conductance was monitored by a home-built I-V converter with a sampling rate of 20 *k*Hz. For each target molecule, the breaking/re-connecting process was repeated for thousands of times, thus thousands of conductance traces recorded for each individual experiment.

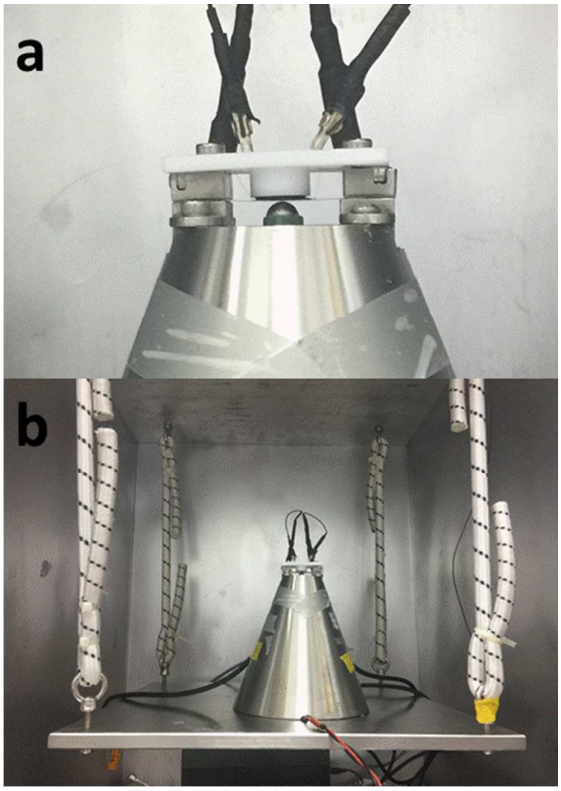

Figure S26. The photos of our MCBJ setup.

6. Data Analysis

Molecular conductance is strongly correlated to the molecular configuration binding on molecule-electrode contact, and the molecular junction conformation of the backbone. The mobility of surface adatom of electrode and the vibration of the molecular junction will influent the conformation to significantly change the charge transport property, especially at room temperature. For single-molecule nanodevice, since each device present different molecular junction configuration, the conductance might vary from device to device. Therefore, in our experiment, we use break-junction technique to fabricate single-molecule nanodevice for thousands of times dynamically, and use statistical approach to determine the most probable conductance-distance features and their variation.

All the conductance traces were used for analysis without data selection as reported in our previous paper[11]. 1D conductance histograms were constructed by collecting all individual traces with a bin size of 1100 for $\log(G/G_0)$ from -10 to +1, and 1000 for Δz from -0.5 to 3 nm. The conductance distribution was extracted by calculating the data density in each bin. The peak shift in a conductance histogram was determined by Gaussian fitting, which represents the most probable molecular conductance.

2D conductance-displacement histograms were generated by overlapping all individual traces with a bin size of 1100 for $\log(G/G_0)$ from -10 to +1, and 1000 for Δz from -0.5 to 3 nm. All traces are aligned with a relative zero point ($\Delta z = 0$) at $G = 0.5\ G_0$. Then the 2D conductance distribution versus the relative distance was constructed by the data counts in each bin.

To construct the displacement distribution histograms, firstly the relative stretching distance, Δz, was determined from the position where the conductance is 0.5 G_0 (after the rupture of gold-gold atomic break at G_0), to the molecular conductance region, just before the end of molecular plateau. The peak represents the most probable plateau length. To find the absolute displacement, z^*, which is related to the most

probable length of molecular junction, the relative displacements were corrected by adding the snap-back distance, Δz_{corr}, to the relative displacement Δz, namely, $z^* = \Delta z + \Delta z_{corr}$. Referring to our previous work[11], Δz_{corr} was determined experimentally to be 0.5 ± 0.1 nm.

7. Control Experiment

The target molecules for MCBJ experiments should be designed with anchoring groups that it can be captured by two gold electrodes. Anchoring groups have strong interaction with gold atoms and provide efficient electronic coupling, and the most widely used anchoring group is thiol, pyridine or amine. In this work, we studied the charge transport of osmacycles complexes. Complex **2**, **3** and **4** have been specially designed, which use thiophene group and sulfur methyl group as anchoring groups. As the -PPh_2 and -PMe_2 group could be used as anchoring groups, control experiment of complex **1** are performed to test whether phosphonium group could be used as anchoring group.

We use MCBJ technique to investigate the charge transport property of complex **1**. 0.1 mM solution of target molecule was prepared in a mixture of tetrahydrofuran (THF) and 1, 3, 5-trimethylbenzene (TMB) solvent (v: v=1: 4). The corresponding conductance histogram and 2D conductance-displacement histogram were shown in Figure S27. There's no significant molecular peak in conductance histogram, which means phosphonium group could not connect to gold electrodes. And, no clear molecular plateau could be found in 2D conductance-displacement histogram, which is in good agreement with the conductance histogram analysis. Thus for complex **2**, **3** and **4**, only the sulfur methyl group could be used as anchoring group.

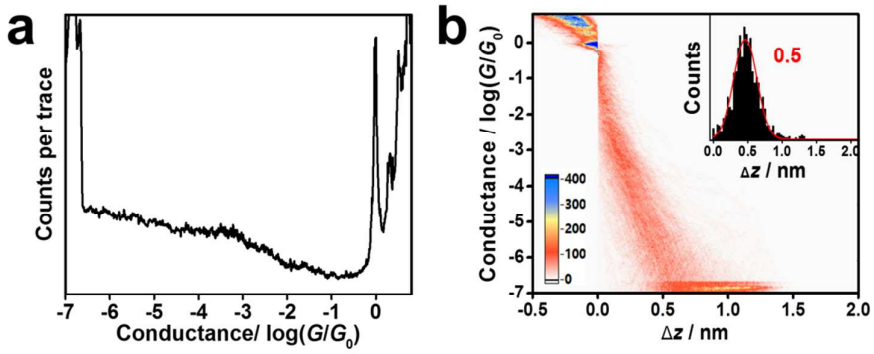

Figure S27. The conductance histogram (a) and 2D conductance-displacement histogram (b) of complex **1**.

8. References

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