Electronic Supplementary Information

A Four-State Fluorescent Molecular Switch

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Experimental

Materials and Methods. 1-[(4-Bromomethyl)phenyl]-1,2,2-triphenylethene (**9**)¹ and 1-chloro-2-diphenylphosphinoethane² were prepared according to modified literature procedures. All other chemicals and anhydrous solvents were purchased from Sigma-Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer, a Bruker Advance III 500 MHz spectrometer, and an Agilent DD2 500 MHz spectrometer. ¹H NMR spectra were referenced to residual protons in the deuterated solvents [CDCl₃, δ 7.26; CD₂Cl₂, δ 5.32; (CD₃)₂SO, δ 2.50] internally. ¹³C NMR spectra were referenced to residual carbons in the deuterated solvents (CDCl₃, δ 77.16) internally. Atmospheric pressure photoionization (APPI) and electrospray ionization (ESI) mass spectrometry (MS) spectra were recorded on a Bruker Impact-II in positiveion mode and an Agilent 6210 LC-TOF in positive-ion mode, respectively.

UV-vis absorption measurements were performed on a Shimadzu UV-1800 spectrophotometer using a 10 mm cell-path quartz cuvette (VMR). Fluorescence emission measurements were acquired using HORIBA Nanolog spectrofluorimeter equipped with a 450-W Xe lamp excitation source and a photomultiplier tube (PMT) detector. The spectra were corrected for the monochromator wavelength dependence and photomultiplier response functions provided by the manufacturer. The widths for either the entrance or exit slits were less than 5 nm. Absolute photoluminescence quantum yields of both solution and solid states were determined using an integrating sphere (Horiba Quanta $-\phi$). For solution samples, the spectra of solvent blank were first measured with the entrance and exit slits adjusted to make the pump scatter intensity less than 2×10^{6} counts at the excitation wavelength. With the same entrance and exit slits, the spectra of the sample solutions were measured under highly diluted conditions (optical density less than 0.1) to avoid self-absorption. Then, the fluorescence quantum yields and the absolute errors of the measurements were calculated using the 2-curve analysis, in which the Rayleigh line and luminescence band were included together in the sample's and blank's data with the "Quantaphi LiquidCorrect 695" as the sphere correction method. For solid samples, the spectra of the solid blank [a powder cup with a quartz coverslip purchased from HORIBA Scientific (item # 5500000064)] were first measured with the entrance or exit slits adjusted to make the pump scatter intensity less than 2×10^6 counts at the excitation wavelength. Then, the DCM solutions of samples were drop-casted on the powder cup with a quartz coverslip and inserted into the integration sphere. Under the same conditions as the solid blank, the spectra of the solid samples were measured, and the fluorescence quantum yields and the absolute errors of the measurements were calculated using the 2-curve analysis, in which the Rayleigh line and luminescence band are included together in the sample's and blank's data with the "Quanta-phi SolidCorrect 695" as the sphere correction method. All spectra were plotted using Origin (OriginLab) and were smoothed using the built-in adjacent-averaging method with a 10-point window.

DFT calculations were made using the Amsterdam Density Functional (ADF2017.111) suite³⁻⁵ on a 16-core computational cluster. Geometry optimizations were made without restraint in the ADF GUI using basis sets containing triple- ζ functions with two polarization function (TZ2P),⁶ and the local density approximations of Generalized Gradient Approximation: Perdew-Burke-Ernzerhof (GGA:PBE).⁷

Synthesis. *1-(4-Thiomethylphenyl)-pyrene (6).* 1-Bromopyrene (281 mg, 1.00 mmol), 4-(thiomethyl)phenylboronic acid (185 mg, 1.10 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (41 mg, 0.05 mmol), and Na₂CO₃ (318 mg, 3.00 mmol) were added into a mixture of 1,2-dimethoxyethane (DME)/H₂O

(10 mL, DME/H₂O = 3/1) under N₂. The resulting mixture was refluxed at 95 °C for 16 hours, and the reaction was quenched with 1.0 M HCl solution at room temperature, at which time the precipitates were observed and removed by filtration. The filtrate was extracted with Et₂O (3 x 10 mL), washed with brine, and dried over MgSO₄. The solvent was removed under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (Hexane/ethyl acetate = 100/1) to afford the desired product **6** in 73% yield (237 mg, 0.73 mmol). ¹H NMR (500 MHz, CDCl₃): δ 8.23–8.16 (m, 4H), 8.10 (s, 2H), 8.04–7.96 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 2.61 (*s*, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 138.12, 137.76, 137.25, 131.65, 131.16, 131.13, 130.75, 128.65, 127.67, 127.59, 127.56, 126.63, 126.19, 125.32, 125.29, 125.15, 125.07, 125.00, 124.83, 16.06.

1-(4-Thiophenyl)-pyrene (5). Compound **6** (100 mg, 0.31 mmol) and sodium ethanethiolate (90%, 145 mg, 1.55 mmol) were added to DMF (2 mL) N₂. The resulting mixture was refluxed at 155 °C overnight, and the reaction was quenched with 1.0 M HCl solution at room temperature, at which time yellow precipitates were formed. The mixture was extracted with Et₂O (3 x 10 mL), washed with H₂O (2 x 10 mL) and brine, and dried over MgSO₄. The solvent was removed under reduced pressure to afford yellow solid as the crude product **5** in 97% yield (93 mg, 0.30 mmol), which was confirmed by ¹H NMR and carried to next step without purification. ¹H NMR (500 MHz, CDCl₃): δ 8.22–8.14 (m, 4H), 8.10 (s, 2H), 8.04–8.00 (m, 2H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H).

(*P*,*S*)-*Pyrene* (*3*). Compound **5** (93 mg, 0.30 mmol), 1-chloro-2-diphenylphosphinoethane (81 mg, 0.33 mmol), and Cs₂CO₃ (111 mg, 0.34 mmol) were stirred in MeCN (4 mL). The resulting mixture was refluxed at 82 °C for 15 hours, at which time the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (Hexane/ ethyl acetate = 95/5) to afford the desired ligand **3** in 72% yield (116 mg, 0.22 mmol). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.25–8.16 (m, 5H), 8.12 (s, 2H), 8.06–8.02 (m, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.48–7.44 (m, 4H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.39–7.35 (m, 5H), 3.11–3.07 (m, 2H), 2.51–2.47 (m, 2H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ -17.24. HRMS (APPI+): *m/z* calcd for C₃₆H₂₇PS [M]⁺: 522.1566; found: 522.1556.

1-[(4-S-Methyl thiourea)phenyl]-1,2,2-triphenylethene (8). 1-[(4-Bromomethyl)phenyl]-1,2,2-triphenylethene (9) (100 mg, 0.24 mmol) and thiourea (21 mg, 0.28 mmol) were added to ethanol (3 mL) under N₂. The resulting mixture were refluxed at 80 °C for 4 hours and cooled to room temperature. The solution was concentrated under reduced pressure, and hexane (10 mL) was added to initiate precipitation. The precipitates were filtered and washed with hexane (3 x 10 mL) to afford white solid as the crude product **8** in 85% yield (100 mg, 0.2 mmol), which was confirmed by ¹H NMR and carried to next step without purification. ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.11–8.94 (m, 4H), 7.17–7.10 (m, 11H), 6.98–6.95 (m, 8H), 4.38 (s, 2H).

1-[(4-methylthiol)phenyl]-1,2,2-triphenylethene (7). Compound **8** (100 mg, 0.2 mmol) was dissolved in a mixture of ethanol/H₂O (6 mL, Ethanol/H₂O = 3/1), and the resulting solution was saturated with N₂ for 20 min before 1.0 M solution of sodium hydroxide (9.6 mg, 0.24 mmol) was added. The reaction mixture was heated to 70 °C under N₂ for 5 hours, at which time the reaction was cooled to room temperature and quenched with saturated ammonium chloride solution until the pH of the solution reached about 6.5. The resulting mixture was extracted with CH₂Cl₂ (3 x 20 mL), washed with brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure to afford light yellow solid as the crude product 7 in 91% yield (69 mg, 0.181 mmol), which was

confirmed by ¹H NMR and carried to next step without purification. ¹H NMR (500 MHz, CDCl₃): δ 7.11–7.08 (m, 9H), 7.06–7.00 (m, 8H), 6.97–6.96 (m, 2H), 3.65 (d, *J* = 7.5 Hz, 2H).

(*P*,*S*)-*TPE* (4). Compound 7 (100 mg, 0.26 mmol) and potassium tert-butoxide (31 mg, 0.28 mmol) were stirred in MeCN (10 mL) at room temperature for 15 min before 1-chloro-2-diphenylphosphinoethane (62 mg, 0.25 mmol) was added. The resulting mixture was refluxed at 82 °C for 15 hours, at which time the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (Hexane/ethyl acetate = 95/5) to afford the desired ligand 4 in 79.5% yield (118 mg, 0.20 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.42–7.37 (m, 3H), 7.34–7.32 (m, 5H), 7.11–7.07 (m, 10H), 7.03–7.01 (m, 7H), 6.95–6.90 (m, 4H), 3.60 (s, 2H), 2.47–2.41 (m, 2H), 2.31–2.27 (m, 2H). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -16.79. HRMS (APPI+): *m/z* calcd for C₄₁H₃₆PS [M+H]⁺: 591.2270; found: 591.2255.

Semi-open complex (1). A solution of (P,S)-TPE (4) (8 mg, 0.014 mmol) in 1 mL of CH₂Cl₂ was added dropwise to a solution of dichloro(1,4-cyclooctadiene)platinum-(II) (5 mg, 0.014 mmol) in 1 mL of CH₂Cl₂. The solution was stirred at room temperature for 5 min, and a solution of (P,S)-pyrene (**3**) (7 mg, 0.014 mmol) in 1 mL of CH₂Cl₂ was added. The resulting mixture was stirred for additional 30 min. The solution was then concentrated under reduced pressure, and hexane (10 mL) was added to initiate precipitation. The precipitates were filtered and washed with hexane (3 x 10 mL) to afford light yellow solid as the product **1** in >95% yield (20 mg, 0.014 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.26–7.94 (m, 9H), 7.53–7.27 (m, 25H), 7.09–6.96 (m, 18H), 3.16–3.10 (m, 2H), 2.84–2.78 (m, 2H), 2.44 (br, 1H), 1.91 (br, 1H), 1.26 (s, 2H), 0.89–0.83 (m, 2H). ³¹P {¹H} NMR (162 MHz, CD₂Cl₂): 42.6 (d, *J*_{P-P} = 14 Hz, *J*_{P-Pt} = 3500 Hz, 1P), 8.6 (d, *J*_{P-P} = 14 Hz, *J*_{P-Pt} = 3171 Hz, 1P). HRMS (ESI+): *m/z* calcd for C₇₇H₆₂P₂S₂Pt [M-Cl]⁺: 1342.310; found: 1342.311.

Fully closed complex (2). Semi-open complex **1** (20 mg, 0.014 mmol) and silver tetrafluoroborate (8.6 mg, 0.028 mmol) were mixed in CH₂Cl₂ (1 mL). The resulting mixture was stirred at room temperature for 20 min in the absence of light. The mixture was then filtered, and the filtrate was dried under reduced pressure to afford the desired product **2** as a yellow solid in >95% yield (21 mg, 0.014 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.27–7.81 (m, 13H), 7.53 (br, 20H), 7.09–6.91 (m, 19H), 3.18 (br, 4H), 1.27 (s, 4H), 0.90–0.83 (m, 2H). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 46.3 (d, *J*_{P-P} = 12 Hz, *J*_{P-Pt} = 3105 Hz, 1P), 44.6 (d, *J*_{P-P} = 12 Hz, *J*_{P-Pt} = 3129 Hz, 1P). HRMS (ESI+): *m/z* calcd for C₇₇H₆₂P₂S₂BF₄Pt [M-BF₄]⁺: 1394.344; found: 1394.345.

Procedure. *Tritration experiment for Figure 2*. A DCM solution (2.5 mL) of the fully closed complex **2** (3.8 μ M) was added to the cuvette at room temperature. The fluorescence measurement of this solution was recorded as the first data point (0.0 eq. of TBACl). Then, 5 μ L of a DCM solution of TBACl (200 μ M) was added to the cuvette, providing 0.1 eq. of Cl⁻ ion with respect to complex **2**. The resulting mixture was shaken gently, and the fluorescence was measured. This procedure was repeated for 10 times until 1.0 eq. of Cl⁻ was added to the cuvette. 10 μ L of a DCM solution of TBACl (200 μ M) was next added to the cuvette, providing 0.2 eq. of Cl⁻ ion with respect to complex **2**, and the fluorescence was recorded following the aforementioned procedures. Upon the addition of 2.0 eq. of TBACl, 25 μ L of a DCM solution of TBACl (200 μ M) was added to the cuvette, providing 0.5 eq. of Cl⁻ ion. Then, the fluorescence was recorded following the aforementioned procedure until 4.5 eq. of TBACl was added. Finally, 50 μ L and 100 μ L of a DCM solution of TBACl (200 μ M) were added sequentially, and the fluorescence measurement of the solution was recorded as the data points for 5.5 eq. and 7.5 eq. of TBACl, respectively.

Fluorescence measurements for Figure 3 and Figure S2. The DCM solution (2.5 mL) of complexes 1 (4 mM) and 2 (5 mM) are prepared at room temperature as the stock solution. To each vial was added 0.1 mL of the stock solution, and then, different amount of DCM and hexane was added to make 1 mL of the final volume with various hexane fraction (0 vol% to 90 vol%). For the measurement, the solutions or the suspensions were transferred to the cuvette with a stir bar at the bottom, and the fluorescence was recorded with gentle stirring.

Syntheses of (P,S)-Ligands



Scheme S1. Syntheses of (P,S)-ligands with pyrene and TPE moieties

Synthesis of Homoligated Complexes



Scheme S2. (a) Syntheses of the homoligated Pt^{II}-WLA complexes **S1** and **S2** from (P,S)-pyrene ligand **3**. (b) Syntheses of the homoligated Pt^{II}-WLA complexes **S3** from (P,S)-TPE ligand **4**.

Table for Optical Properties

Compound, State	$\lambda_{em} (nm)$	Quantum Yield, Φ (%)
1, solution	407	10.5 (± 0.15)
1, solid	475	29.8 (± 0.10)
2 , solution	404	0.9 (± 0.13)
2, solid	470	$10.0 (\pm 0.03)$
S1, solution	391	1.9 (± 0.27)
S2, solution	386	NA^d
S3, solid	481	15.2 (± 0.02)

Table S1. Optical properties^{*a*} of complexes **1**, **2**, **S1**, **S2** and **S3** in solution^{*b*} and solid^{*c*} states

^{*a*} Excitation wavelength: 344 nm for 1, 2, S1, and S2; 311 nm for S3. ^{*b*} In DCM solution at room temperature. Concentration: 1 (3.4 μ M), 2 (3.5 μ M), S1 (1.6 μ M), and S2 (1.4 μ M). ^{*c*} Solid samples drop-casted on powder cups with a quartz coverslip. ^{*d*} No measurable quantum yields were recorded for S2 in solution.

Energy minimized DFT Models of Complex 1 and 2



Fig. S1. Calculated structures of (a) 1 and (b) 2. The distances were measured between the Pt^{II} center and the center of the pyrene moiety. Counterions have been omitted for clarity.



Photographs and Fluorescence Spectra of Solutions or Suspensions of 1 and 2

Fig. S2. Formation of aggregates resulted in enhanced fluorescence emission. Photographs of the solutions or suspensions of (a) 1 and (b) 2 in DCM/hexane mixtures with different volumetric fractions of hexane. Stacked fluorescence emission spectra of the solutions or suspensions of (c) 1 and (d) 2 in DCM/hexane mixtures. Concentration: 1 (0.4 mM); 2 (0.5 mM). Excitation wavelength: 344 nm.

Absorption Spectra



Absorption spectra of 1 (16.8 μ M), 2 (8.8 μ M), S1 (1.6 μ M), S2 (1.4 μ M), and S3 (2.7 μ M) in DCM at room temperature.



Absorption spectrum of 16.8 μ M solution of the semi-open complex 1 in DCM at room temperature. The maximum λ_{abs} : 344 nm. Calculated molar absorptivity constant for 1: $\epsilon = 2.6E4$ M⁻¹·cm⁻¹.



Absorption spectrum of 8.8 μ M solution of the closed complex 2 in DCM at room temperature. The maximum λ_{abs} : 344 nm. Calculated molar absorptivity constant for 2: $\epsilon = 2.14E4 \text{ M}^{-1} \cdot \text{cm}^{-1}$.



Absorption spectrum of 1.6 μ M solution of **S1** in DCM at room temperature. The maximum λ_{abs} : 344 nm.



Absorption spectrum of 1.4 μ M solution of **S2** in DCM at room temperature. The maximum λ_{abs} : 344 nm.



Absorption spectrum of 2.7 μ M solution of **S3** in DCM at room temperature. The maximum λ_{abs} : 311 nm.

Fluorescence Spectra



Fluorescence emission spectra of (a) a DCM solution of **1** (3.4 μ M). The maximum λ_{em} : 407 nm; (b) a DCM solution of **2** (3.5 μ M). The maximum λ_{em} : 404 nm; (c) a DCM solution of **S1** (1.6 μ M). The maximum λ_{em} : 391 nm; (d) a DCM solution of **S2** (1.4 μ M). The maximum λ_{em} : 386 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectra of (a) solid-state **1** drop-casted on powder cups. The maximum λ_{em} : 475 nm; (b) solid-state **2** drop-casted on powder cups. The maximum λ_{em} : 470 nm; (c) solid-state **S3** drop-casted on powder cups. The maximum λ_{em} : 481 nm. Excitation wavelength: 344 nm for **1** and **2**; 311 nm for **S3**.



Fluorescence emission spectrum of a DCM solution of semi-open complex 1 (3.4 μ M). The maximum λ_{em} : 407 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of solid-state semi-open complex 1 drop-casted on powder cups. The maximum λ_{em} : 475 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of a DCM solution of closed complex 2 (3.5 μ M). The maximum λ_{em} : 404 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of solid-state closed complex 2 drop-casted on powder cups. The maximum λ_{em} : 470 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of a DCM solution of **S1** (1.6 μ M). The maximum λ_{em} : 391 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of a DCM solution of S2 (1.4 μ M). The maximum λ_{em} : 386 nm. Excitation wavelength: 344 nm.



Fluorescence emission spectrum of solid-state **S3** drop-casted on powder cups. The maximum λ_{em} : 481 nm. Excitation wavelength: 311 nm.

High Resolution Mass Spectra





















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