

Supporting Information for:

Chromophore-Radical Excited State Antiferromagnetic Exchange Controls the Sign of Photoinduced Ground State Spin Polarization.

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General Considerations Reagents and solvents were used as received and purchased from commercial vendors. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. ¹H and ¹³C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Infrared spectra were recorded on a Brüker Vertex 80v spectrometer with Brüker Platinum ATR attachment. Elemental analyses were performed by Atlantic Microlabs, Inc. Mass spectra were obtained at the NCSU Mass Spectrometry Facility located in the Department of Chemistry. Compounds **mPh-Pt**,¹ **MOM₂CATBpin**,² 2,3-dimethyl-2,3-bis(hydroxyamino)butane (**BHA**),³ and **Tp^{Cum,Me}Zn(OH)**,⁴ were prepared as previously reported.

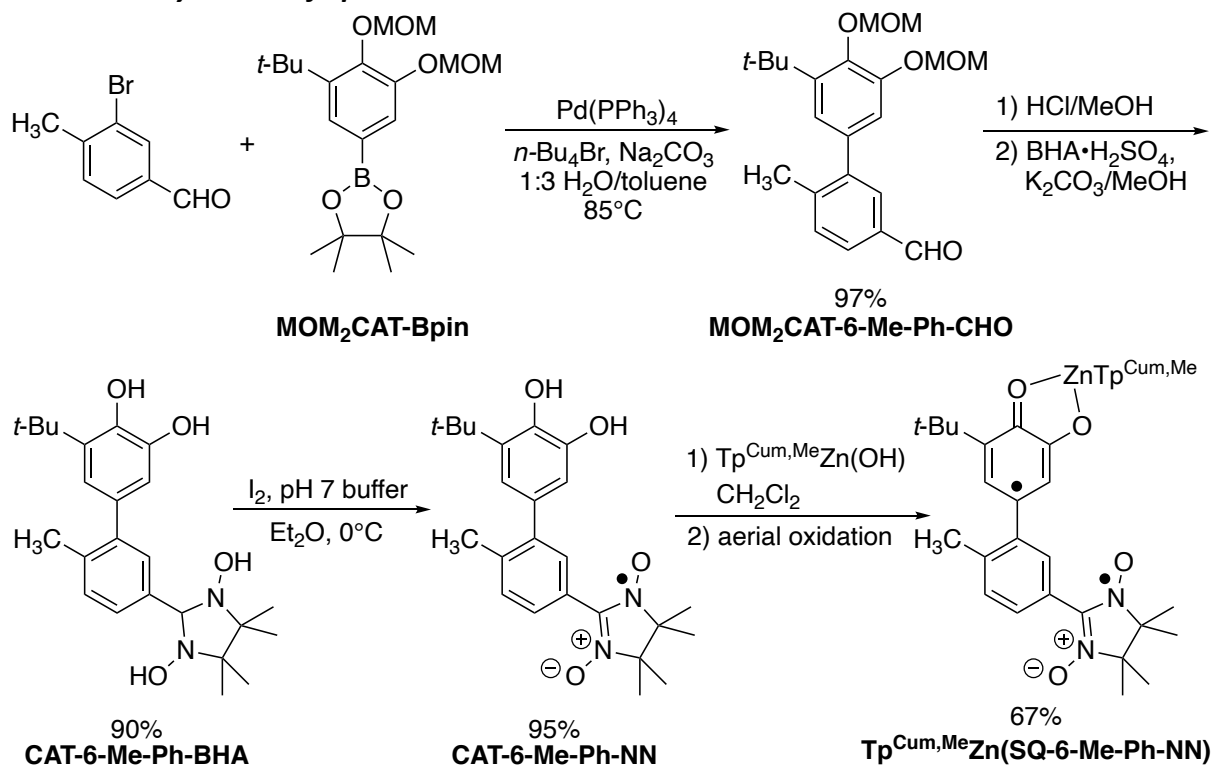
Table S1. Parameters used to simulate the cw-EPR spectrum of **(bpy)Pt(Cat-mPh-NN)** in MTHF at 20 K (Figure 2B in text).

Principal g-values	$g_{xx} = 2.0029$	$g_{yy} = 2.01079$	$g_{zz} = 2.00927$
Hyperfine coupling to two equivalent ¹⁴ N nuclei (MHz)	$A_{xx} = 50.632$	$A_{yy} = 0.191$	$A_{zz} = 7.559$
Lorentzian linewidth (FWHM) (mT)	2.33		
Modulation amplitude (mT)	0.80		
Microwave frequency (GHz)	9.779		

Synthesis of $\text{Tp}^{\text{Cum,Me}}\text{ZnSQ-6-Me-mPh-NN}$. Scheme S1 illustrates the preparation of the zinc complex of the biradical which serves as the donor half of the Pt complex and provides the $J_{\text{SQ-NN}}$ coupling constant. The synthesis begins with Suzuki coupling **MOM₂CAT-Bpin** and commercially available 3-bromo-4-methylbenzaldehyde, followed by cleavage of the MOM groups under acidic conditions and condensation with **BHA•H₂SO₄**. From here, the NN is made by oxidation with molecular iodine and the catechol is complexed with **Tp^{Cum,Me}Zn(OH)** followed by aerial oxidation to the semiquinone.

3'-(*tert*-Butyl)-4',5'-bis(methoxymethoxy)-6-methyl-[1,1'-biphenyl]-3-carbaldehyde (MOM₂CAT-6-Me-mPh-CHO). A solution of 3-bromo-4-methylbenzaldehyde (103 mg, 0.518 mmol), **MOM₂CATBpin** (191 mg, 0.502 mmol), Pd(PPh₃)₄ (10 mg, 0.009 mmol), Na₂CO₃ (109 mg, 1.03 mmol) and Bu₄NBr (18 mg, 0.56 mmol) in 6 mL of toluene and 2 mL of water were heated to 85°C for 40h. The reaction was cooled to room temperature, then transferred to a separatory funnel where it was diluted with ca. 10 mL of EtOAc and washed with ca. 10mL of brine. The organic layer was separated, dried with Na₂SO₄ and concentrated under reduced pressure. The title compound was isolated as a colorless oil (181 mg, 97% yield) by purification with silica chromatography (silica deactivated by 1% Et₃N/hexanes) with 20% EtOAc/80% hexanes. ¹H NMR (400MHz, CDCl₃) δ = 10.01 (s, 1 H), 7.81 - 7.70 (m, 2 H), 7.42 (d, *J* = 7.6 Hz, 1 H), 7.01 (d, *J* = 2.0 Hz, 1 H), 6.94 (d, *J* = 2.0 Hz, 1 H), 5.28 (s, 2 H), 5.20 (s, 2 H), 3.69 (s, 3 H), 3.53 (s, 3 H), 2.37 (s, 3 H), 1.46 (s, 9 H). ¹³C NMR (101MHz, CDCl₃) δ = 192.1, 149.8, 145.3, 143.3, 143.1, 142.8, 135.2, 134.4,

Scheme S1. Synthesis of $\text{Tp}^{\text{Cum,Me}}\text{ZnSQ-6-Me-mPh-NN}$.



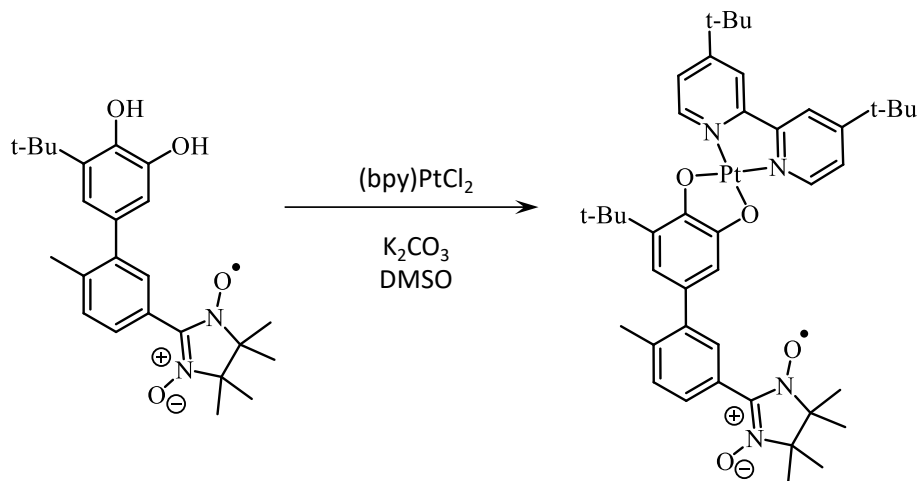
131.3, 131.1, 128.0, 121.4, 115.4, 99.1, 95.5, 57.6, 56.3, 35.3, 30.6, 21.1. HRMS (ESI) m/z: [M+H]⁺ Calculated for C₂₂H₂₈O₅ 373.20095; Found 373.20110.

2-(3'-(*tert*-butyl)-4',5'-dihydroxy-6-methyl-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (CAT-6-Me-*mPh*-BHA). MOM₂CAT-6-Me-*mPh*-CHO (181 mg, 0.486 mmol) was dissolved in 10 mL of MeOH and placed under nitrogen. 1 mL of 12 M HCl was added and the reaction was stirred for 48h at room temperature. TLC with FeCl₃ stain and ¹H NMR confirmed deprotection and then the reaction was transferred to a separatory funnel, diluted with ca. 20 mL of hexanes and washed with ca. 20 mL of brine. The organic layer was separated, dried with Na₂SO₄ and concentrated under reduced pressure. To the residue was added BHA•H₂SO₄ (180 mg, 0.731 mmol) and K₂CO₃ (68 mg, 0.49 mmol). The flask was purge-pumped three times; backfilling with nitrogen. 5 mL of anhydrous, deoxygenated MeOH were added and the reaction was stirred for 2 days at room temperature. After confirming completion by ¹H NMR in DMSO, the reaction was poured into ca. 100 mL of stirring brine and then filtered through a Büchner funnel. The product was collected by redissolving in Et₂O, dried with Na₂SO₄ and concentrated to give the title compound as a colorless solid (181mg, 90%). ¹H NMR (DMSO-d₆) δ = 9.52 (br s, 1H), 8.14 (br s, 1H), 7.77 (s, 2H), 7.62 (s, 1H), 7.35 (m, 2H), 6.95 (s, 1H), 6.89 (s, 1H), 4.53 (s, 1H), 1.38 (s, 9H), 1.08 (d, 3J 4.4 Hz, 12H). ¹³C NMR (DMSO-d₆) δ = 145.2, 143.6, 142.2, 140.5, 135.8, 130.6, 127.8, 126.4, 126.3, 124.8, 90.3, 66.0, 34.3, 29.4, 24.3, 17.1.

(CAT-6-Me-*mPh*-NN) To a 100 mL round bottom flask, 49 mg (0.12 mmol) **CAT-6-Me-*mPh*-BHA** was added with 20 mL diethyl ether, 10 mL fresh pH 7 buffer, and magnetically stirred at 0°C. To a 60 mL separatory funnel, 47 mg (0.18 mmol) I₂ was added with 30 mL diethyl ether and shaken. The solution of I₂ was added dropwise with stirring to the reaction mixture. After all of the iodine was added, the reaction stirred for 15 minutes then 100 mL pH 7 buffer was added. The reaction was transferred to a separatory funnel and washed with 50 mL saturated thiosulfate solution twice followed by 50 mL saturated sodium chloride solution. The organic phase was collected, dried over magnesium sulfate, and the solvent removed under reduced pressure to yield 53 mg of **Cat-*m6MePh*-NN** (>95% yield). HRMS (ESI) m/z: [M+H]⁺ Calculated for C₂₄H₃₂N₂O₄ 412.23566; Found 412.23431

Tp^{Cum,Me}Zn(SQ-6-Me-*mPh*-NN). To an oven dried 25 mL Schlenk flask, 95 mg (0.23 mmol) of **CAT-6-Me-*mPh*-NN** was added with 156 mg (0.23 mmol) Tp^{Cum,Me}Zn(OH) and pump purged with nitrogen five times. Using a nitrogen purged syringe, 5 mL of dry and nitrogen bubbled dichloromethane was added to the reaction mixture under a nitrogen atmosphere. The reaction was stirred under nitrogen for 3 hours the opened to air overnight. The solvent was removed under reduced pressure and the product purified by column chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield 165 mg (67%) of **Tp^{Cum,Me}Zn(SQ-6-Me-*mPh*-NN)** as a green solid. Crystals of **Tp^{Cum,Me}Zn(SQ-6-Me-*mPh*-NN)** were grown from slow evaporation of a methanol/dichloromethane solution in air at room temperature. IR (solid) ν_{max} (cm⁻¹): 3182, 2955, 2869, 1657, 1602, 1486, 1438, 1345, 1256, 1204, 1155, 1129, 1074, 1022, 958, 921, 865, 813, 758, 732, 698, 665, 631, 601, 542, 471, 449. EPR: (ca. 0.2 mM in 2-methyltetrahydrofuran): apparent a_N = 3.63 G. Mass spectrometry (m/z) calculated for C₆₃H₇₅BN₈O₄Zn: 1083.5368 (M+H)⁺, found: 1083.5386 (M+H)⁺.

Scheme S2. Synthesis of bpyPt(CAT-6-Me-mPh-NN).



Synthesis of $bpyPt(CAT-6-Me-mPh-NN)$. **CAT-6-Me-mPh-NN** (49 mg, 0.12 mmol) and $BpyPtCl_2$ (51 mg, 0.12 mmol) were added to a 10 mL round-bottom flask with 2 mL of DMSO. The solution was purged with argon via balloon for 0.5 h and then K_2CO_3 (25 mg, 0.18 mmol) was added and the reaction was stirred at room temperature under argon for 19 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in Et_2O , then dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound (85 mg, 81%) as a dark purple solid. HRMS (ESI) m/z : $[M+H]^+$ Calculated for $C_{42}H_{54}N_4O_4Pt$ 873.37873; Found 873.37721.

X-ray diffraction structural analysis. Thermal ellipsoid plot of $Tp^{Cum,Me}Zn(SQ-6-Me-mPh-NN)$, and $Tp^{Cum,Me}Zn(SQ-mPh-NN)$ are shown in Figure S3 with hydrogen atoms and cumenyl groups removed for clarity and relevant crystallographic data for $Tp^{Cum,Me}Zn(SQ-6-Me-mPh-NN)$ are listed in Table S2.

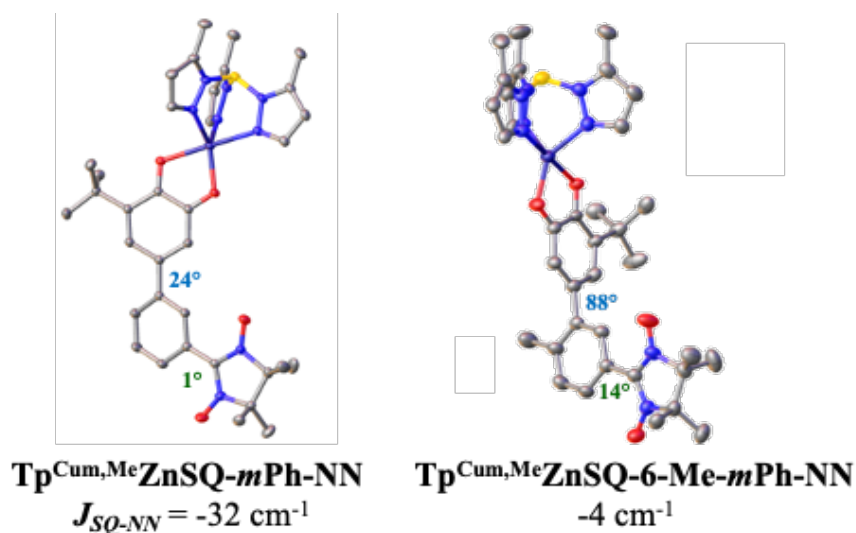


Figure S1. Thermal ellipsoid plots of **Tp^{Cum,Me}ZnSQ-*m*Ph-NN**, and **Tp^{Cum,Me}ZnSQ-6-Me-*m*Ph-NN**. Hydrogen atoms and cumenyl groups have been removed for clarity. These biradicals serve as analogs of the donor halves of the charge-separated LL'CT excited states of the Pt^{II} complexes discussed in the text.

Table S2. Crystal Data for **Tp^{Cum,Me}Zn(SQ-6-Me-*m*Ph-NN)**

Designation	1-Me
Formula	C ₆₃ H ₇₅ BN ₈ O ₄ Zn
Formula Weight (<i>g/mol</i>)	1084.49
Crystal Dimensions (<i>mm</i>)	0.60 x 0.21 x 0.24
Crystal System, Space Group	Monoclinic, P ₁ 2 ₁ /c 1
Temperature, K	110
<i>a</i> , Å	14.4507(7)
<i>b</i> , Å	18.2789(7)
<i>c</i> , Å	22.7894(10)
α , °	90
β , °	97.460(2)
γ , °	90
<i>V</i> , Å ³	5968.7(5)
<i>Z</i>	4
ρ (<i>g/cm</i>)	1.207
κ , Å	0.71073 (MoK α)
μ , (<i>cm</i> -1)	0.464
R1	0.0866
wR2	0.1891

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