# Heterospin Biradicals Provide Insight into Molecular Conductance and

# Rectification

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**Magnetic Susceptibility and Magnetization.** Magnetic susceptibility measurements were collected on a Quantum Design MPMS-XL7 SQUID magnetometer with an applied field of 0.7 T. A crystalline sample (~20 mg) was loaded into a gelcap/straw sample holder and mounted to the sample rod with Kapton tape for variable temperature measurements. Raw data were corrected with Pascal's constants as a first approximation for molecular diamagnetism followed by a straight line correction to all data for diamagnetic response of sample container where the slope of the line represents the residual diamagnetic correction. The Magnetic susceptibility data were fit using a field-independent van Vleck expression,  $\chi_{eff}T = \frac{2zJ'_{inter}}{2}$  and  $\chi = \frac{0.75g^2}{2}$  and  $J_{eff}$  is the SO Bridge NN magnetic orchange

 $[\chi/(1-\theta\chi)]$ T, where  $\theta = \frac{2zJ'_{inter}}{Ng^2\beta^2}$ , and  $\chi = \frac{0.75g^2}{3+exp(\frac{-2J_{SQBNN}}{0.695\cdot T})}$ , and  $J_{SQNN}$  is the SQ-Bridge-NN magnetic exchange

parameter.<sup>1</sup> The origin of  $zJ'_{inter}$  may be zero-field splitting, intermolecular interactions, saturation effects, or some combination of all three.<sup>1,2</sup> The  $\chi$ T plots and fit parameters for **SQ-PT-NN** and **SQ-TP-NN** are shown in Fig. S1A and B, respectively. In our data, collected above 10 K, the effects of  $zJ'_{inter}$  are negligible. The small deviation of the *g*-values from the expected spin-only value of ~2.00 can be the result of minute (~1%) weighing errors. We note that excellent fits required no "*J*-strain," suggesting that thermal (de)population of torsional levels have no effect on the magnetic data, in accord with our published results<sup>3</sup> on other SQ-Bridge-NN molecules.





**Figure S1.** Paramagnetic susceptibility-temperature product plots for **SQ-PT-NN** (**A**) and **SQ-TP-NN** (**B**) shown as blue diamond data points and blue fit lines. Each plot includes theoretical  $\chi T$  plots (red and green lines) for the *J*-values indicated in the legend. The *g*-values used in the theoretical plots were the same as those determined by the fitting of the experimental data. (**C**) and (**D**) Paramagnetic susceptibility-temperature product plot for **SQ-PT-NN** and **SQ-T-P-NN**, respectively, with a fixed  $J = 59 \text{ cm}^{-1}$  (**C**) and 49 cm<sup>-1</sup> (**D**) and letting *g* float. As can be seen, the fits are not as good in the low-temperature region (where the *J*-value dominates) as those in **A** and **B**.

The *J*-values from the fits are 56.5±0.5 cm<sup>-1</sup> for **SQ-PT-NN** (Fig. S1A) and 51.2±0.6 cm<sup>-1</sup> for **SQ-TP-NN** (Fig. S1B). The small errors listed are derived from the nonlinear least squares fit routine. In addition, theoretical lines for J = 59 and 53 cm<sup>-1</sup> for **SQ-PT-NN** and J = 54 and 49 cm<sup>-1</sup> for **SQ-PT-NN**. Finally, Figs. S1C and D show plots of the experimental data in Figs. S1A and B respectively, but holding J fixed at 59 cm<sup>-1</sup> (the "high" J-value from Fig. S1A chosen arbitrarily, but the result is the same if the "low" value had been chosen) for **SQ-PT-NN** and holding J fixed at 49 cm<sup>-1</sup> (the "low" J-value from Fig. S1B chosen arbitrarily, but the result is the same if the "high" value had been chosen). The latter two plots show that fixing the J-values to  $\pm 3$  cm<sup>-1</sup> of those from the fits in Figs. S1A and B give poorer fits in the low-temperature regions where the J-value dominates the fit quality. This is compared to the fits in Figs. S1A and B are certainly better than a  $\pm 3$  cm<sup>-1</sup> error and although our conclusions do not rely on a difference in the two J-values, the data illustrates that 56.5 cm<sup>-1</sup> and 51.2 cm<sup>-1</sup> are indeed different.

Magnetization data (Fig. S2) were collected from the same samples as the magnetic susceptibility (see text Fig. 2A,B and Fig. S1A,B), and the former data were collected at 2 K with applied magnetic fields of 0 to 7 T.



*Figure S2.* Saturation magnetization plots for **SQ-T-P-NN** and **SQ-P-T-NN**. The molar magnization is 1.704 for **SQ-T-P-NN** and 1.730 for **SQ-P-T-NN** when H/T = 3.5, ~95% of the theoretical value of 1.796 when S= 1 at H/T = 3.5.

# **References for Magnetometry**

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*Figure S3.* Electron density difference maps (EDDMs) for **SQ-P-T-NN** and **SQ-T-P-NN**. Red indicates a loss of electron density in the transition and green indicates a gain of electron density in the transition. Note the similar  $SQ(SOMO) \rightarrow B-NN(LUMO)$  character in the intraligand charge transfer transition.



Figure S4. Computed rectification ratio as a function of bias voltage for SQ-T-P-NN and SQ-P-T-NN.

**Electronic Absorption Spectroscopy.** Electronic absorption spectra were recorded on a Shimadzu UV-3600 UV-Visible Spectrophotometer instrument in purified CH<sub>2</sub>Cl<sub>2</sub> solvent.

**X-ray Crystallography.** The X-ray diffraction data for **SQ-P-T-NN** were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K<sub>a</sub> INCOATEC Imus micro-focus source ( $\lambda = 1.54178$  Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013 [7] (full-matrix least-squares on F<sup>2</sup>) contained in APEX2 [1,7], WinGX v1.70.01 [4,5,6,7] and OLEX2 [7,8]. All non-hydrogen atoms were refined anisotropically. Disordered atoms of isopropyl and phenyl groups were refined using restraints for geometry and ADPs. Crystal has been refined as pseudo merohedral twin with (-1.0, 0.0, 0.0, 0.0, -1.0, 0.0, 0.273, 0.0, 1.0) twin law and BASF =0.0264(5) (1% drop in R-factor, minor twinning). Hydrogen atoms of -CH, -CH<sub>3</sub> and -BH groups were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2(1.5)Ueq(-CH,(-CH<sub>3</sub>)). There are two molecules of substrate in the asymmetric unit together with disordered water molecules. Crystal data and refinement conditions are shown in Table S1.

A brown plate-like specimen of **SQ-T-P-NN**, approximate dimensions 0.126 mm x 0.228 mm x 0.244 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 29.92 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 106893 reflections to a maximum  $\theta$  angle of 23.25° (0.90 Å resolution), of which 10221 were independent (average redundancy 10.458, completeness = 100.0%,  $R_{int}$  = 3.65%,  $R_{sig}$  = 2.69%) and 8308 (81.28%) were greater than  $2\sigma(F^2)$ . The final cell constants of <u>a</u> = 22.0024(13) Å, <u>b</u> = 16.5492(12)

Å, <u>c</u> = 21.1852(8) Å,  $\beta$  = 112.792(2)°, volume = 7111.7(7) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9827 reflections above 20  $\sigma$ (I) with 4.477° < 2 $\theta$  < 49.82°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.925. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9040 and 0.9490.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit,  $C_{65}H_{74}BN_9O_4SZn$ . The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 746 variables converged at R1 = 5.28%, for the observed data and wR2 = 16.04% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.714 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.558 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of0.063 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.077 g/cm<sup>3</sup> and F(000), 2440 e<sup>-</sup>.

### **References for Crystallography**

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Identification code	SQ-P-T-NN	SQ-T-P-NN	
Empirical formula	C <sub>65</sub> H <sub>74</sub> BN <sub>9</sub> O <sub>4.28</sub> SZn	C <sub>65</sub> H <sub>74</sub> BN <sub>9</sub> O <sub>4</sub> SZn	
Formula weight	1158.01	1153.57	
Temperature/K	100(2)	110	
Crystal system	monoclinic	monoclinic	
Space group	P2 <sub>1</sub> /c	P21/c	
a/Å	13.6329(4)	22.0024(13)	
b/Å	14.5215(4)	16.5492(12)	
c/Å	63.8849(18)	21.1852(8)	
α/°	90	90	
β/°	91.6616(12)	112.792(2)	
γ/°	90	90	
Volume/Å <sup>3</sup>	12642.0(6)	7111.7(7)	
Z	8	4	
$\rho_{calc}g/cm^3$	1.217	1.077	

Table S1. Crystallographic details of SQ-P-T-NN and SQ-T-P-NN.

µ/mm <sup>-1</sup>	1.269	0.422	
F(000)	4898.0	2440	
Crystal size/mm <sup>3</sup>	0.130 × 0.090 × 0.040	0.24 × 0.23 × 0.13	
Radiation	CuKα (λ = 1.54178)	ΜοΚα(λ = 0.71073)	
Reflections collected	103469	10221	
Goodness-of-fit on F <sup>2</sup>	1.131	1.059	
Final R indexes	$R_1 = 0.0901$ , $wR_2 = 0.2021$	R <sub>1</sub> = 0.053, wR <sub>2</sub> = 0.1604	
Largest diff. peak/hole / e Å <sup>-3</sup>	0.97/-0.50	0.71/-0.56	

The exact torsion angles in **SQ-T-P-NN** were directly measured using the dihedral angle between the mean planes of the SQ ring and thiophene ring ( $\phi_{SQ-B}$ ), the thiophene ring and pyridine ring ( $\phi_{B-B}$ ), and the pyridine ring and O-N-C-N-O atoms of NN ( $\phi_{B-NN}$ ). **SQ-P-T-NN** has two molecules in the unit cell, and the torsion angles were calculated as the mean value of the corresponding torsional angle in each structure.

Table S2. Select Torsion Angles for Complexes SQ-T-P-NN and SQ-P-T-NN.

Complex	<b>ф</b> <sub>SQ-B</sub> (°)	<b>ф</b> <sub>В-В</sub> (°)	$\mathbf{\phi}_{\text{B-NN}}$ (°)
SQ-T-P-NN	14.87(0.16)	26.38(0.15)	35.81(0.35)
SQ-P-T-NN	15.72(0.25)	11.55(0.23)	10.54(0.23)

Estimated standard deviations in parentheses after each torsion angle value.

**Synthesis.** Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. <sup>1</sup>H and <sup>13</sup>C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. EPR spectra were recorded on an IBM ER200D-SRC EPR spectrometer in CH<sub>2</sub>Cl<sub>2</sub> solution. Infrared spectra were recorded on a Brüker Vertex 80v spectrometer with Brüker Platinum ATR attachment. Mass spectra were obtained at the NCSU Mass Spectrometry Facility located in the Department of Chemistry. Compound **3**<sup>1</sup>, compound **9**<sup>2</sup>, compound **10**<sup>3</sup>, 2,3-dimethyl-2,3-bis(hydroxyamino)butane<sup>4</sup>, and **Tp<sup>Cum,Me</sup>Zn(OH)**<sup>5</sup> were prepared as previously reported.

## Scheme S1.





**5-(thiophen-2-yl)pyridinecarboxaldehyde (1).** To a 250 mL Schlenk flask were added 1.20 g (6.45 mmol) of 5-bromo-2-pyridinecarboxaldehyde, 0.87g (6.77 mmol) of 2-thienylboronic acid, and the reaction vessel was transferred to a glove box where 0.28 g (0.34 mmol) of Pd(dppf)Cl<sub>2</sub>•CH<sub>2</sub>Cl<sub>2</sub> complex were added with 100 mL THF. The Schlenk flask was transferred out and added 6.77mL (13.54 mmol) of degassed 2M K<sub>2</sub>CO<sub>3</sub> solution. The reaction flask was fit with a condenser under nitrogen and reflux for 40 h. The reaction was then cooled, poured into a separatory funnel and washed with 100 mL of saturated NaCl solution twice. The organic layer was collected and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 10% ethyl acetate in hexanes) to yield 1.06 g (87%) of compound **1**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.08 (s, 1H), 9.04 (d, *J* = 1.5 Hz, 1H), 8.06-7.97 (m, 2H), 7.54-7.47 (m, 2H), 7.20-7.17 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 192.88, 151.48, 147.21, 139.32, 134.48, 133.46, 128.99, 128.19, 126.20, 122.22. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1699 (s, C=O). Mass spectrometry (*m/z*): calculated for C<sub>10</sub>H<sub>8</sub>NOS (M+H)<sup>+</sup>: 190.03211, found: 190.03204 (M+H)<sup>+</sup>.

**5-(5-bromothiophen-2-yl)pyridinecarboxaldehyde (2).** To a N<sub>2</sub> filled 100 mL round bottom flask, 0.80 g compound **1** (4.23 mmol), 0.79 g N-bromosuccinimide (4.44 mmol) and 50 mL anhydrous DMF were added. The mixture was covered with aluminum foil and stirred at 40 °C for 5 hours. The reaction mixture was poured into a separatory funnel containing and 200 mL saturated NaCl solution and the mixture was extracted with ethyl acetate three times. The organic layers were collected and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 20% ethyl acetate in hexanes) to yield 1.11 g (98%) of compound **2**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.07 (s, 1H), 8.95 (d, *J* = 2.1 Hz, 1H), 8.00-7.90 (m, 2H), 7.27 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 3.9 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 192.71, 151.69, 146.79, 140.68, 133.59, 133.19, 131.82, 126.45, 122.25, 115.38. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1699 (s, C=O). Mass spectrometry (*m/z*): calculated for C<sub>10</sub>H<sub>7</sub>NOSBr (M+H)<sup>+</sup>: 267.94262, found: 267.94235 (M+H)<sup>+</sup>.

**5-(5-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)thiophen-2-yl)pyridinecarboxaldehyde** (4). To a 250 mL Schlenk flask were added 1.30 g (3.42 mmol) of compound **3**, 1.01 g (3.76 mmol) of compound **2** and several pieces of 4Å molecular sieves, and then transferred to the glove box where 0.28 g (0.34 mmol) of Pd<sub>2</sub>(dppf)Cl<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub> complex were added with 120 mL THF. The Schlenk flask was transferred out of the glovebox and 3.42 mL (6.84 mmol) of degassed 2M K<sub>2</sub>CO<sub>3</sub> solution were added. The reaction flask was fitted with a condenser under nitrogen and heated to reflux for 48 h. The reaction was then cooled, filtered into a separatory funnel and washed with 100 mL of saturated NaCl solution twice. The organic layers were collected and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 25% ethyl acetate in hexanes) to yield 0.92 g (61%) of compound **4**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.07 (s, 1H), 9.04 (d, *J* = 2.1 Hz, 1H), 8.10-7.96 (m, 2H), 7.49 (d, *J* = 3.9 Hz, 1H), 7.33-7.25 (m, 3H), 5.25 (s, 4H), 3.67 (s, 2H), 3.55 (s, 2H), 1.47 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 192.87, 151.28, 150.75, 147.64, 146.81, 146.67, 144.31, 137.71, 134.53, 132.90, 128.73, 127.15, 124.49, 122.28, 118.77, 112.48, 99.39, 95.71, 57.91, 56.66, 35.53, 30.62. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1710 (s, C=O). Mass spectrometry (*m*/*z*): calculated for C<sub>24</sub>H<sub>28</sub>NO<sub>5</sub>S (M+H)<sup>+</sup>: 442.16827, found: 442.16741 (M+H)<sup>+</sup>.

**5-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)pyridinecarboxaldehyde (5).** To a 250 mL round bottom flask were added 1.12 g (2.54 mmol) **3a** and 50 mL ethyl acetate. The mixture was added 4M HCl solution in ethyl acetate and stirred for 30 min. To the reaction was added saturated NaHCO<sub>3</sub> solution until pH of aq. phase was 9. The mixture was then transferred to a separatory funnel. The organic layer was washed once with saturated NaHCO<sub>3</sub> solution and followed by another wash of saturated NaCl solution. The organic layer was dried with NaSO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 30% ethyl acetate in hexanes) to yield 0.57 g (64%) of compound **5**. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 10.08 (s, 1H), 9.03 (s, 1H), 8.03-7.96 (m, 2H), 7.48 (d, *J* = 3.9 Hz, 1H), 7.21 (d, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 1.46 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 10.94, 35.06, 29.91. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 2996 (br, OH), 1698 (s, C=O). Mass spectrometry (*m*/*z*): calculated for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>S (M+H)<sup>+</sup>: 354.11584, found: 354.11532 (M+H)<sup>+</sup>.

#### 2-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)pyridin-2-yl)-4,4,5,5-tetramethylimidazolidine-

**1,3-diol (6).** To a 25 mL Schlenk flask were added 0.30 g compound **5** (0.85 mmol) and 0.19 g 2,3-dimethyl-2,3-bis(hydroxyamino)butane (1.27 mmol). The flask was pump purged three times and filled with  $N_2$ . Then 10 mL anhydrous methanol was added to the reaction flask via syringe. The reaction flask was stirred in the dark for 72 h, and then solvent was removed under reduced pressure. The crude product **6** was collected and used for next step without further purification.

### 2-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)pyridin-2-yl)-4,4,5,5-

**tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (7).** To a 250 mL round bottom flask, 0.38 g (0.79 mmol) of compound **6** was added with 80 mL diethyl ether, 40 mL aq. phosphate buffer (pH = 7), and then cooled to 0 °C. To a 60 mL separatory funnel, 0.30 g (1.18 mmol)  $I_2$  was added with 30 mL diethyl ether and added

dropwise to the stirring reaction mixture at 0 °C. After all of the I<sub>2</sub> solution was added, the reaction was warmed to room temperature and transferred to a separatory funnel containing 100 mL aq. phosphate buffer (pH = 7). The organic layer was washed once with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution followed by another wash of saturated NaCl solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure to yield 0.27 g (71%) of compound **7** as brown solid. IR (solid)  $v_{max}$  (cm<sup>-1</sup>): 3049 (br, OH). EPR (X-Band, 298 K):  $a_N = 7.45$  G (1:2:3:2:1). Mass spectrometry (*m*/*z*): calculated for C<sub>26</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub>S (M+H)<sup>+</sup>: 481.20298, found: 481.20202 (M+H)<sup>+</sup>.

**Tp**<sup>Cum,Me</sup>**Zn(SQ-T-P-NN) (8).** To an oven dried 25 mL Schlenk flask, 0.13 g (0.26 mmol) of compound **7** was added with 0.18 g (0.26 mmol) of Tp<sup>Cum,Me</sup>Zn(OH) and pump purged with nitrogen three times. Then 10 mL anhydrous  $CH_2Cl_2$  was added to the Schlenk flask. In the dark, the reaction was stir for 1 h under nitrogen then opened to air and stirred for additional 12h. The solvent was removed under reduced pressure and the product purified by column chromatography (basic alumina, 30% ethyl acetate in hexanes) to yield 0.09 g (33%) of **Tp**<sup>Cum,Me</sup>**Zn(SQ-T-P-NN)**. Crystals were grown from slow evaporation of  $CH_2Cl_2$  in methanol. IR (solid)  $v_{max}$  (cm<sup>-1</sup>): 2537 (w, BH). EPR (~0.2 mM in  $CH_2Cl_2$ ): apparent  $a_N = 3.73$  G. Mass spectrometry (*m/z*): calculated for  $C_{65}H_{75}N_9O_4SBZn$  (M+H)<sup>+</sup>: 1152.50418, found: 1152.50253 (M+H)<sup>+</sup>.

### Scheme S2.





**5-(6-(tert-butoxy)pyridin-3-yl)thiophene-2-carbaldehyde (11).** To a 250 mL Schlenk flask were added 1.24 g (5.20 mmol) compound **9** and 1.20 g (5.20 mmol) of compound **10**, then transferred to the glove box where 0.28 g (0.34 mmol) of Pd<sub>2</sub>(dppf)Cl<sub>2</sub>•CH<sub>2</sub>Cl<sub>2</sub> complex were added along with 100 mL THF. The Schlenk flask was transferred out of the glovebox and 5.20 mL (10.40 mmol) of degassed 2M aq. K<sub>2</sub>CO<sub>3</sub> solution were added. The reaction flask was fitted with a condenser under nitrogen and heated to reflux for 16 h. The reaction was then cooled, transferred into a separatory funnel and washed twice with 100 mL of saturated aq. NaCl solution. The organic layer was collected, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 20% ethyl acetate in hexanes) to yield 1.06 g (79%) of compound **11**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.88 (s, 1H), 8.47 (d, *J* = 2.7 Hz, 1H), 7.79-7.72 (m, 2H), 7.30 (d, *J* = 3.9 Hz, 1H), 6.70 (d, *J* = 9.3 Hz, 1H), 1.62 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 182.83, 164.81, 151.64, 144.56, 142.27, 137.77, 136.32, 123.60, 122.15, 113.75, 80.56, 28.82. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1643 (s, C=O). Mass spectrometry (*m/z*): calculated for C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 262.08963, found: 262.08878 (M+H)<sup>+</sup>.

**5-(6-oxo-1,6-dihydropyridin-3-yl)thiophene-2-carbaldehyde (12).** To a 100 mL round bottom flask were added 0.50 g (1.92 mmol) **11** and 30 mL THF. To this solution was added 1 mL trifluoroacetic acid in 10 mL THF and 1 mL H<sub>2</sub>O. The reaction was stirred at room temperature for 2h, then 10 mL of 2M HCl solution was added and stirred for an additional 16h. To the reaction was added saturated aq. NaHCO<sub>3</sub> solution until the pH of the aqueous phase was 9. The mixture was then filtered, and the filter cake was washed with 100 mL H<sub>2</sub>O then 100 mL diethyl ether. The solid was collected and dried under reduced pressure at 40 °C to yield 0.37 g (95%) of compound **12**. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ): 9.84(s, 1H), 8.00-7.96 (m, 2H), 7.83 (dd, *J* = 9.6 Hz, *J* = 2.7 Hz, 1H), 7.55 (d, *J* = 3.9 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ): 183.21, 162.60, 150.29, 140.90, 140.05, 139.44, 135.00, 124.17, 120.91, 112.17. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 2652 (br, NH), 1663(s, C=O), 1642 (s, C=O). Mass spectrometry (*m*/*z*): calculated for C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>S (M+H)<sup>+</sup>: 206.02703, found: 206.02685 (M+H)<sup>+</sup>.

**5-(5-formylthiophen-2-yl)pyridin-2-yl trifluoromethanesulfonate (13).** To a 100 mL Schlenk flask, 0.50 g (2.44 mmol) of compound **12** was added and pump-purged with N<sub>2</sub> three times. To the Schlenk flask, 30 mL of dried and degassed pyridine was added and the mixture was chilled to -20 °C. Using a N<sub>2</sub> purged syringe, 0.61 mL (3.65 mmol) of trifluoromethanesulfonic anhydride was added to the mixture in one portion. The reaction mixture was stirred at -20 °C for 30 min then allowed to warm to room temperature. After 2 hours,

the reaction was opened to air and 30 mL of H<sub>2</sub>O were added, transferred into a separatory funnel and washed with 100 mL of saturated NaHCO<sub>3</sub> solution three times. The aqueous layer was extracted with diethyl either twice, then the combined organic layers were removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 20% ethyl acetate in hexanes) to yield 0.63 g (77%) of compound **13**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.95 (s, 1H), 8.70 (d, *J* = 2.7 Hz, 1H), 8.12 (dd, *J* = 8.6 Hz, *J* = 2.7 Hz, 1H), 7.80 (d, *J* = 3.9 Hz, 1H), 7.47 (d, *J* = 3.9 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 182.83, 155.95, 147.27, 146.15, 144.72, 138.73, 137.28, 130.44, 126.32, 120.40, 115.86. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1664 (s, C=O). Mass spectrometry (*m*/*z*): calculated for C<sub>11</sub>H<sub>7</sub>F<sub>3</sub>NO<sub>4</sub>S<sub>2</sub> (M+H)<sup>+</sup>: 337.97631, found: 337.97586 (M+H)<sup>+</sup>.

**5-(6-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)pyridin-3-yl)thiophene-2-carbaldehyde (14).** To a 250 mL Schlenk flask were added 0.71 g (1.87 mmol) of compound **3** and 0.60 g (1.78 mmol) of compound **13**, and then transferred to the glove box where 0.1 g (0.044 mmol) of the Pd<sub>2</sub>(dppf)Cl<sub>2</sub> • CH<sub>2</sub>Cl<sub>2</sub> complex was added with 120 mL THF. The Schlenk flask was transferred out of the gloveobx and 1.87 mL (3.74 mmol) of degassed 2M K<sub>2</sub>CO<sub>3</sub> solution was added. The reaction flask was fit with a condenser under nitrogen and heated to reflux for 96 h. The reaction was then cooled, transferred into a separatory funnel and washed with 100 mL of saturated NaCl solution twice. The organic layer was collected and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 40% ethyl acetate in hexanes) to yield 0.67 g (85%) of compound **14**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.91 (s, 1H), 8.98 (d, *J* = 2.4 Hz, 1H), 7.95 (dd, *J* = 8.1 Hz, *J* = 2.4 Hz, 1H), 7.78-7.70 (m, 4H), 7.46 (d, *J* = 3.9 Hz, 1H), 5.28 (s, 4H), 3.67 (s, 2H), 3.55 (s, 2H), 1.49 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 182.83, 157.88, 150.61, 150.46, 147.71, 147.15, 143.87, 143.30, 137.54, 134.27, 133.34, 127.13, 124.83, 120.37, 119.48, 113.25, 99.33, 95.60, 57.85, 56.65, 35.57, 30.64. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 1660 (s, C=O). Mass spectrometry (*m*/*z*): calculated for C<sub>24</sub>H<sub>28</sub>NO<sub>5</sub>S (M+H)<sup>+</sup>: 442.16827, found: 442.16773 (M+H)<sup>+</sup>.

**5-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)pyridin-3-yl)thiophene-2-carbaldehyde (15).** To a 250 mL round bottom flask were added 1.20 g (2.71 mmol) **14** and 50 mL ethyl acetate. The mixture was added 12M hydrochloric acid and stirred for 30 min. To the reaction was then added saturated NaHCO<sub>3</sub> solution until pH of the aqueous phase was 9. The mixture was then transferred to a separatory funnel. The organic layer was washed once with saturated aq. NaHCO<sub>3</sub> solution and followed by another wash of saturated aq. NaCl solution. The organic layer was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 75% ethyl acetate in hexanes) to yield 0.67 g (70%) of compound **15**. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 9.93 (s, 1H), 9.03 (d, *J* = 2.1 Hz, 1H), 8.17 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 4.2 Hz, 1H), 7.85-7.83 (m, 2H), 7.49 (s, 2H), 1.40 (s, 9H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 184.63, 157.81, 149.89, 147.24, 146.74, 145.99, 142.94, 139.79, 136.38, 134.88, 128.24, 126.42, 126.37, 119.68, 116.63, 111.86, 35.15, 30.01. IR (solid) v<sub>max</sub> (cm<sup>-1</sup>): 3108 (br, OH), 1655 (s, C=O). Mass spectrometry (*m*/z): calculated for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>S (M+H)<sup>+</sup>: 354.11584, found: 354.11532 (M+H)<sup>+</sup>.

**2-(5-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)pyridin-3-yl)thiophen-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (16).** To a 50 mL Schlenk flask were added 0.67 g compound **15** (1.89 mmol) and 0.42 g 2,3-dimethyl-2,3-bis(hydroxyamino)butane (2.84 mmol). The flask was pump purged three times and filled with  $N_2$ . Then 10 mL anhydrous benzene was added to the reaction flask via syringe. The reaction mixture was heated to reflux under  $N_2$  and monitored by <sup>1</sup>H NMR until the absence of starting material **15** was observed. The reaction was stopped after 2 days, and solvent was removed under reduced pressure. The crude product **16** was collected and used for next step without further purification.

**2-(5-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)pyridin-3-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-4,5-dihydroim idazol-3-oxide-1-oxyl (17).** To a 100 mL round bottom flask, 0.17 g (0.34 mmol) of compound **16** was added with 30 mL CH<sub>2</sub>Cl<sub>2</sub>, 20 mL buffer (pH = 7), and then cooled to 0 °C. To a 60 mL separatory funnel, 0.17 g (0.68 mmol) I<sub>2</sub> was added to 10 mL diethyl ether and the solution was added dropwise to the stirring reaction mixture at 0 °C. After all of the I<sub>2</sub> was added, the reaction was stirred at 0 °C for 1 h and then warmed to room temperature. The reaction mixture was transferred to a separatory funnel containing 100 mL aq. phosphate buffer (pH = 7). The organic layer was washed once with 5 mL saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution followed by another wash of saturated aq. NaCl solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure to yield 0.11 g (64%) of compound **17** as a green solid. IR (solid)  $v_{max}$  (cm<sup>-1</sup>): 3083 (br, OH). EPR (X-Band, 298 K):  $a_N = 7.45$  G (1:2:3:2:1). Mass spectrometry (*m/z*): calculated for C<sub>26</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub>S (M+H)<sup>+</sup>: 481.20298, found: 481.20247 (M+H)<sup>+</sup>.

**Tp**<sup>cum,Me</sup>**Zn(SQ-P-T-NN) (18).** To an oven dried 25 mL Schlenk flask, 0.084 g (0.17 mmol) of compound **17** was added with 0.18 g (0.26 mmol) of Tp<sup>Cum,Me</sup>Zn(OH) and pump purged with nitrogen three times. Then 10 mL anhydrous  $CH_2Cl_2$  was added to the Schlenk flask. In the dark, the reaction was stir for 1 h under nitrogen then opened to air and stirred for additional 12h. The solvent was removed under reduced pressure and the product purified by column chromatography (basic alumina, 30% ethyl acetate in hexanes) to yield 0.05 g (25%) of **Tp**<sup>Cum,Me</sup>**Zn(SQ-P-T-NN)**. Crystals were grown from slow evaporation of  $CH_2Cl_2$  in methanol. IR (solid)  $v_{max}$  (cm<sup>-1</sup>): 2541 (w, BH). EPR (~0.2 mM in  $CH_2Cl_2$ ): apparent  $a_N = 3.80$  G. Mass spectrometry (*m/z*): calculated for  $C_{65}H_{75}N_9O_4SBZn (M+H)^+$ : 1152.50418, found: 1152.50277 (M+H)<sup>+</sup>.

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**Computational Details.** Spin unrestricted gas-phase geometry optimizations for **SQ-T-P-NN**, **SQ-P-T-NN**, and the thiophene-pyridine (**T-P**) bridge were performed at the density functional level of theory using the Gaussian 09W software package<sup>1</sup>. Input files were prepared using the molecular builder function in GaussView. Complexes were optimized with and without constraints to achieve planar geometries as

well as fully optimized geometries. Calculations employed the B3LYP hybrid exchange-correlation functional. A 6-31g(d',p') split valence basis set with polarizability functions was used for all light atoms. The LANL2DZ basis set, which includes an effective core potential, was used for the Zn ion. The *tert*-butyl substituent on **SQ** were modeled as a methyl substituent. Frontier molecular orbitals (MOs) were generated from fully optimized ground states.

# **Computational References**

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