Supporting Information:

Stabilization of a Zn(II) Hydrosulfido Complex Utilizing a Hydrogen-Bond Accepting Ligand

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Table of Contents...Page

Experimental details

General considerations. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or an Innovative Atmospheres N_2-filled glove box unless otherwise noted. Tetrabutylammonium chloride and butane thiol were purchased from TCI Chemicals and used without purification. 1,3,5-Trimethoxybenzene was purchased from Sigma Aldrich and used without further purification. Sodium hydride was purchased from TCI chemicals, taken into a dry glove box and washed several times with hexanes before use. Tetrabutylammonium hydrosulfide (NBu_4SH) was prepared as described in the literature.[1] *Note*: Hydrogen sulfide and its salts are highly toxic and should be handled carefully to avoid exposure. Zn(didpa)Cl_2 and Zn(^{iPr}PDI)Cl_2 were prepared according to reported methods.[2-3] Spectroscopic grade acetonitrile and dichloromethane were degassed by sparging with argon followed by passage through a Pure Process Technologies solvent purification system to remove water and stored over 4 Å molecular sieves in an inert atmosphere glove box. Acetonitrile-d_3 and dichloromethane-d_2 were purchased from Cambridge Isotope laboratories and distilled from calcium hydride, deoxygenated by three freeze-pump-thaw cycles, and stored in an inert atmosphere glove box. Zn(didpa)Cl_2 and NBu_4SH stock solutions were prepared in dry acetonitrile and stored in an inert atmosphere glove box until immediately prior to use. Concentrations of Zn(didpa)Cl_2 were corrected to account for uncoordinated Zn(II) as determined by titration with *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), *vide infra*. Dichloromethane stock solutions of NBu_4SH were always prepared immediately prior to use.

Spectroscopic Methods. UV-Vis measurements were acquired on an Agilent Cary 100 UV-Vis spectrophotometer equipped with a QNW dual cuvette temperature controller at 25.00 ± 0.05°C. All spectroscopic samples were prepared under an inert atmosphere in septum-sealed cuvettes obtained from Starna Scientific. NMR spectra were acquired on a Brüker Avance-III-HD 600 spectrometer with a Prodigy multinuclear broadband cryoProbe or Varian INOVA 500 MHz spectrometer at 25.0°C unless otherwise indicated. Chemical shifts are reported in parts per million (δ) and are referenced to the residual solvent resonances.

UV-Vis Titrations. In a glove box, Zn(didpa)Cl_2 stock solutions were diluted to the desired concentration by addition to a 3.0 mL of solvent in a septum-sealed cuvette and removed from the glove box. NBu_4SH stock solutions were prepared approximately 10^5 times more concentrated than the Zn solution to provide minimal dilution during addition, and were added to the septum-sealed cuvettes by gas-tight syringe. Sodium butane thiolate solutions were prepared immediately prior to use by injecting butane thiol into a suspension of sodium hydride in acetonitrile. After shaking and a cessation of bubbling, the suspension was allowed to settle before aliquots were removed from the supernatant. Control experiments of sodium hydride suspensions and butane thiol solutions were conducted as well, and showed no reactivity.

NMR experiments. In a glove box, a 10 mM Zn(didpa)Cl_2 solution was prepared in either acetonitrile-d_3 or dichloromethane-d_2 and added to a septum-capped NMR tube. Stock solutions of NBu_4SH (~0.5 M in acetonitrile-d_3) were prepared. Aliquots of the NBu_4SH stock solutions were added to the NMR tube by gas-tight syringe.

Determination of excess Zinc in Zn(didpa)Cl_2. Stock solutions of *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) and Zn(didpa)Cl_2 were prepared in CD_3CN, with each stock solution containing 50.5 mM 1,3,5-trimethoxybenzene as an internal standard. Two equivalents of TPEN from the stock solution were added to the Zn(didpa)Cl_2 solution, and the spectrum was measured. Integration of the signals corresponding to free TPEN and Zn(TPEN) against the internal standard established that 6.0% free zinc was present, which is due to small excess of zinc being present regardless of purification method.

Additional UV-Vis experiments

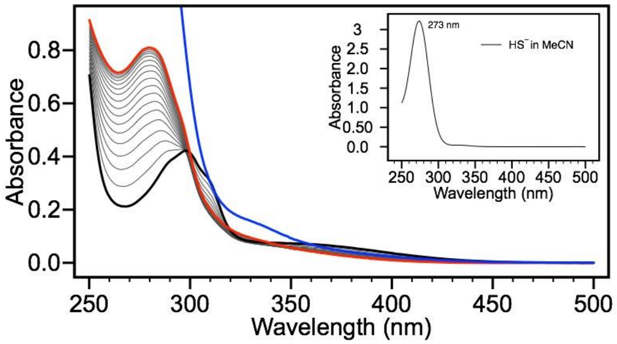

Figure S1. Titration of a 88 µM solution of Zn(didpa)Cl_2 in MeCN (black) with NBu_4SH added in 0.1 equiv. increments up to 1.5 equiv. (red). The titration was continued up to 5 equiv. (blue) of NBu_4SH, which results in a spectrum primarily dominated by the absorption of free HS^-, which has an absorbance at 273 nm (inset) in MeCN. Attempts to fit this data to a 1:1 or 1:2 binding model were unsuccessful due to overlapping peaks.

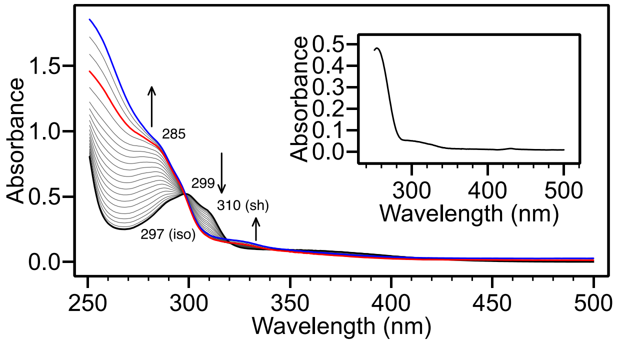

Figure S2. Titration of a 87 µM solution of Zn(didpa)Cl_2 in MeCN (black) with sodium butylthiolate added in 0.3 equiv. increments up to 6 equivalents (red). Further increase in the spectrum at 250 nm is due to sodium butane thiolate (blue). The spectrum of sodium butylthiolate is shown in the inset for comparison. Attempts to fit this data to a 1:1 or 1:2 binding model were unsuccessful.

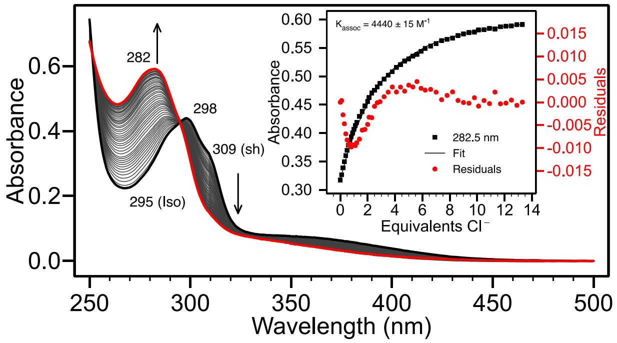

Figure S3. Titration of a 88 µM solution of Zn(didpa)Cl_2 in MeCN with NBu_4Cl added in 0.1 equiv. increments of NBu_4Cl up to 13.6 equivalents (red). Inset shows the binding isotherm at 282 nm with fit of 4,440 ± 15 M^{-1}. Residuals are assigned to the right y-axis.

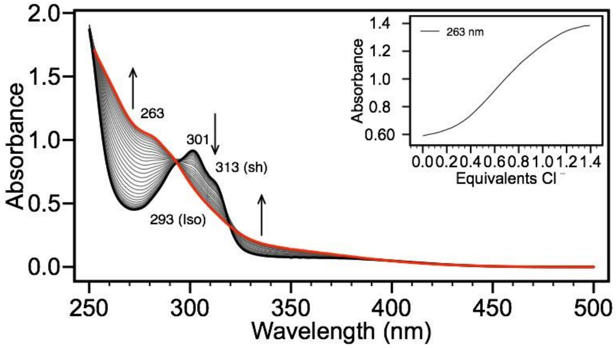

Figure S4. Titration of 175 µM solution of Zn(didpa)Cl_2 in DCM with NBu_4Cl added in 0.1 equiv. increments of NBu_4Cl up to 4.0 equivalents (red). Inset shows the binding isotherm at 263 nm and was unable to be fit due to its sinusoidal nature. The apparent induction behavior could be due to chloride binding free zinc (see methods); however, removal of these initial points does not provide reasonable fits to a 1:1 or 1:2 model.

Additional NMR experiments

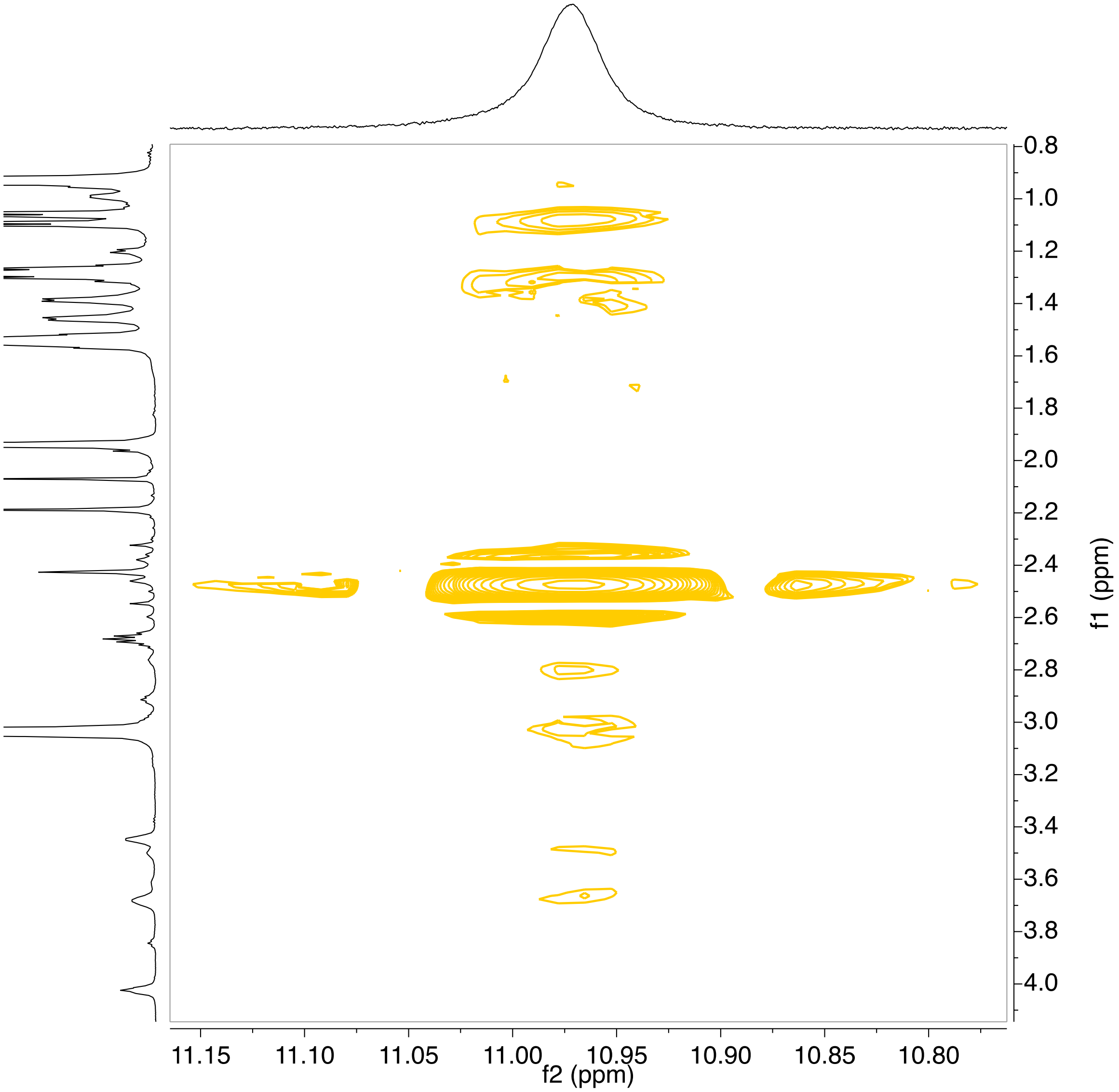

Figure S5. NOESY spectrum of 11.6 mM Zn(didpa)Cl_2, and 18.9 mM NBu_4SH (1.6 equiv.) in CD_3CN recorded at -35 °C. The spectra were recorded with a 2.0 s relaxation delay and a 0.4 s mixing time. The largest observed peak is an exchange peak with residual water.

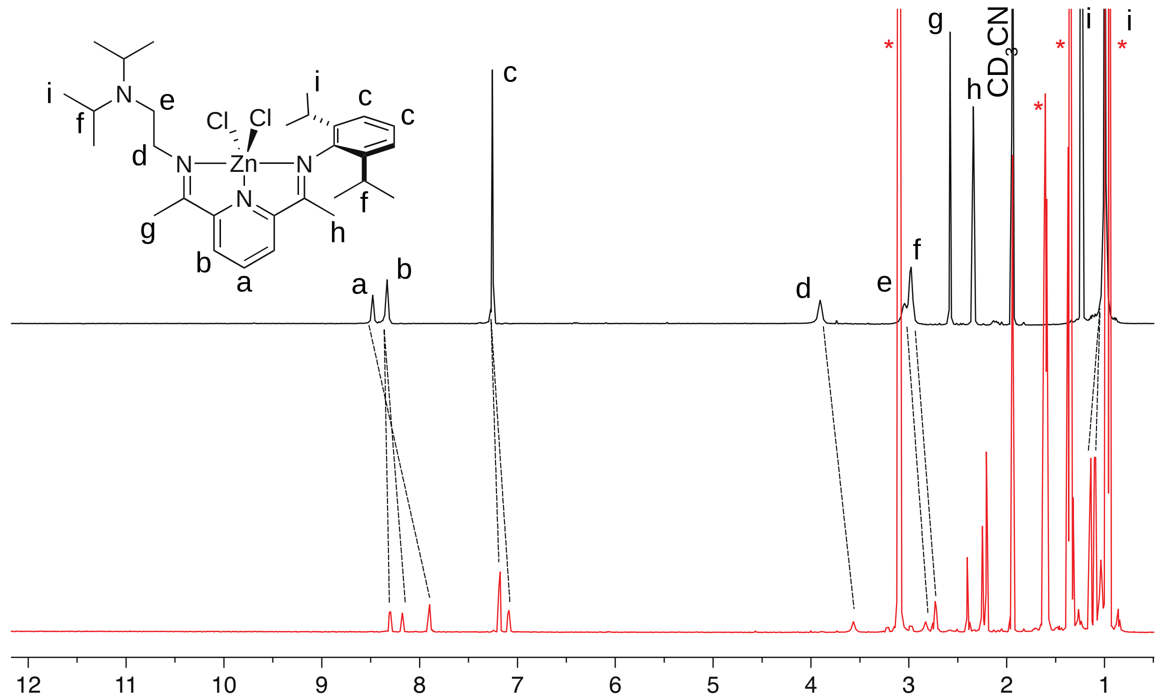

Figure S6. ^{1}H NMR spectra of Zn(didpa)Cl$_2$ (5.8 mM in CD$_3$CN) before (top, black spectrum) and after (bottom, red spectrum) addition of 5.7 equiv. of NBu$_4$Cl. The (*) correspond to NBu$_4^+$.

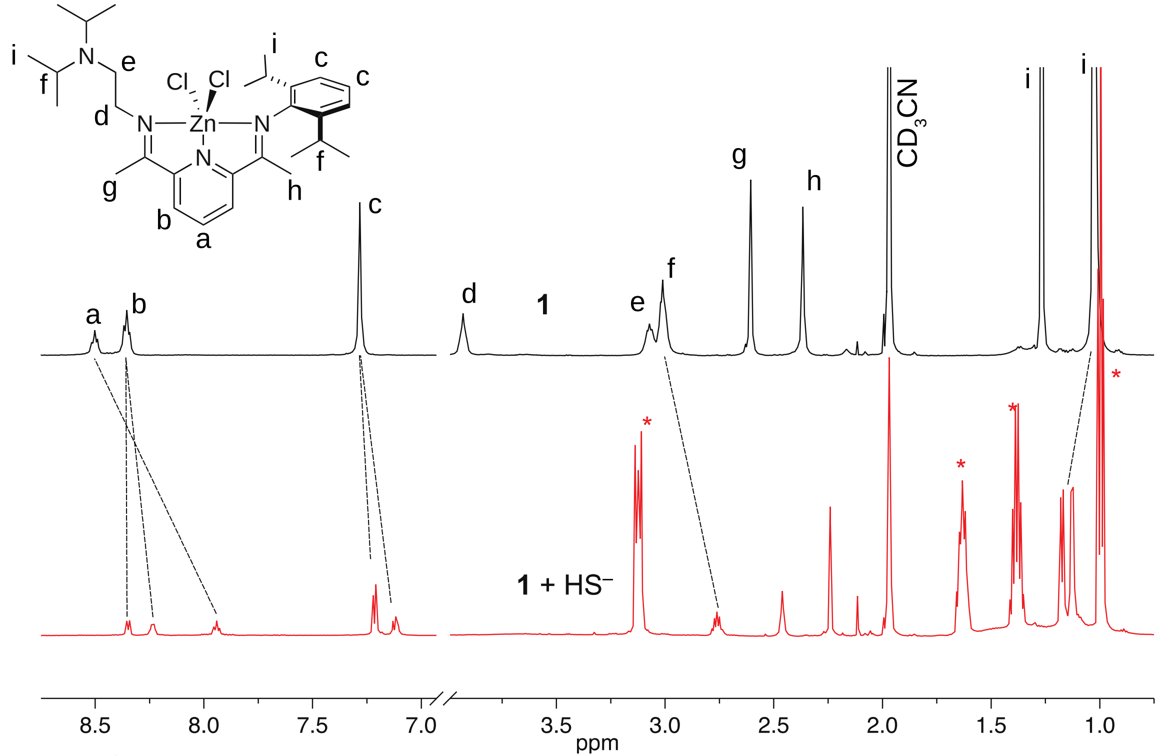

Figure S7. ^{1}H NMR spectra of **1** (11.8 mM in CD$_3$CN before (top, black) and after (bottom, red) addition of 1.5 equiv. of NBu$_4$SH. Peaks denoted with (*) correspond to the NBu$_4^+$ counterion. (reprint of figure 2)

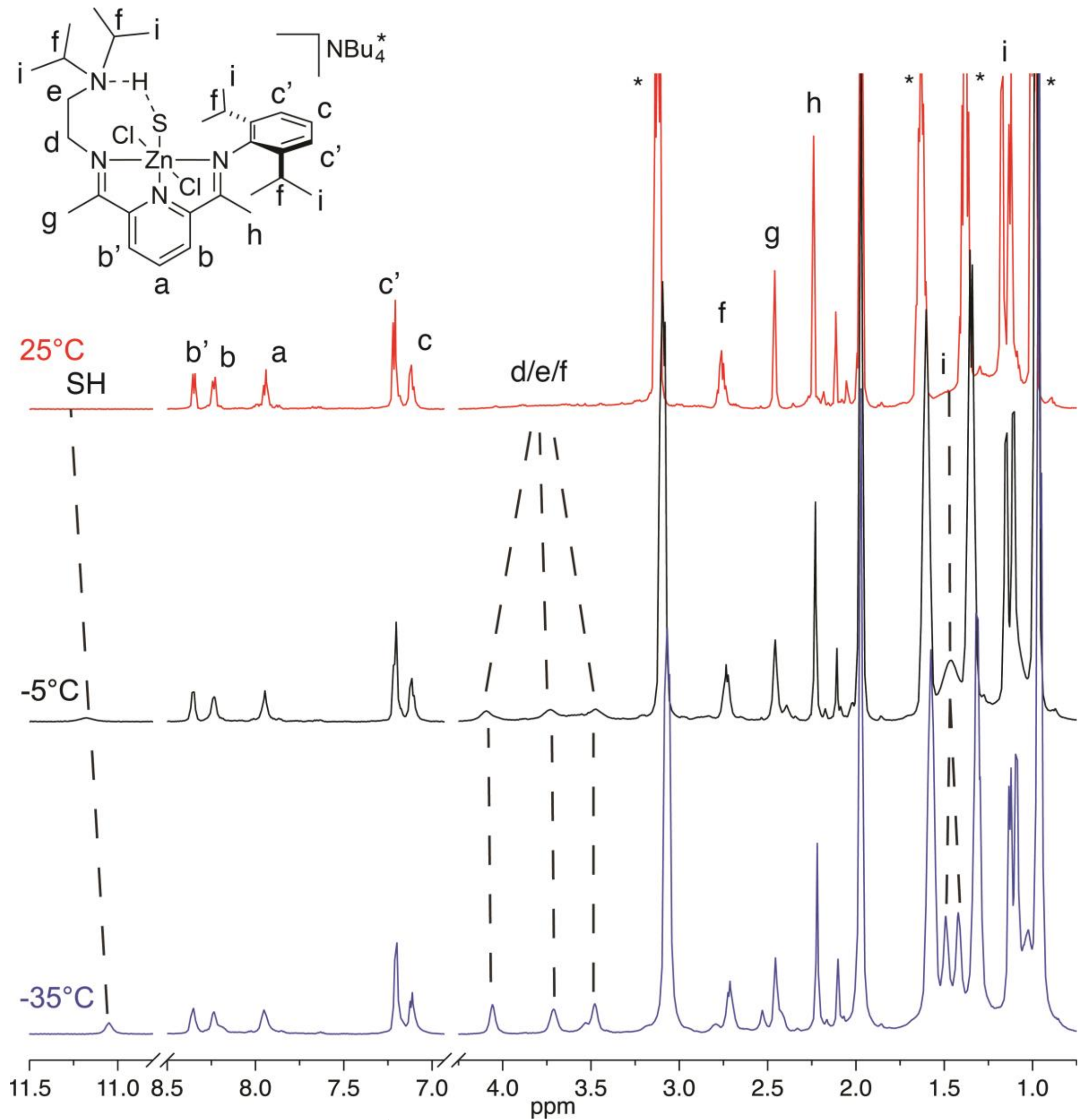

Figure S8. Variable temperature ^1H NMR spectra of 11.4 mM Zn(didpa)Cl_2, and 1.5 equiv. NBu_4SH in CD_3CN. Cooling to -35 °C results in sharpening and an upfield shift of the broad SH peak to 11.05 ppm. See Figure S6 for an expanded view of the SH peak.

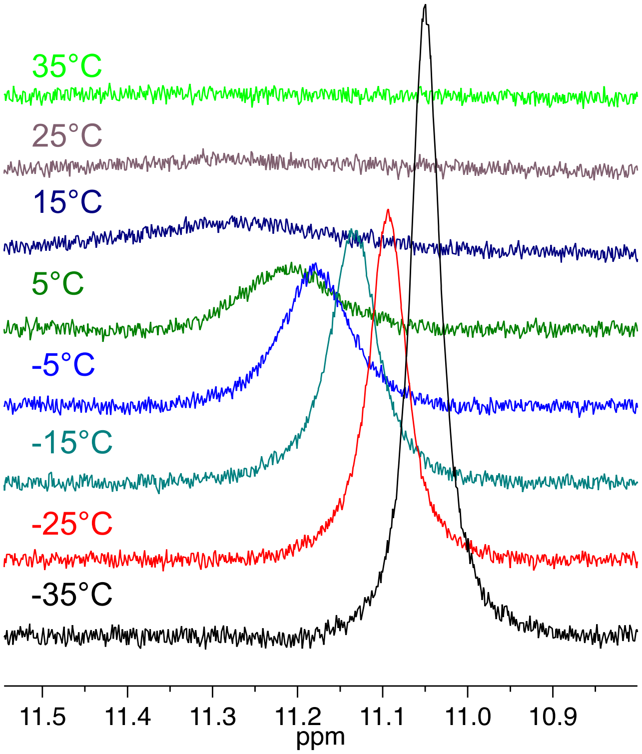

Figure S9. ^{1}H NMR spectra of 11.4 mM Zn(didpa)Cl_2, and 16.7 mM NBu_4SH (1.5 equiv.) in CD_3CN showing the SH resonance upon cooling. All spectra were measured with a 5 second relaxation delay.

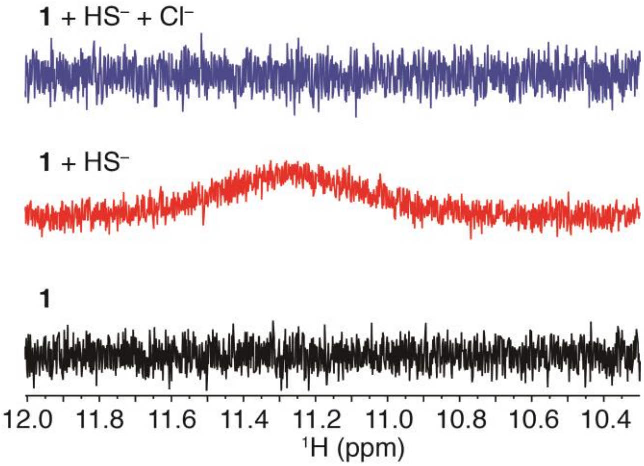

Figure S10. ^{1}H NMR spectra of 10.3 mM **1** (black) at 25 °C. Addition of 1.5 equivalents NBu_4SH at 25 °C (red). Addition of 20 equiv. of NBu_4Cl at 25 °C (blue).

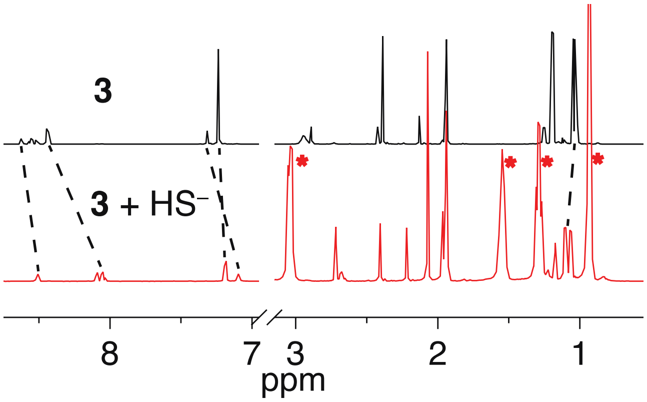

Figure S11. ^{1}H NMR spectra of 2.63 mM Zn(^{iPr}PDI)Cl$_2$ and 4.85 mM NBu$_4$SH in CD$_3$CN. Formation of a white precipitate was observed during addition of the first two equivalents of sulfide.

Job Plot

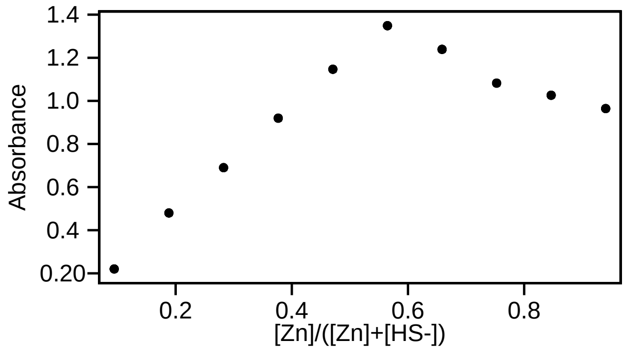

Figure S12. Job plot of Zn(didpa)Cl_2 with NBu_4Cl in MeCN at an overall concentration of 412 µM. The break is consistent with a 1:1 binding event. The plot was corrected for 6.0% excess zinc as determined by addition of TPEN by subtraction of that percentage from the mol ratio of zinc as described in the experimental details above.

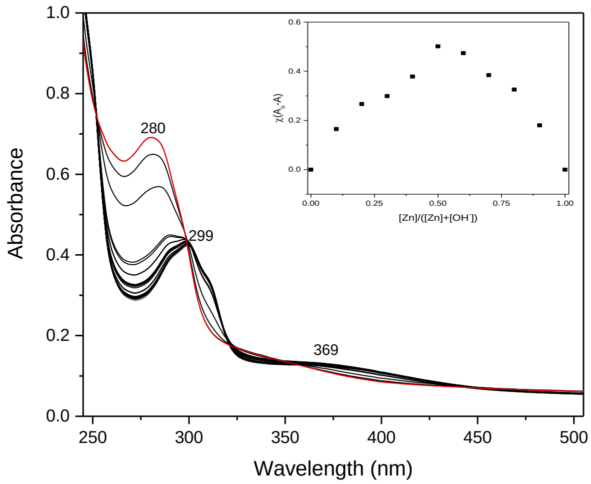

Figure S13. Titration of Zn(didpa)Cl_2 (85.5 µM, CH_2Cl_2, black) with tetramethylammonium hydroxide pentahydrate (0.1 equiv. increments up to 3 equivalents, red). The inset shows the Job plot of **1** with tetramethylammonium hydroxide pentahydrate in MeCN at a total concentration of 413 µM. The break is consistent with 1:1 binding.

Additional References

1. M. D. Hartle, D. J. Meininger, L. N. Zakharov, Z. J. Tonzetich and M. D. Pluth, *Dalton Trans.*, 2015, **44**, 19782-19785.
2. M. Delgado, S. K. Sommer, S. P. Swanson, R. F. Berger, T. Seda, L. N. Zakharov and J. D. Gilbertson, *Inorg. Chem.*, 2015, **54**, 7239-7248.
3. R. Fan, D. Zhu, H. Ding, Y. Mu, Q. Su and H. Xia, *Synt. Met.*, 2005, **149**, 135-141.