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I. Materials and Characterization

The molecular formulae and structures of the three studied complexes are shown in fig. S1. The three complexes are THF-adduct monomer, (thiolfan)YbCl(THF) (**1**), chloride-bridged dimer, [(thiolfan)YbCl]₂ (**1'**), and a variation with a shortened carbon bridge, (thiolfan*)YbCl(THF)₂ (**2**). The Yb³⁺ complex [(thiolfan)YbCl]₂ (thiolfan = 1,1'-bis(2,4-di-*tert*-butyl-6-thiomethylenephenoxy)ferrocene) was synthesized by deprotonating H₂(thiolfan) with an alkali metal hydride, followed by a reaction with YbCl₃(THF)₃ (THF = tetrahydrofuran) at -78 °C (section I-A, B). Complexes **1** and **1'** were synthesized using similar methods. To investigate the relationship between the structural and spectroscopic properties of this class of Yb³⁺ compounds, an additional derivative of **1**, (thiolfan*)YbCl(THF)₂, **2**, thiolfan* = 1,1'-bis(2,4-di-*tert*-butyl-6-thiophenoxy)ferrocene, was synthesized for comparison by modifying the supporting ligand. All reaction schemes were detailed in section I-B and laid out in fig. S2-S4. All solid-state molecular structures were confirmed by single crystal X-ray diffraction (fig. S5-S7). Details corresponding to the obtained structures can be found in table S1. Further characterization of the compounds was accomplished by nuclear magnetic resonance (NMR; fig. S8-S10) spectroscopy, elemental analysis (section I-A, B), diffusion-ordered spectroscopy (DOSY; fig. S11-14) and FTIR (fig. S33-34). The *in situ* monomeric and dimeric behavior of the ytterbium chloride complexes in solutions of toluene and THF were investigated *via* absorption, NMR, and DOSY (section I-F). We note that the spectral measurements in the main text were performed after dissolving samples in THF or 2-MeTHF (2-methyltetrahydrofuran), in which both compounds exist as a monomer, (thiolfan)YbCl(THF).

The magnetic properties were investigated using a superconducting quantum interference device (SQUID) in the solid state and the Evans method in solution (12). A magnetic susceptibility value of $\chi_m T = 4.77 \text{ emu} \cdot \text{K/mol}$ was obtained for the solid sample crushed out of toluene from direct current susceptibility measurements at 290 K after a diamagnetic correction. This is in line with the reported $\chi_m T = 5.14 \text{ emu} \cdot \text{K/mol}$ for two Yb³⁺ centers ($^2F_{7/2}$, $g_J = 8/7$) (further details in section I-F). The paramagnetic properties of the monomer, (thiolfan)YbCl(THF), were evaluated in THF-d₈ revealing $\chi_m T = 2.47 \text{ emu} \cdot \text{K/mol}$ at room temperature, in line with the reported value for a single Yb³⁺ center ($\chi_m T = 2.57 \text{ emu} \cdot \text{K/mol}$). This suggests minimal interaction of the Yb³⁺ center(s) in both the monomer and dimer.

A. General Synthetic Considerations

All compounds were manipulated and handled under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs and transferred to the glovebox without exposure to air (39). 2-Methyltetrahydrofuran (2-MeTHF) was distilled over calcium hydride under nitrogen. All solvents were stored on activated molecular sieves and/or sodium for at least a day prior to use. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use.

Nuclear magnetic resonance spectra were recorded on Bruker AV300, Bruker DRX500, and Bruker AV500 spectrometers at 298 K in C₆D₆, THF-d₈ and toluene-d₈ unless otherwise specified. Chemical shifts are reported with respect to solvent residual peaks (C₆D₆ at 7.16 ppm, C₄D₈O at 1.73 ppm, C₇D₈ at 2.08, 6.97, 7.01, and 7.09 ppm). YbCl₃(THF)₃ was prepared by stirring YbCl₃ in THF. H₂(thiolfan) (1,1'-bis(2,4-di-*tert*-butyl-6-thiomethylenephenoxy)ferrocene) and H₂(thiolfan*) (thiolfan* = 1,1'-bis(2,4-di-*tert*-butyl-6-thiophenoxy)ferrocene) were synthesized according to the literature (40, 41).

DOSY experiments were conducted on an AV300 instrument. In our hands, no DOSY signal was observed on higher field instruments (e.g., DRX500). By using a lower magnetic field instrument, spin-lattice relaxation (T_1) can be enhanced, allowing for a shorter acquisition time and thus more scans that can be used to compensate partially for a lower signal to noise ratio when using a lower field instrument. Additionally, lower magnetic fields increase the efficiency of spin-spin relaxation (T_2), minimizing the effect of spin dephasing during the echo formation in the DOSY experiments. This results in narrower and more pronounced DOSY signals than when higher magnetic fields are used. All DOSY experiments were conducted with a pulse length of 1.25 ms ($\delta = 1250 \mu\text{s}$), diffusion time of 55 ms ($\Delta = 0.055 \text{ s}$), and acquisition time of 0.60 s, except for **1'**, where a diffusion time of 32 ms ($\Delta = 0.032 \text{ s}$) was used. For all experiments, the linear gradient was split to 32 steps from 2% to 95% strength. It is important to note that, while multiple paramagnetic ^1H peaks are observed in the regular ^1H spectra, only the peak around -8 ppm yielded a DOSY signal.

IR spectra were measured on an Agilent Technologies Cary 620 Fourier transform infrared spectrometer (FTIR) fitted with a Cary 600 Series FTIR Microscope using Nujol mulls sandwiched between NaCl optical plates. CHN analyses were performed in house on a CE-440 elemental analyzer manufactured by Exeter Analytical, Inc. Magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 2 and 300 K for direct-current (DC) applied fields ranging from -7 to +7 T. DC analyses were performed on polycrystalline samples sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and temperatures between 1.8 and 300 K. In addition, data were collected on different batches to check for consistency. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants) (42).

Continuous-wave (CW) X-band (9.6 GHz) EPR spectra were acquired using a Bruker EMX CW-EPR spectrometer equipped with an ER-4116DM Dual Mode resonator operating in perpendicular mode. Temperature control was achieved through use of an Oxford Instruments ESR-900 liquid helium flow cryostat and an ITC-503 temperature controller. Pulse EPR data were acquired using a Bruker ELEXSYS E-580 pulse EPR spectrometer operating at X-band with a microwave frequency of 9.36 GHz using a MS-5 split ring resonator, with temperature control achieved through use of an Oxford Instruments CF-935 liquid helium flow cryostat and a Mercury temperature controller. Electron spin-echo (ESE) detected field-swept EPR spectra were collected using a Hahn-echo pulse sequence ($\frac{\pi}{2} - \tau - \pi - \tau - \text{echo}$) where τ is a fixed time delay of 300 ns, and $\frac{\pi}{2}$ and π pulse lengths were 40 and 80 ns, respectively.

X-ray quality crystals were obtained from various concentrated solutions placed in a -36 °C freezer in the glovebox. Inside the glovebox, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker SMART 1000 single crystal X-ray diffractometer using Mo or Cu $K\alpha$ radiation and a SMART APEX CCD detector. The data were reduced by SAINTPLUS, and an empirical absorption correction was applied using the package SADABS (43). The structure was solved and refined using SHELXTL via OLEX 2 as a graphical user interface. The structures were then visualized using ORTEP 3 (44, 45).

B. Synthesis of Ytterbium Complexes

[(thiolfan)YbCl]₂ (1'): In a nitrogen filled glovebox, 179.5 mg (0.26 mmol, 1 equiv.) of H₂(thiolfan) was dissolved in 3 mL of THF and added dropwise to a stirring slurry of NaH (63.0 mg, 10 equiv., 2.6 mmol) in 2 mL of THF. The mixture was stirred at room temperature for 2 h then filtered through glass fiber twice. The filtrate was cooled to -78 °C and added to the stirring slurry of YbCl₃(THF)₃ (128.9 mg, 1 equiv., 0.26 mmol). The reaction was stirred at -78 °C for 15 min then slowly brought to room temperature and stirred for another 2 h. The volatiles were removed under a reduced pressure and the residue was extracted with toluene and filtered through glass fiber twice. The filtrate was concentrated, then stored at -36 °C. Yellow crystals were obtained in moderate yield (151.0 mg, 65 %). X-ray quality single crystals of [(thiolfan)YbCl]₂ were grown from a solution of toluene layered with *n*-pentane at -36 °C. Due to the paramagnetic nature of the ytterbium complex, peaks are not assigned in the ¹H NMR spectrum. However, a peak at -8.66 ppm and a shoulder at -10.6 ppm were observed in C₆D₆ (fig. S8). Elemental analysis for [C₄₀H₅₂FeClO₂S₂Yb]₂, calculated: C, 53.78%, H, 5.87%, N, 0.00%; found: C, 53.35%, H, 6.04%, N, 0.00%. The reaction scheme is shown in fig. S2.

(thiolfan)YbCl(THF) (1): The procedure is analogous to the synthesis of 1'. X-ray quality single crystals of (thiolfan)YbCl(THF) were grown from a solution of THF layered with hexanes in a 2 mL glass vial at -36 °C. Due to the paramagnetic nature of the ytterbium complex, peaks are not assigned in the ¹H NMR spectrum. However, a peak at -8.66 ppm and a shoulder at -10.6 ppm were observed in C₆D₆ (fig. S9). Elemental analysis for C₄₄H₆₀FeClO₃S₂Yb, calculated: C, 54.74%, H, 6.26%, N, 0.00%; found: C, 54.59%, H, 6.30%, N, 0.15%. The reaction scheme is shown in fig. S3.

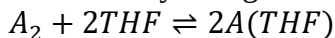
(thiolfan*)YbCl(THF)₂ (2): In a nitrogen filled glovebox, 108.7 mg (0.16 mmol, 1 equiv.) of H₂(thiolfan*) was dissolved in 3 mL of THF and added dropwise to a stirring slurry of NaH (40.0 mg, 10 equiv., 1.6 mmol) in 2 mL of THF. The mixture was stirred at room temperature for 2 h then filtered through glass fiber twice. The filtrate was cooled to -78 °C and added to a stirring slurry of YbCl₃(THF)₃ (81.3 mg, 1 equiv., 0.16 mmol). The reaction was stirred at -78 °C for 15 min then slowly brought to room temperature and stirred for another 2 h. The volatiles were removed under a reduced pressure and the residue was extracted with toluene and filtered through glass fiber twice. The filtrate was dried and dissolved in 0.5 mL of THF and 5 mL of hexanes, then stored at -36 °C. Yellow crystals were obtained in moderate yield (58.0 mg, 41%). Due to the paramagnetic nature of the ytterbium complex, peaks are not assigned in the ¹H NMR spectrum (fig. S10). Elemental analysis for C₄₆H₆₄FeClO₄S₂Yb, calculated: C, 54.73%, H, 6.39%, N, 0.00%; found: C, 54.59%, H, 5.97%, N, 0.10%. The reaction scheme is shown in fig. S4.

C. Discussion on the Monomer vs. Dimer Equilibrium

As shown in fig. S5-S7, the solid-state molecular structure of [(thiolfan)YbCl]₂ shows a dimer bridged by two chlorides (fig. S5), while that of (thiolfan)YbCl(THF) shows a monomer with a single THF ligand coordinated (fig. S6). For the dimer, the compound was crystallized from toluene in order to perform NMR and single crystal X-ray diffraction measurements. Single crystals of (thiolfan)YbCl(THF) were obtained from a saturated THF solution layered with hexanes (fig. S6). THF is a coordinating solvent, leading to a change from the dimeric to the monomeric structure. In the following section, we lay out our observations that elaborate on the monomer vs. dimer equilibrium (fig. S15).

First, we performed a titration experiment by introducing stoichiometric amounts of THF to the sample in toluene and observed a shift in absorption features that trend toward the feature observed when THF is used as a solvent. As shown in fig. S16, shifting from 1:1, 1:2, 1:4, and 1:10 ratios of (thiolfan)YbCl monomer to THF shifts the absorption spectra from bimodal to unimodal peaks that reflect the spectra of the sample in THF, even in excess toluene. We added the absorption spectra in toluene and in THF at the top and bottom of the figure to make this trend clear.

The change in absorption of these two peaks aligns with an equilibrium constant of 1. The monomer vs. dimer equilibrium that is caused by a single THF coordination can be expressed as:



Where A = (thiolfan)YbCl, A_2 = [(thiolfan)YbCl]₂, and $A(THF)$ = (thiolfan)YbCl(THF). The equilibrium constant (K_{eq}) can be written out as:

$$K_{eq} = \frac{[A(THF)]^2}{[A_2][THF]^2}$$

The monomer and dimer concentrations can be related by the total amount of sample added (1.3 mM), either in monomer or dimer forms. This equation can be rearranged to express the monomer concentration as a function of the dimer concentration.

$$[Total\ Yb\ centers\ added] = [A] + 2[A_2] = 1.3\ mM$$

With the above two equations, solving for $[A_2]$ gives:

$$[A_2] = \frac{1}{40} \left(5K_{eq}[THF]^2 \pm \sqrt{5K_{eq}[THF]^2(5K_{eq}[THF]^2 + 52)} + 26 \right)$$

And, solving for $[A(THF)]$ gives:

$$[A(THF)] = \frac{1}{20} \left(\pm \sqrt{25K_{eq}^2[THF]^4 + 260K_{eq}[THF]^2 + 5K_{eq}[THF]^2} \right)$$

The calculated monomer and dimer concentrations, corresponding to $[A(THF)]$ and $[A_2]$ above, are plotted against $[THF]$ for $K_{eq} = \{0.1, 1, 10\}$ in fig. S17. The integrated absorption areas of the peak at 980 nm and 983 nm are plotted, which reflects the concentration of monomer and dimer in the solution, according to Beer's law. The absorption trend corresponds best to $K_{eq} \sim 1$.

Similar to the Yb complex, [(thiolfan)YCl]₂ also crystallizes as a dimer with chlorides bridging the two yttrium centers (46). Critically, previous work showed that [(thiolfan)YCl]₂ coordinates THF when dissolved in THF (46). A DOSY experiment was conducted on [(thiolfan)YCl]₂ in THF-d₈ with tetrakis(trimethylsilyl)silane (TMSS) used as an internal standard (fig. S18). The hydrodynamic radius (r_H) of (thiolfan)YCl(THF) was derived from the Stokes-Einstein equation.

$$D_t = \frac{k_B T}{6\pi\eta r_H}$$

Where k_B is the Boltzmann constant, T is the temperature, and η is the solution viscosity (298 K, 0.46 mPa·s, respectively) (47). Radius $r_H = 6.70\ \text{\AA}$ was calculated using this equation and compared to the radius of the dimeric structure in the solid state ($r_{X-ray} = 11.20\ \text{\AA}$ estimated by measuring the distance from the center of the dimeric molecule to the farthest atom using X-ray crystallographic data), which is 1.67 times of that in solution. The integration of THF to Y proton signals in the ¹H NMR spectrum of (thiolfan)YCl(THF) in C₆D₆ was found to be consistent with one coordinated THF to yttrium in prior studies, indicating that the Y analogue of the ytterbium complex also exists as a monomer in THF (46).

The solution-state molecular radii obtained from the DOSY experiments for the (thiolfan) and (thiolfan*) Yb complexes in presence and absence of THF are presented in tables S2 and S3, respectively. For the (thiolfan) complexes, DOSY experiments suggest that (thiolfan)YbCl dimerizes in solution in the absence of a coordinating substrate such as THF and exists as [(thiolfan)YbCl]₂ (**1'**). However, in the presence of THF, it will form a monomeric THF-adduct (**1**). We can verify these experiments by comparing r_H values to their respective solid-state structures' radii. Given the solid-state structure's "globular" geometry for **1** and **1'**, the radius of a complex can be obtained by measuring the distance between the center of mass and the furthest point on the molecule from the center of mass. The coordinates for the center of mass are calculated using:

$$\bar{x} = \frac{\sum_{i=1}^N m_i x_i}{MW}, \bar{y} = \frac{\sum_{i=1}^N m_i y_i}{MW}, \bar{z} = \frac{\sum_{i=1}^N m_i z_i}{MW}$$

Where ($\bar{x}$, $\bar{y}$, $\bar{z}$) is the coordinates of the center of mass, m_i is the atomic mass of the atoms corresponding to the (x_i , y_i , z_i) coordinates, and MW is the molecular weight of the complex. The calculated r_H values of 7.1 Å for **1** and 10.2 Å for **1'** are in near perfect agreement with their solid-state counterparts, 7.2 Å and 10.3 Å respectively.

Similarly, the (thiolfan*) complexes exhibit the same trend in their r_H values in d₈-toluene and d₈-THF, with the THF compound being slightly smaller. However, the difference between the two radii is not as significant as the (thiolfan) complexes. At first glance, the calculated radii of 5.2 Å (toluene solution) and 4.6 Å (THF solution) seem small, however it is important to note that these compounds are assumed to be spherical/globular in the Stokes-Einstein equation. In contrast to **1** and **1'**, the solid-state structure of (thiolfan*)YbCl(THF)₂ exhibits a "cylindrical" geometry. Therefore, to approximate the compound as a spherical object, one can calculate the compound's radius of gyration (r_g) using:

$$r_g^2 = \frac{1}{MW} \sum_i^N m_i [(x_i - \bar{x})^2 + (y_i - \bar{y})^2 + (z_i - \bar{z})^2]$$

The calculated r_g value of 4.5 Å is now in great agreement with the 4.6 Å radius obtained from DOSY experiments, suggesting that (thiolfan*)YbCl exists as a bis-THF adduct. Unfortunately, as we have no data on the solid-state structure of (thiolfan*)YbCl, we are unable to assign this compound's *in situ* state in the absence of a coordinating solvent. Visualization of the radial and center-of-mass analyses are shown in fig. S19, and the calculated radii are tabulated for toluene-d₈ (table S2) and THF-d₈ (table S3).

Furthermore, a variable temperature ¹H NMR experiment was conducted to investigate the equilibrium between the monomeric and dimeric Yb complexes in toluene-d₈ at different temperatures. As the temperature increased, the peak at -8.38 ppm and -10.42 ppm shifted and eventually coalesced into one peak at -7.56 ppm at 354 K (fig. S20). In addition, a small peak at -1.34 ppm and a bump at -18.6 ppm appeared and became obvious at elevated temperatures. A similar trend was observed when THF was added to a sample in C₆D₆, where the bump at -10.5 ppm started to disappear and merged with the peak at -8.32 ppm, but the intensity of the peaks at -1.86 ppm and -17.8 ppm both increased (fig. S21). In addition, the ¹H NMR spectrum of (thiolfan)YbCl(THF) taken in THF-d₈ displayed a sharp peak at -8.92 and a small peak at -17.9 ppm (fig S9). Despite the slight difference in the chemical shifts due to different deuterated solvents being employed, we hypothesize that increasing temperature and having THF present, either as the NMR solvent or added intentionally to an NMR sample, cause the shift in equilibrium from the dimeric to the monomeric form of the ytterbium complex.

Lastly, theoretical calculations of the monomeric (thiolfan)YbCl(THF) showed remarkable alignment with the experimental spectra using THF as a solvent. Unfortunately, performing calculations on the ytterbium dimer was too expensive, given the presence of two ytterbium and two iron atoms. In conclusion, our data indicated that (thiolfan)YbCl(THF) was a monomer in THF solution, based on single crystal X-ray diffraction, absorption, DOSY of the ytterbium and yttrium complexes, NMR, and theoretical calculations.

D. Magnetic Properties

The magnetic properties of all three ytterbium compounds in the solid state were investigated using a superconducting quantum interference device (SQUID). Analyses were performed on crushed polycrystalline samples obtained from a solution of toluene/hexanes and sealed in a polyethylene membrane under an inert atmosphere. Direct current (dc) susceptibility measurements were performed in a magnetic field, B , of 1000 Oe and at a temperature range of 2 K to 290 K. Solid-state molecular structure of [(thiolfan)YbCl]₂ revealed a dinuclear complex, therefore, at 290 K, $\chi_m T = 4.77 \text{ emu} \cdot \text{K/mol}$ after diamagnetic correction is comparable with the reported two ytterbium centers ($5.14 \text{ emu} \cdot \text{K/mol}$, $^2F_{7/2}$, $g_J = 8/7$) at room temperature (48-54). Upon cooling, $\chi_m T$ decreased gradually to $3.67 \text{ emu} \cdot \text{K/mol}$ at 2 K as a result of depopulation of the excited crystal field sublevels of Yb³⁺ and/or antiferromagnetic interactions between the two Yb³⁺ centers (fig. S22). At low temperature, the magnetization value rose rapidly at low fields, and increased slowly at high fields, then reached a maximum of $3.76 \mu_B$ at 7 T (fig. S23a). Such field dependence of the magnetization of [(thiolfan)YbCl]₂ is typically observed for weakly interacting Yb³⁺ ions (49, 51, 52, 55). Attempts to fit the field dependent magnetization data using a Brillouin function of two non-interacting Yb³⁺ ions gave incongruent results. The saturation limit at 7 T and 2 K for [(thiolfan)YbCl]₂ was lower than expected for two uncoupled Yb³⁺ centers. This discrepancy may be due to exchange interactions or the presence of low-lying excited states (54, 56). The discrepancy between Brillouin function of two uncoupled $J = \pm 7/2$ states versus the experimental data of [(thiolfan)YbCl]₂ may also be attributed to magnetic anisotropy. The lack of perfect superimposition of the M versus H/T curves at 2, 4, 6, 8, and 10 K (fig. S23b) suggests the presence of magnetic anisotropy and/or low-lying excited states for the ytterbium complex. However, the measurement was performed on a polycrystalline sample which is insufficient to probe the orientation sensitivity of the anisotropic exchange contribution.

A linear curve was observed in $1/\chi$ vs T and a Curie constant was calculated based on the linear fit ($c = 4.39 \text{ emu K/mol}$). According to the Curie-Weiss law, a negative Weiss constant ($\theta = -4.46 \text{ K}$) was obtained from the graph, indicating anti-ferromagnetic coupling (fig. S24). A linear curve was also observed in the M vs H measurement passing through the origin, confirming the paramagnetic properties of the compound. No hysteresis in isothermal magnetization measurements was observed (fig. S25).

Similarly, direct current (DC) susceptibility measurements in a magnetic field, B , of 1000 Oe and at a temperature range of 2 K to 300 K were also conducted for (thiolfan*)YbCl(THF)₂. For (thiolfan*)YbCl(THF)₂, the room temperature molecular susceptibility and effective magnetic moment $\chi_m T = 2.11 \text{ emu} \cdot \text{K/mol}$ and $\mu_{eff} = 4.11$ per ytterbium center were calculated based on experimental results which are comparable to the expected values for one ytterbium center ($2.57 \text{ emu} \cdot \text{K/mol}$ and $\mu_{eff} = 4.54$) assuming a $J = 7/2$ ($S = 1/2$, $L = 3$, $g_J = 8/7$) ground state (20, 57). Interestingly, upon cooling, $\chi_m T$ of (thiolfan*)YbCl(THF)₂ first decreases gradually as temperature decreases to $1.73 \text{ emu} \cdot \text{K/mol}$ at 17 K, then slowly increased to $1.75 \text{ emu} \cdot \text{K/mol}$ at 6 K, followed by a sharp decrease to $1.69 \text{ emu} \cdot \text{K/mol}$ at 2 K (fig. S26). A linear curve was

observed in $1/\chi$ vs T . The Curie constant was calculated based on the linear fit ($c = 2.13 \text{ emu K/mol}$), which is comparable to the value of $\chi_m T = 2.11 \text{ emu} \cdot \text{K/mol}$ previously calculated for one ytterbium center. According to the Curie-Weiss law, a negative Weiss constant ($\theta = -5.89 \text{ K}$) was obtained from the graph, indicating a net anti-ferromagnetic coupling in the bulk sample (fig. S27). A linear curve was also observed in the M vs H measurement passing through the origin, confirming the paramagnetic properties of this compound (fig. S28).

The magnetic susceptibility of each ytterbium compound in solution was measured by NMR spectroscopy using the Evans method in designated deuterated solvents (12). The molar susceptibility and effective magnetic moment (μ_{eff}) of each compound was calculated based on the following formulae (58):

$$\chi_m T = \frac{3 \times 10^3 \Delta f}{4\pi f_m c} - \chi_D$$

$$\mu_{eff} = 2.827 \sqrt{\chi_m T}$$

where χ_m is the corrected paramagnetic molar susceptibility, T (in K) is the absolute temperature at which the NMR spectrum was taken, Δf (in Hz) is the chemical shift difference of the NMR reference in the presence and absence of the paramagnetic compound (shift of the deuterated solvent referencing peak), f_m (in Hz) is the external magnetic field, C (in mol/L) is the concentration of the sample, and χ_D is the diamagnetic susceptibility. For simplicity, χ_D of (thiolfan*)YbCl(THF)₂ is estimated based on:

$$\chi_D \approx -\frac{M}{2} \times 10^{-6}$$

where M (in g/mol) is the molecular mass.

The paramagnetic properties of **1** and **1'** were investigated in THF-d₈, C₆D₆, and Tol-d₈ (fig. S29-S31). A $\chi_m T = 2.68 \text{ emu} \cdot \text{K/mol}$ was calculated along with a $\mu_{eff} = 4.63$ based on the difference in δ observed in the ¹H NMR spectrum after diamagnetic correction in THF-d₈, as expected for one ytterbium center ($2.57 \text{ emu} \cdot \text{K/mol}$ and $\mu_{eff} = 4.54$) assuming a $J = 7/2$ ($S = 1/2$, $L = 3$, $g_J = 8/7$) ground state (19, 57). Similar results were obtained using other two solvents, $\chi_m T = 2.08 \text{ emu} \cdot \text{K/mol}$ was calculated for C₆D₆, and $2.68 \text{ emu} \cdot \text{K/mol}$ was calculated for Tol-d₈ per ytterbium center. The effective magnetic moment of (thiolfan)YbCl(THF) was calculated based on the formulae above suggesting $\mu_{eff} = 4.63$ in THF-d₈, 4.08 in C₆D₆, and 4.63 in Tol-d₈.

Similarly, the molar susceptibility and effective magnetic moment were calculated for (thiolfan*)YbCl(THF)₂ in C₆D₆. A $\chi_m T = 2.05 \text{ emu} \cdot \text{K/mol}$ and $\mu_{eff} = 4.05$ per ytterbium center was found for (thiolfan*)YbCl(THF)₂ (fig. S32). This is consistent with the findings for (thiolfan)YbCl(THF), and previously reported values per ytterbium center (19, 57).

II. Details of Electronic Spectroscopy

A. Further Details on Sample Absorption

The absorption band around 400-600 nm is assigned to the supporting ligand, as evident by the comparison between the absorbance of the sample vs. that of H₂(thiolfan) (fig. S35). The wide-field absorption in Fig. 1c is reproduced in molar absorptivity units (M⁻¹ cm⁻¹) in fig. S36. The peak absorptivity is $64 \text{ M}^{-1} \text{ cm}^{-1}$ with a FWHM of 3.13 meV, which is about 5 times broader than the linewidth of 0.6 meV obtained from high-resolution transmission. The molar absorptivity spectrum of the high-resolution transmission reported in Fig. 3b (same spectrum as the one shown

in Fig. 1c) has a peak height of around $300 \text{ M}^{-1} \text{ cm}^{-1}$. Accounting for the five-fold broadening of the linewidth, the ratio of the peak amplitudes 300:64 is expected.

B. High Resolution Transmission/Absorption Setup

The broad band absorption spectra reported in the manuscript were collected using the Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer. A high-resolution transmission/absorption spectrum of the sample was measured with a tunable narrow band CW laser (M Squared SolsTis Ti:Sapph laser). The laser beam is split into two paths by a polarizing beam splitter (PBS). One beam measures the absorption of the solvent and the other measures the absorption of the sample. The quarter waveplate is used to change the polarization of the laser beam so that we can measure the absorption of σ^+ and σ^+ light. The two permanent magnets create a strong static magnetic field to induce Zeeman splitting. The translational stage allows us to control the distance between the magnet and the sample and to vary the strength of the magnetic field at the sample's location. The setup is shown in fig. S37.

C. Discussion on the Sources of Linewidth Broadening

As shown in fig. S38, over a range of 300 K, the absorption linewidth narrows by 0.1 meV as a function of temperature, but once the sample is frozen, it appears to have no change in linewidth. This suggests that the room temperature linewidth has some component of homogeneous broadening, while the 77 K linewidth consists of many narrower transitions, as evident in the linewidth obtained in spectral hole burning (fig. S39). If the 0.6 meV linewidth is limited by the excited state lifetime, it would correspond to a lifetime of 1.1 ps (where lifetime $\tau = \hbar/\Gamma$, linewidth $\Gamma = 0.6 \text{ meV}$ and $\hbar = 6.6 \times 10^{-16} \text{ eV} \cdot \text{s}$). However, the Einstein A_{21} coefficient can be extracted from the experimental oscillator strength of 9.36×10^{-6} (59). The corresponding expected excited state decay rate is 912 Hz, which translates to a lifetime of 1.1 ms. Therefore, the 0.6 meV linewidth is not limited by the excited state lifetime.

We also measured the fluorescence lifetime of the room-temperature sample in solution (fig. S40). Because there is minimal Stokes shift from the 980 nm absorption and emission peaks, as shown in Fig. 1 in the manuscript, we excited into the ligand absorption band at 420 nm to be able to spectrally filter the excitation from the emission. The resulting lifetime then would include not only the excited state decay rate of the 980 nm transition, but also the time it takes for the excited electron to decay from the ligand-dominated states to the Yb^{3+} -dominated electronic states, from which the emission originates. The measured lifetime was 3.2 μs , which rules out lifetime broadening as the major source of the room-temperature linewidth. The 3.2 μs lifetime would correspond to a 0.2 neV linewidth, which is far narrower than the observed 0.6 meV and close to the 0.41 neV SHB linewidth (Fig. 2e). Therefore, we conclude that the 0.6 meV linewidth of the room-temperature solution consists of many transitions and some amount of ligand fluctuations, which cause a broader linewidth than the transform-limit.

We also investigated the hyperfine contribution to the spectral linewidth. The isotopic distribution of Yb can be divided into 7 stable isotopes with 3 nuclear spin values $\{S = 0, 1/2, 5/2\}$. We obtained ground state g-values and hyperfine (A) parameters by fitting the X-band (9.638 GHz) CW-EPR spectrum as shown in fig. S41a. For the excited state, we employ the calculated g-values based on CASSCF/RASSI level of theory (section III-B). With these parameters, we are able to plot a calculated hyperfine splitting as a function of the external magnetic field strength, as shown in the fig. S41b. At zero field, the hyperfine splitting for $\{S = 0, 1/2, 5/2\}$ is [0, 20.7, 27.2] GHz for the ground state and [0, 14.8, 19.4] GHz for the excited state. Considering all the spin-allowed

zero-field transitions, the energy spread shows a minuscule effect compared with the 150 GHz optical peak, this reveals that zero-field hyperfine broadening may not be a major line-broadening contributor. Besides hyperfine splitting, the isotope shift caused by reduced mass is calculated to be around 23 MHz, and the volume effect is around 4 MHz. Overall, the isotopic contributions are found to be orders of magnitude smaller compared to the 150 GHz absorption linewidth of the (thiolfan)YbCl(THF) and are not expected to be the major broadening sources.

Furthermore, we investigated the superhyperfine contributions to the spectral linewidth. A superhyperfine interaction occurs when an unpaired electron couples to multiple nuclei. As it applies to our sample, a deuterated THF coordinating to the Yb³⁺ may cause a change in superhyperfine splitting. In addition, spin-spin dipolar interaction may occur if some other magnetic moment near the Yb³⁺ nucleus interacts with the magnetic dipole that couples to the electronic states involved in transition IV. In general, the magnitude of these effects can be gauged by taking the absorption of the sample in THF and deuterated THF. The linewidth of our sample saw an increase in linewidth from 0.6 meV to 0.7 meV and a decrease in molar absorptivity when using the deuterated solvent (fig. S42). The sample concentrations were 3.1 mM in THF and 3.7 mM in THF-d₈. The linewidth stays similar with solvent deuteration, which indicates that superhyperfine interactions do not make up the dominant contributions to the inhomogeneous broadening observed in THF.

A comparison of reported linewidths of Yb³⁺ and other lanthanide transitions in a variety of temperatures and environments are shown in table S4 (18-21, 60-71). The wide range of linewidths listed in the table demonstrate the effect of temporal and environmental dephasing, especially when comparing solution vs. solid phase samples.

III. Theoretical Calculations

A. Magnetic Dipole Calculations

The transitions between states with the same orbital-angular momentum quantum number are electric dipole (E1) disallowed. Therefore, operators with even symmetry (e.g. magnetic dipole (M1)) might assist in mediating the transitions. However, the theoretical limit for an Yb³⁺ ion M1 transition ($f \sim 10^{-8}$) is considerably smaller than that measured in (thiolfan)YbCl(THF) ($f \sim 10^{-6}$) as shown in table S5 (56). With the assumption that the f-f transition occurs between two pure 4f atomic orbitals, the transition is expected to be only magnetic-dipole-allowed (23). The magnetic dipole moment operator, $\hat{M}$ can be written as (72):

$$\hat{M} = -\frac{\mu_B}{\hbar} \sum_i (\hat{l}_i + 2\hat{s}_i),$$

The magnetic dipole oscillator strength $M1$ is therefore

$$M1_{f \leftarrow i} = \frac{2m_e(E_f - E_i)}{3\hbar^2 e^2 c^2} \frac{n_r}{2J + 1} |\langle f | \hat{M} | i \rangle|^2,$$

or

$$M1_{f \leftarrow i} = \frac{2m_e(E_f - E_i)}{3\hbar^2 e^2 c^2} \frac{n_r}{2J + 1} |\langle f | \hat{M}_x \mathbf{i} + \hat{M}_y \mathbf{j} + \hat{M}_z \mathbf{k} | i \rangle|^2,$$

Where

$$\hat{M}_z = -\frac{\mu_B}{\hbar} \sum_i (\hat{l}_{zi} + 2\hat{s}_{zi}),$$

$$\hat{M}_x = -\frac{\mu_B}{2\hbar} \sum_i (\hat{l}_+ + \hat{l}_- + 2\hat{S}_+ + 2\hat{S}_-)_i,$$

$$\hat{M}_y = -\frac{\mu_B}{2i\hbar} \sum_i (\hat{l}_+ - \hat{l}_- + 2\hat{S}_+ - 2\hat{S}_-)_i.$$

From this model, considering only the $M1$ transition is not enough to reproduce the experimental oscillator strength, therefore, a mixing of orbitals with different angular momenta is needed to allow $E1$ (the electric dipole) transition, and $E1$ should be the principal contributor to the transition strength. The Judd-Ofelt perturbation theory has been used previously to explain the enhancement of $E1$ oscillator strengths in lanthanide systems by invoking mixing with the virtual $5d$ orbitals via artificially lowering the $5d$ energy to enhance the electronic $4f/5d$ interaction (7, 24). However, this approach does not fully account for how the transition energies and oscillator strengths are altered by the ligand field, and the single electron-hole picture does not provide enough fitting parameters to use the Judd-Ofelt theory for the Yb^{3+} ion.

B. Electronic Structure Calculations

The ground state of (thiolfan) $\text{YbCl}(\text{THF})$ was optimized in Turbomole (73), using the TPSSh functional (74), the ANO-RCC basis set (75, 76) (ANO-RCC-VTZP for Yb, ANO-RCC-VDZP for Fe, ANO-RCC-VTZ for Cl, O, S, and ANO-RCC-VDZ for C and H), and the D3 dispersion correction (77). The effect of solvation on geometry optimizations was included by employing the conductor-like screening model (COSMO) with a dielectric constant of $\epsilon = 7.58$ to model THF (78). From this optimized geometry, a reduced model was used for multireference calculations below. In the truncated model, the ferrocene unit was removed, and the sulfur atoms were capped with hydrogens, after which the reduced structure was reoptimized.

As implemented in Openmolcas (79), the multireference CASSCF/MS-CASPT2 methods (80-83) were used in combination with the same ANO-RCC basis set. The second-order Douglas-Kroll-Hess (DKH2) one-electron spin-less Hamiltonian was applied for all wave function theory calculations to allow for spin-free relativistic effects (84-86). A complete active space used in the CASSCF calculations comprised of 13 electrons in 12 orbitals (7 x Yb $4f$ -like orbitals and 5 x Yb $5d$ -like orbitals, tables S6 and S7). All orbitals were generated with Visual Molecular Dynamics with an isosurface of 0.01 (87). The state-averaged (SA-)CASSCF formalism was used, including 20 lowest-lying states. The dynamic MS-CASPT2 correlation was then included via the CASPT2 module. Spin-orbit coupling was added through the RASSI-SOC module (88, 89), where oscillator strengths and transition energies were calculated for electric and magnetic dipole transitions.

Finally, g tensors and spin-orbit coupling matrix elements were computed with the EPRG (RASSI module for EPR g -factor calculations) and SOC functions in the RASSI-SOC module after applying spin-orbit effects on the basis of the Kramers doublet (90). Length dipole oscillator strengths were reported in the main text, the length and velocity dipole results are listed in table S8. Most dominant orbitals involved in the electronic transition from CASSCF and RASSI-SOC calculations are shown in table S9. SOC matrix elements between RASSI-SOC states are listed in tables S10 and S11. We see the CAS(12,13) active space produces different spin-orbit couplings between RASSI-SOC states than CAS(7,13). In table S10, we probed how orbital composition affected these SOC matrix elements. SA-7-CASCI takes the orbitals from the CAS(12,13) active space, and does not reoptimize them, computing SOC matrix elements for the first 7 RASSI-SOC states, corresponding to the f - f transitions. SA-7-CASSCF takes the orbitals from the CAS(12,13) active space and reoptimizes them based on the first seven transitions. Since these transitions are

dominated by f-f transitions, the orbitals become more f-like in character, i.e., less mixing with 5d. We see the SA-7-CASSCF SOC matrix elements look more like the CAS(7,13) matrix elements in table S11, while SA-7-CASCI look like the CAS(12,13) matrix elements. This underscores the importance of 4f/5d orbital mixing's effect on spin orbit coupling, which in turn mediates oscillator strength. Recent findings suggest that f-orbitals are quite sensitive to SOC and these orbitals should be optimized with SOC-included (91). One way to include this effect is through an exact two-component transformation (X2C) but the quantitative importance of including SOC via X2C vs. other methods requires further study (92).

Several limitations of our theoretical calculations should be mentioned. Due to the large system size and number of electrons, the active space used in the CASSCF calculations is still fairly limited, prohibiting us from including all the ligand-metal bonding orbitals. We thus cannot accurately capture the covalency of metal-ligand bonds and how much the pure 4f states are influenced by the ligand. Additionally, spin-orbit coupling is added for calculating transitions and oscillator strengths, but (thiolfan)YbCl(THF) orbitals are not optimized to include spin-orbit coupling. This could allow for an increased 4f/5d mixing in our complete active space orbitals that we currently do not observe, and could also alter the symmetry of the 4f orbitals involved in transitions **II-V**. Furthermore, the multireference calculations are performed in the gas phase and as a static approximation. Dynamic calculations of the molecular vibrational structure and solvent contributions and fluctuations will help aid additional understanding of the nature of the target transition **IV**, such as its linewidth. Theoretical and Experimental Spectra of Reported Compounds

According to the methods detailed above, the ground state geometries, transition energies, and oscillator strengths were computed for **1-2**. The theoretical results are plotted against absorption (for **1-2**) and emission (for **1**) measurements at room temperature for sample concentrations around 3 mM (figure S43). For all compounds, the theoretical transition energies and oscillator strengths align to the relative intensities observed experimentally.

The Einstein A_{21} coefficients can be extracted from the calculated oscillator strengths of **1** and **2** (2.5×10^{-6} and 3.0×10^{-6} , respectively), which correspond to 244 and 295 Hz (59). The corresponding expected excited state decay rates translate to lifetimes of 4.1 and 3.4 ms. Therefore, the observed absorption linewidths for all three compounds are not limited by the excited state lifetime.

C. Measured vs. Calculated g Factors

Continuous-wave (CW) EPR spectra of (thiolfan)YbCl were first measured in 2-MeTHF as a frozen glass, and exhibit prominent, narrow positive features centered around a peak at $g_x = 7.486 \pm 0.008$ (figs. S44-45). It should be noted that CW-EPR spectroscopy uses modulation of the static magnetic field (B_1) by a small oscillating magnetic field (B_{mod} , typically ± 0.1 to 2 mT in magnitude) to detect the first derivative of the EPR absorption spectrum. As such, if all molecular orientations exhibit resonance within the magnetic fields accessible by the instrumentation (1-1000 mT, in this case) the entire EPR spectrum should have approximately equal intensity above and below the baseline. The fact that the most prominent features have purely positive intensity, and that there are no resolved negative features or features which cross the baseline with similar linewidths implies that such resonances are outside of the accessible magnetic field range of our instrumentation or are inhomogeneously broadened beyond detection due to the limitations of field modulation.

In order to further evaluate these questions, we turned to pulse EPR spectroscopy – specifically, field swept electron spin echo (ESE) EPR spectroscopy. In contrast to CW-EPR

spectroscopy, pulse EPR spectroscopy enables more direct measurement of the EPR absorption spectrum without the use of field modulation, enabling the measurement of features with extremely broad linewidths in comparison to CW-EPR spectroscopy. Indeed, the X-Band ESE-EPR spectrum of (thiolfan)YbCl (fig. S46) exhibits broad linewidths ($lw_{pp} \sim 120\text{-}400$ mT), with intensity starting near 140 mT ($g = 4.78$) and continuing up to the high-field limit of our electromagnet at 1478.5 mT ($g = 0.45$). This indicates that the majority of molecular orientations exhibit significant inhomogeneous broadening in the field ranges accessible, and that there is significant spectral intensity above the field ranges accessible by our instrumentation. The latter point is in line with calculations of the full ground state g-matrix, which indicates two principal components may fall below $g = 0.45$ (table S12), or at least a significant portion of molecular orientations exhibit resonant fields below this g-value. Spin relaxation measurements using pulse EPR spectroscopy (inversion recovery for T_1 and Hahn Echo decay for T_m) were performed at 320 and 1200 mT (Fig. S47) in order to evaluate whether spin relaxation is responsible for the extremely broad linewidths of the CW- and pulse EPR spectra. In general, at temperatures where the spin-lattice relaxation time (T_1) is much longer than the phase memory time (T_m), EPR spectra typically exhibit Lorentzian line shapes with approximate homogenous peak-peak linewidths proportional to $\frac{2}{\sqrt{3}T_m}$. The shortest T_m value we measure is 0.82 μs at 320 mT, which corresponds to a linewidth of approximately 2 mT. This is in agreement with the peak-peak linewidth of the sharp transitions resolved at $g = 7.486$ in the CW-EPR spectrum ($lw_{pp} = 1.6$ mT), corresponding to a small subset of molecular orientations around g_x , but two orders of magnitude smaller than the observed linewidths at higher fields in the field-swept pulse EPR spectrum. Therefore, the extremely broad linewidths must be due to inhomogeneous broadening, which most likely arises from heterogeneity in g-values of the spin system due to slight variations in spin orbit coupling contributions.

Attempts were also made to resolve other possible features in the spectrum by preparing solid samples of paramagnetically diluted Yb^{3+} complexes by reacting the deprotonated thiolfan ligand with $\text{YbCl}_3\text{THF}_3$ and YCl_3THF_3 in 10:90, 5:95 and 1:99 percentage ratios following the procedure shown in section I-B. The exact concentrations of Yb and Y in the diluted samples were confirmed by inductively coupled plasma (ICP) measurements. EPR measurements on the diluted powder samples were obtained by packing the solid samples into a quartz capillary tube and inserting into a regular EPR tube. The 10%Yb sample was diluted to 1%Yb by mixing the 10%Yb sample with boron nitride, which appeared to have introduced some organic radical impurity at $g = 2.003$. This serial dilution provides magnetic dilution to investigate whether the features observed in the solution spectra are reproducible, as confirmed by the constant feature that remains at $g_x = 7.486 \pm 0.008$. It should be noted that the g factors derived from EPR spectroscopy and MCD are determined by using $E = g\mu_B B$, where ΔE is the Zeeman energy extracted from the absorption spectra. Using the measured ground state g factor of 7.486, we were then able to estimate the excited state g factor as 3.2 ± 0.2 , as shown in table S12.

IV. Magnetic Circular Dichroism Spectroscopy

A. Linear Zeeman Trend

The ground and excited states of (thiolfan)YbCl(THF) are split into two distinct states under an external magnetic field, corresponding to whether the magnetic moment is parallel or antiparallel to the B field. This induced Zeeman splitting is given by $\Delta E = 2g\mu_B B$, where h is the

Planck's constant, g is the Landé g-factor and μ_B is the Bohr magneton. The expected linear relationship is confirmed and demonstrated in fig. S48.

B. Imaging Setup

We use a home-made external cavity diode laser (ECDL) for imaging (fig. S49). The laser is set at the half max of the absorption peak of the sample. We use two lenses to expand the laser beam size to cover the whole cuvette. A permanent magnet is mounted onto a rotating motor beneath the sample. We image the sample with a webcam. Under circularly polarized light, the sample's absorption depends on the strength of the magnetic field, so as we rotate the magnet, the image blink.

The video showing the change in intensity of the transmission image can be found in movie S1.

C. Direct Measurement of DC Field with Oscillating Polarization

An M Squared SolsTis Ti:Sapph laser with a Lighthouse Sprout pump laser system was used to generate 304 THz to 307 THz light. The laser power needed in this measurement is under 30 mW. The beam is split into two paths, each going through an acousto-optic modulator (AOM; Gooch & Housego 2308-1-1.06 and Isomet SR48607) set at f and $f + \Delta f$, and brought together at another polarizing beam splitter (PBS). The resulting beam is oscillating between right- and left-hand circular polarizations at $\Delta f = 100 \text{ kHz}$. The amplitude of the transmitted light was collected with Thorlabs PDA8A. The setup is shown in fig. S50.

D. Direct Measurement of AC Field

The measurement of an AC field was achieved by taking the setup above and adding a Helmholtz coil around the sample holder. This gives rise to two more sidebands at frequency $\Delta f \pm f_{AC}$, and their amplitude is tracked by a spectrum analyzer (Agilent Technologies N9010A). The optical setup is shown in fig. S51, and the collected data is shown in fig. S52, which shows the change in signal as the magnitude of the AC field is brought down below 1G (the values reported in the manuscript accounted for background noise of the gaussmeter, which are slightly lower than what is shown here). The AC magnetic field was generated by taking the output of an arbitrary waveform generator (Agilent 33220A) to run an oscillating current onto the coil. The field was then measured by a gaussmeter (Lakeshore 410) to confirm its magnitude as well as mathematically confirmed by checking the AC current magnitude.

A frequency analyzer was used to track the transmission intensity at the sideband frequency ($\Delta f + f_{AC}$) composed of the frequency at which the polarization of the light is oscillating ($\Delta f = 100 \text{ kHz}$) and the frequency of the AC field generated by helmholtz coils ($f_{AC} = 1 \text{ kHz}$). The dBm reading was converted to change in power ($\text{dBm} = 10 \log P / 1 \text{ mW}$, where P is the measured power), and the power value was then converted to volts by accounting for the equipment resistance ($P = V^2 / R$, where $R = 50 \Omega$). Voltage noise has units of $V \text{ Hz}^{-1/2}$, which was converted to magnetic noise in units of $T \text{ Hz}^{-1/2}$ by measuring the relationship between our voltage reading and the gaussmeter reading that we conducted separately (fig. S53). Using this linear fit, the voltage noise was converted to magnetic noise, which translates to an average sensitivity of $3.3 \mu\text{T Hz}^{-1/2}$.

The error bars in Fig. 5e are calculated from the data shown in fig. S52. The error bars indicate standard deviation above and below mean signal, as given by $\sqrt{1/(N-1) \sum_{i=1}^N |A_i - \mu|^2}$, where N is the total number of data points, A is the read-in signal from the frequency analyzer, and μ is the mean value.

E. Sensor-Sample Distance Estimation

In AVCs, the standoff distance is defined as the distance between the sample and the geometric center of the sensor volume. The spatial resolution is limited by the distance scales set by the diameter of the sensor volume. AVCs face a few practical challenges when it comes to miniaturization. Increasing density (through pressure) requires thicker glass and higher standoff distances, which increases sensor-sample distance. Thus, ALMS is an advantageous alternative to AVCs in that the concentration can be increased drastically without broadening the spectral linewidth as we show in fig. S54. Theoretically, ALMS will have an advantageous tradeoff between density and sensor-sample distance with further device engineering. We demonstrate possible device architectures that will bring ALMS magnetometers to shorter sensor to sample distances than those of AVCs in fig. S55.

F. MCD Signal Analysis

The absorption of the ground electronic transition localized at Yb^{3+} for (thiolfan)YbCl(THF) can be expressed as a Lorentzian.

$$\alpha(x, x_0) = \frac{a}{\pi} \frac{\frac{1}{2}\Gamma}{(x - x_0)^2 + \left(\frac{1}{2}\Gamma\right)^2} + c$$

In this equation, a is a scaling factor, Γ is the full-width at half-maximum, x_0 is the center frequency, and c is a constant offset to account for background. For room temperature absorption, the fit values are:

$$a = 8.8498 \times 10^{-4} \text{ eV}$$

$$\Gamma = 0.00064516 \text{ eV} = 0.65 \text{ meV}$$

$$x_0 = 1.2637 \text{ eV}$$

The MCD signal is a subtraction between the absorption of the sample with σ^+ and σ^- light, which only differ in their center frequency by $\Delta x = g_{eff}\mu_B B$. Thus, the MCD absorption signal can be expressed as:

$$M(x, B) = \alpha(x, x_0 + \Delta x) - \alpha(x, x_0 - \Delta x)$$

where $\alpha(x, x_0 \pm \Delta x)$ indicates the sample absorption with $\sigma^{+/-}$ light.

$$\alpha(x, x_0 \pm \Delta x) = \frac{a}{\pi} \frac{\frac{1}{2}\Gamma}{\left(x - \left(x_0 \pm g_{eff}\mu_B B\right)\right)^2 + \left(\frac{1}{2}\Gamma\right)^2} + c$$

The larger the B-field applied, the further the σ^+ and σ^- absorption peak is split, the larger the MCD signal is. We can backtrack the strength of B field from the measured MCD signal if we know the factor g_{eff} .

For small static magnetic field, we perform a Taylor expansion:

$$M(x, B) = \alpha(x, x_0 + \Delta x) - \alpha(x, x_0 - \Delta x)$$

$$\begin{aligned}
&\approx \alpha(x, x_0) + \frac{\partial \alpha(x, x_0)}{\partial x_0} \Delta x - \alpha(x, x_0) - \frac{\partial \alpha(x, x_0)}{\partial x_0} (-\Delta x) \\
&= 2 \frac{\partial \alpha(x, x_0)}{\partial x_0} g_{eff} \mu_B B
\end{aligned}$$

The MCD signal $M(x, B)$ is proportional to the applied static magnetic field B and sensitivity is described by the slope:

$$k(x, x_0, g_{eff}) = 2 \frac{\partial \alpha(x, x_0)}{\partial x_0} g_{eff} \mu_B$$

where

$$\frac{\partial \alpha(x, x_0)}{\partial x_0} = \frac{a}{\pi} \frac{\Gamma(x - x_0)}{\left((x - x_0)^2 + \left(\frac{1}{2} \Gamma \right)^2 \right)^2}$$

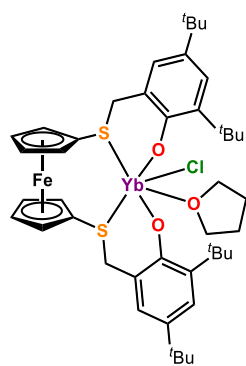
With a laser frequency set at $x = x_0 + \Gamma/\sqrt{12}$, this value reaches a maximum

$$\max \left(\frac{\partial \alpha(x, x_0)}{\partial x_0} \right) = \frac{a}{\pi} \frac{\Gamma \frac{\Gamma}{\sqrt{12}}}{\left(\left(\frac{\Gamma}{\sqrt{12}} \right)^2 + \left(\frac{1}{2} \Gamma \right)^2 \right)^2} = \frac{3\sqrt{3} a}{2} \frac{1}{\pi \Gamma^2}$$

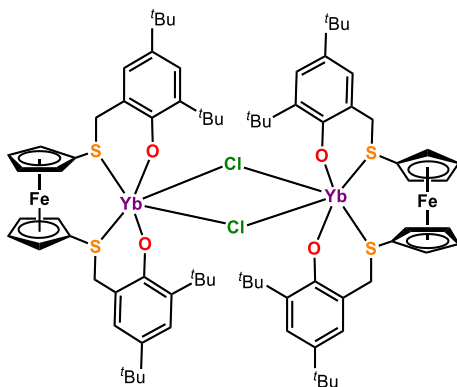
and the slope is

$$k|_{x=x_0+\Gamma/\sqrt{12}} = \frac{3\sqrt{3} a \mu_B}{\pi} \frac{g_{eff}}{\Gamma^2} \propto \frac{g_{eff}}{\Gamma^2}$$

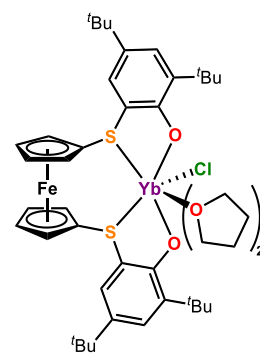
Thus, the sensitivity is proportional to the effective Landé g-factor g_{eff} and is inversely proportional to the square of linewidth Γ . Therefore, for transitions with the same oscillator strength, if the linewidth is halved, the MCD signal will be boosted by a factor of 4. The narrow absorption linewidth of (thiolfan)YbCl(THF) at room temperature makes it a potential interesting candidate in magnetic field sensing.



1 (thiolfan)YbCl(THF)



1' [(thiolfan)YbCl]₂



2 (thiolfan*)YbCl(THF)₂

Fig. S1.

The compound numbers shown in Fig. 3b in the manuscript are clarified above, with exact molecular formula. These numbers refer to the structures we assign the absorption features to, with supporting structural data laid out in section I.

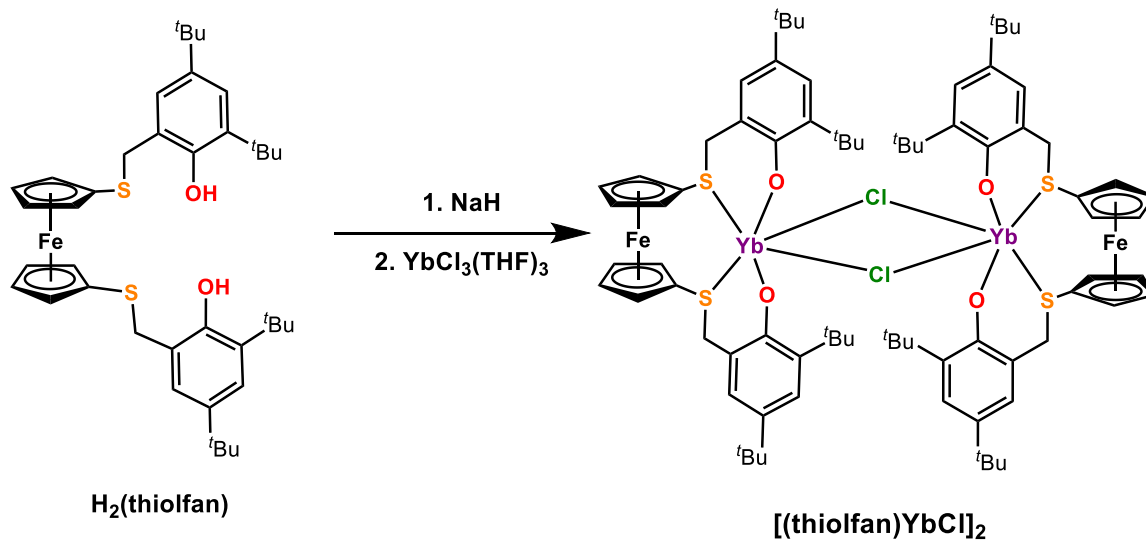


Fig. S2.
 Synthesis of $[(\text{thiolfan})\text{YbCl}]_2$ (**1'**).

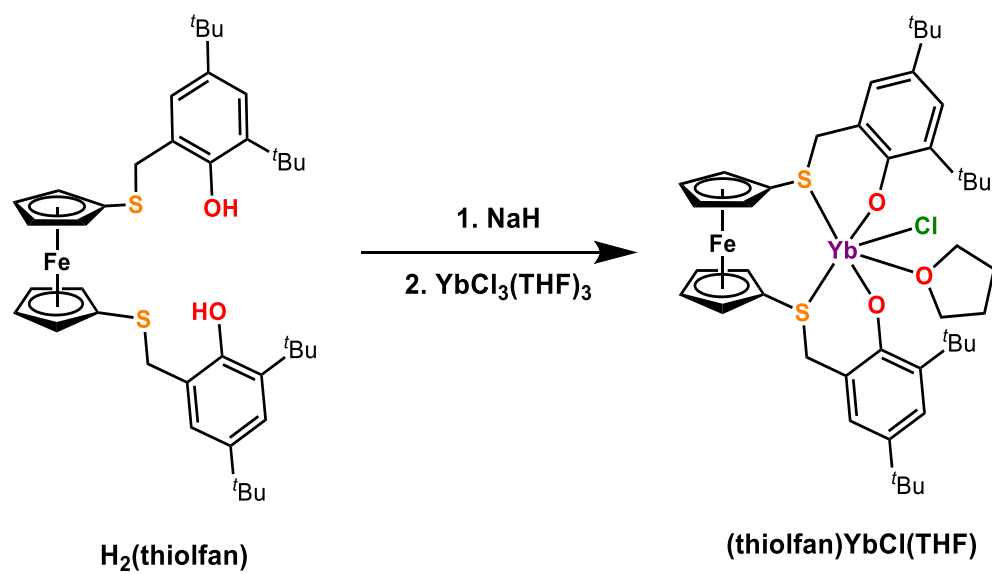


Fig. S3.
 Synthesis of (thiolfan)YbCl(THF) (**1**).

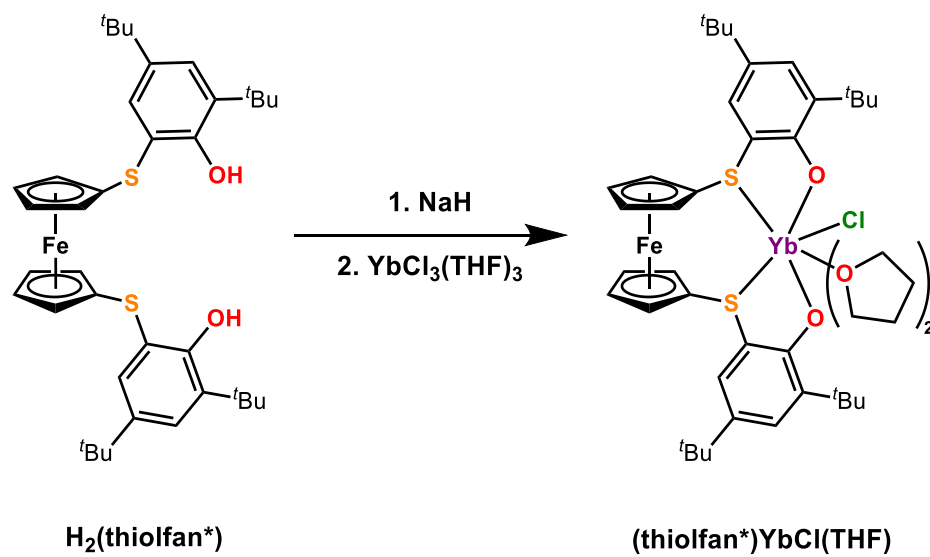
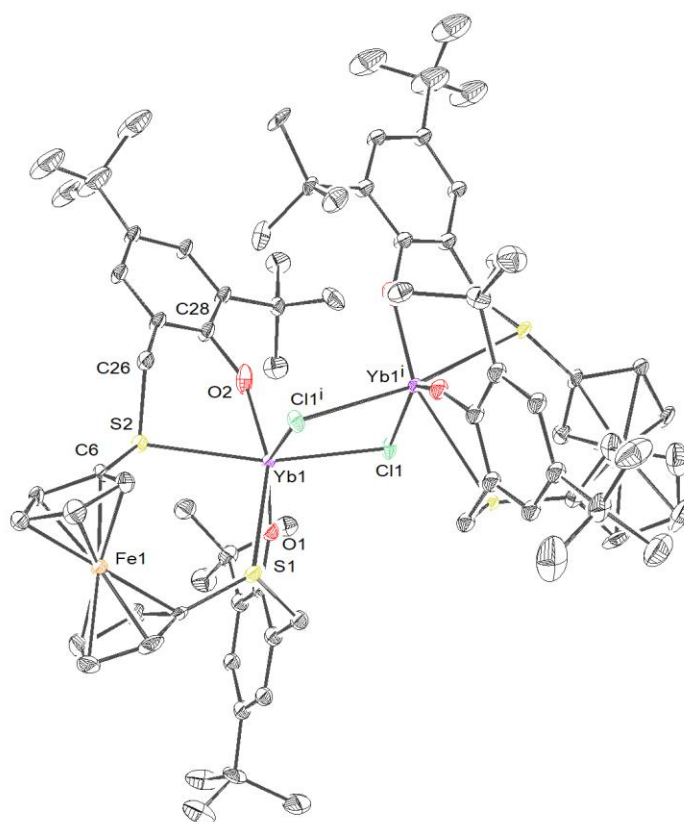
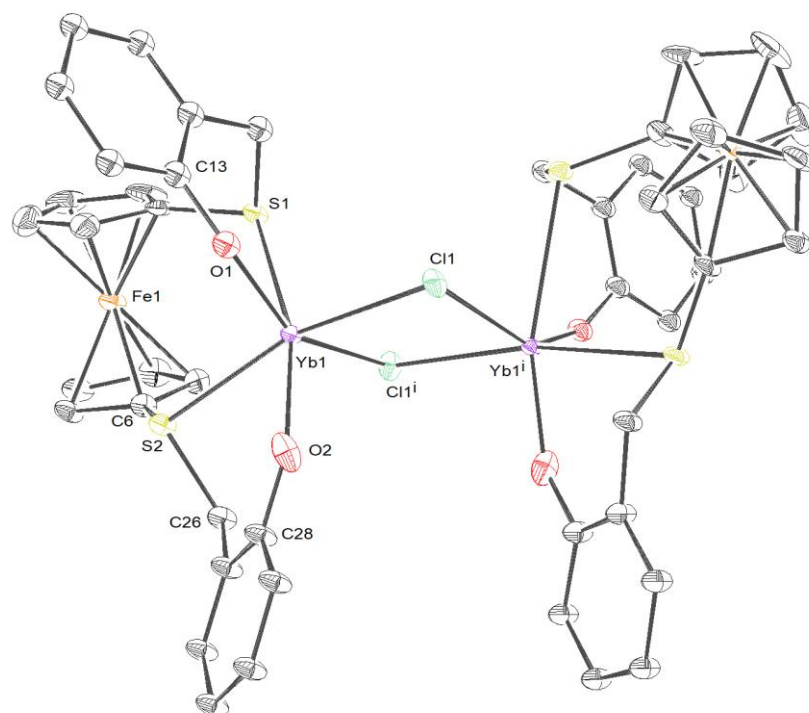


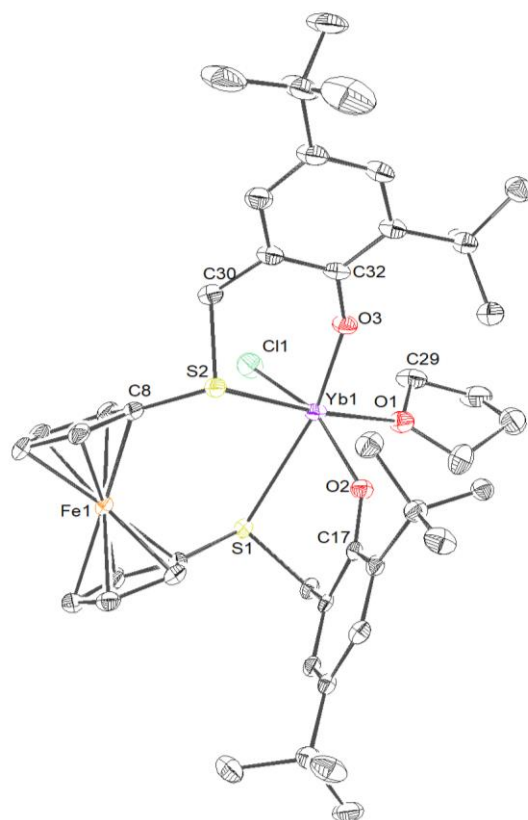
Fig. S4.
 Synthesis of (thiolfan*)YbCl(THF)₂ (2).



Selected distances (Å) and angles (°) of [(thiolfan)YbCl] ₂				
Distances	Yb-Cl ₁	2.654(2)	Yb-S ₂	2.828(2)
	Yb-O ₁	2.041(6)	Yb-Cl ⁱ	2.659(2)
	Yb-O ₂	2.082(8)	Yb-Fe	4.756(2)
	Yb-S ₁	2.931(2)	Yb-Yb ⁱ	4.000(2)
Angles	Cl ₁ -Yb-O ₁	89.9(2)	O ₂ -Yb-S ₁	157.2(2)
	Cl ₁ -Yb-O ₂	96.6(2)	O ₂ -Yb-S ₂	71.5(2)
	Cl ₁ -Yb-S ₁	104.79(7)	S ₁ -Yb-S ₂	86.17(6)
	Cl ₁ -Yb-S ₂	166.08(7)	S ₁ -Yb-Cl ₁	75.35(6)
	Cl ₁ -Yb-Cl ₁ ⁱ	81.22(7)	S ₂ -Yb-Cl ₁	93.57(7)
	O ₁ -Yb-O ₂	111.8(2)	C ₆ -S ₂ -C ₂₆	99.6(4)
	O ₁ -Yb-S ₁	76.4(2)	Yb-O ₁ -C ₁₃	151.9(6)
	O ₁ -Yb-S ₂	101.1(2)	Yb-O ₂ -C ₂₈	154.4(6)

Fig. S5.

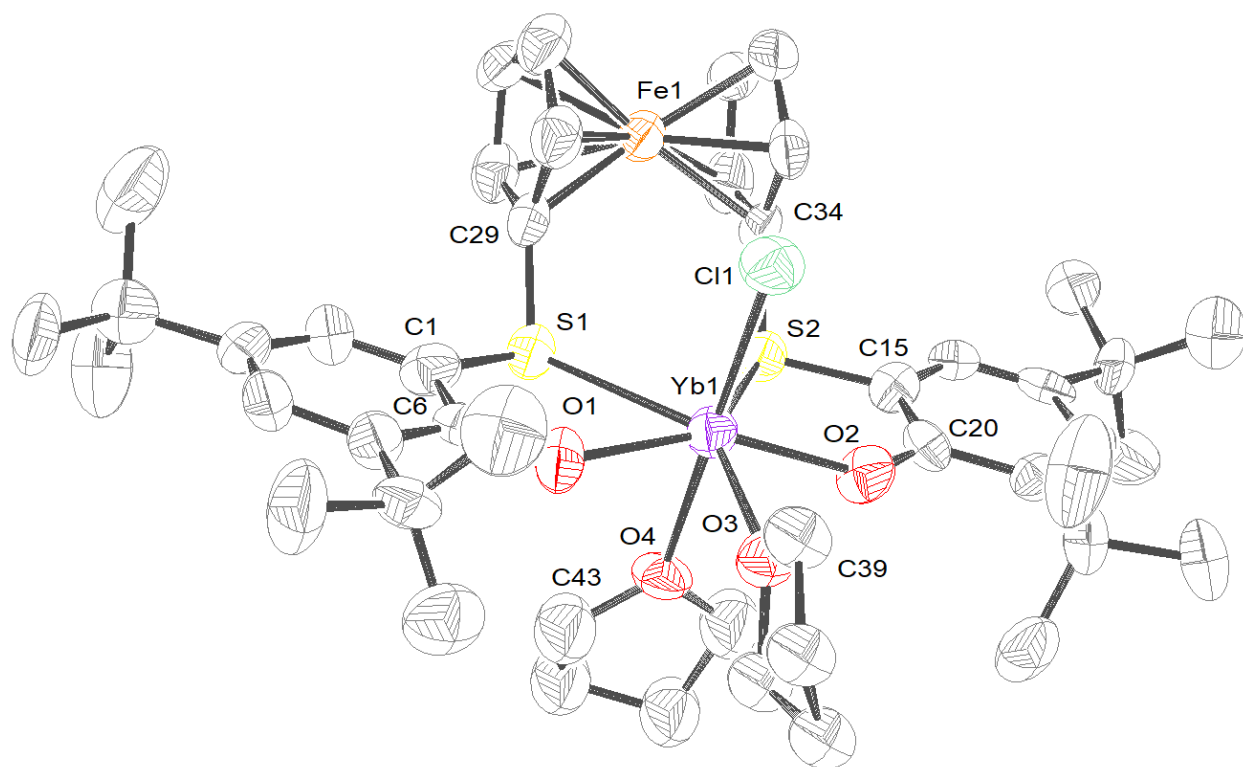
Thermal ellipsoid (50% probability) representation of [(thiolfan)YbCl]₂, without (top) and with (bottom) *t*-butyl groups. Two crystallographically independent molecules are in the unit cell, only one shown here. Hydrogen atoms and solvent molecules (toluene and diethyl ether) are omitted for clarity. Atoms labeled with ⁱ represent the inverted asymmetric unit of the neighboring unit cell.



Selected distances (Å) and angles (°) of (thiolfan)YbCl(THF)				
Distances	Yb-O ₁	2.316(2)	Yb-S ₁	2.9073(7)
	Yb-O ₂	2.087(2)	Yb-S ₂	2.8830(9)
	Yb-O ₃	2.053(2)	Yb-Fe	4.719(7)
	Yb-Cl ₁	2.5534(7)		
Angles	O ₁ -Yb-O ₂	85.83(8)	S ₁ -Yb-S ₂	88.57(2)
	O ₁ -Yb-O ₃	98.47(8)	S ₂ -Yb-O ₁	172.61(6)
	O ₂ -Yb-O ₃	105.00(8)	S ₂ -Yb-O ₂	93.70(6)
	Cl ₁ -Yb-S ₁	80.30(2)	S ₂ -Yb-O ₃	74.51(6)
	Cl ₁ -Yb-S ₂	95.67(2)	C ₈ -S ₂ -C ₃₀	99.7(1)
	Cl ₁ -Yb-O ₁	87.79(6)	Yb-O ₁ -C ₂₉	124.3(1)
	Cl ₁ -Yb-O ₂	154.50(6)	Yb-O ₂ -C ₁₇	146.4(2)
	Cl ₁ -Yb-O ₃	100.35(6)	Yb-O ₃ -C ₃₂	153.7(2)

Fig. S6.

Thermal ellipsoid (50% probability) representation of (thiolfan)YbCl(THF) with selected distances and angles. Hydrogen and disordered atoms are omitted for clarity.



Selected distances (Å) and angles (°) of (thiolfan*)YbCl(THF) ₂				
Distances	Yb-O ₁	2.154(12)	Yb-S ₁	2.956(5)
	Yb-O ₂	2.147(12)	Yb-S ₂	3.012(5)
	Yb-O ₃	2.348(12)	Yb-Fe	4.734(7)
	Yb-O ₄	2.348(12)	Yb-Cl ₁	2.530(5)
Angles	O ₁ -Yb-O ₂	154.5(5)	S ₁ -Yb-S ₂	67.1(1)
	O ₁ -Yb-O ₃	78.7(5)	S ₁ -Yb-O ₁	66.6(3)
	O ₁ -Yb-O ₄	84.0(5)	S ₁ -Yb-O ₂	131.1(3)
	O ₂ -Yb-O ₃	78.8(5)	S ₁ -Yb-O ₃	143.5(4)
	O ₂ -Yb-O ₄	83.1(5)	S ₁ -Yb-O ₄	77.9(3)
	O ₃ -Yb-O ₄	87.5(5)	Yb ₁ -S ₁ -C ₁	98.0(7)
	Cl ₁ -Yb-O ₁	97.2(3)	Yb ₁ -S ₁ -C ₂₉	115.5(6)
	Cl ₁ -Yb-O ₂	96.1(3)	C ₁ -S ₁ -C ₂₉	102.6(9)
	Cl ₁ -Yb-O ₃	93.4(4)	Yb ₁ -O ₁ -C ₆	137.0(1)
	Cl ₁ -Yb-O ₄	178.7(3)	Yb ₁ -O ₂ -C ₂₀	139.0(1)
	Cl ₁ -Yb-S ₁	101.9(1)	Yb ₁ -O ₃ -C ₃₉	127.0(2)
	Cl ₁ -Yb-S ₂	98.5(1)	Yb ₁ -O ₄ -C ₄₃	129.0(1)

Fig. S7.

Thermal ellipsoid (50% probability) representation of (thiolfan*)YbCl(THF)₂ with selected distances and angles. Hydrogen, solvent, and disordered atoms are omitted for clarity. Please note that this structure is presented as a connectivity-only structure.

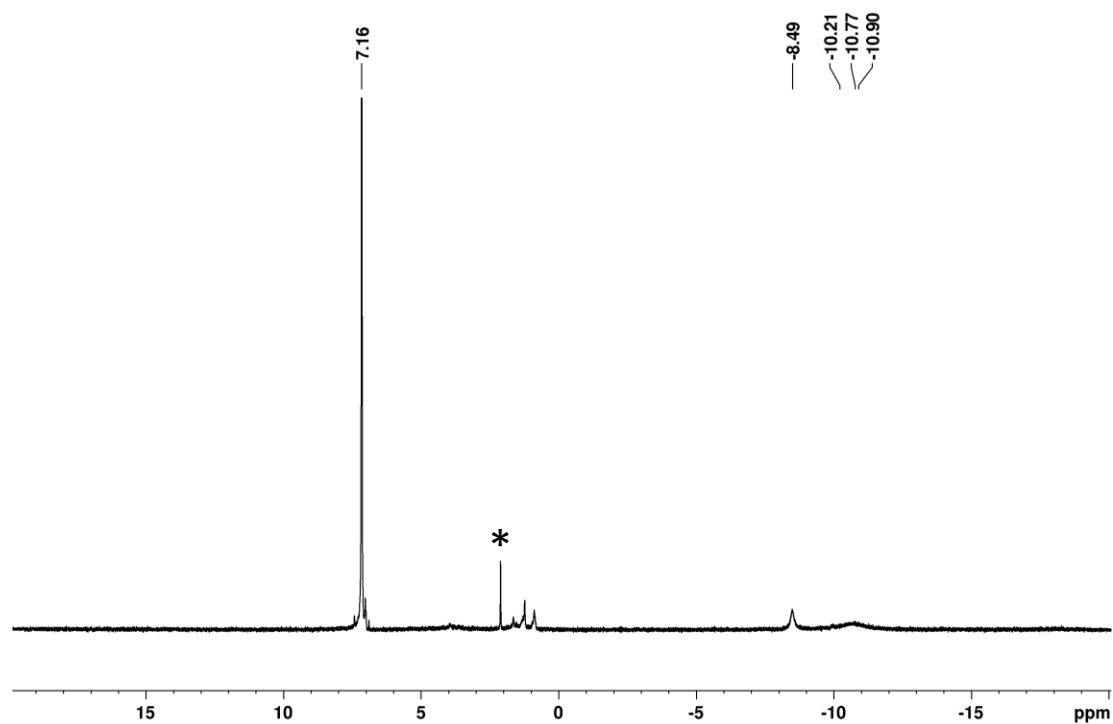


Fig. S8.

^1H NMR spectrum (298 K, 500 MHz, C_6D_6) of $[(\text{thiolfan})\text{YbCl}]_2$ (*residual toluene).

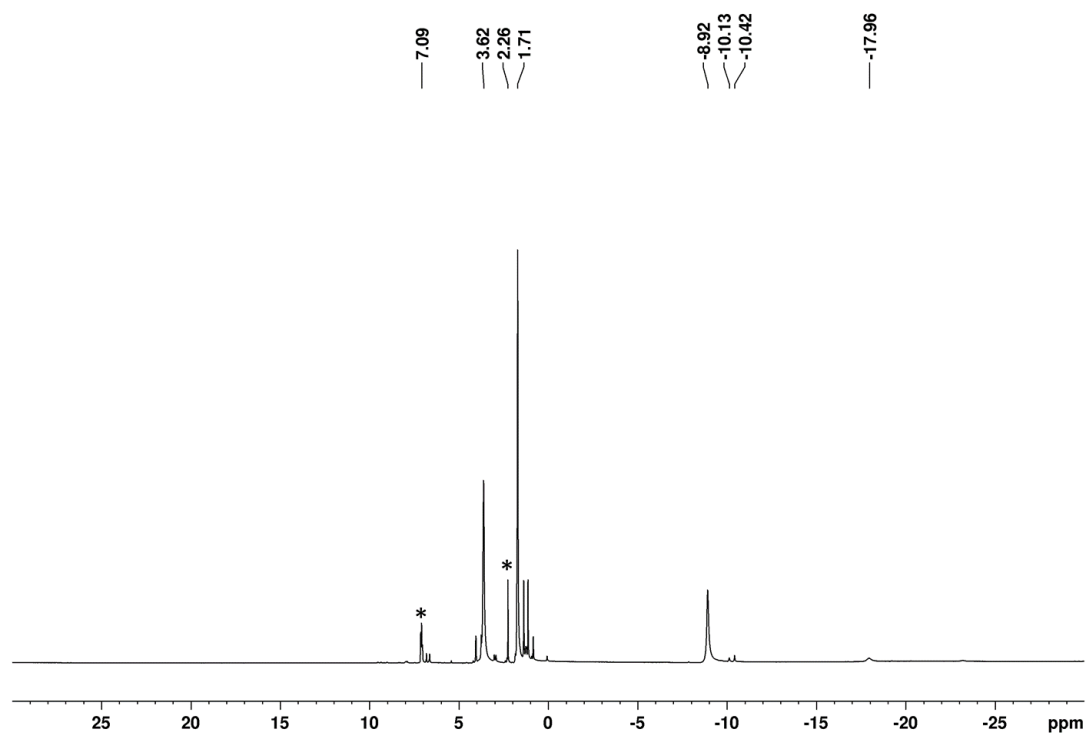


Fig. S9.

^1H NMR spectra (298 K, 500 MHz, THF-d_8) of (thiolfan) YbCl(THF) (*residual toluene).

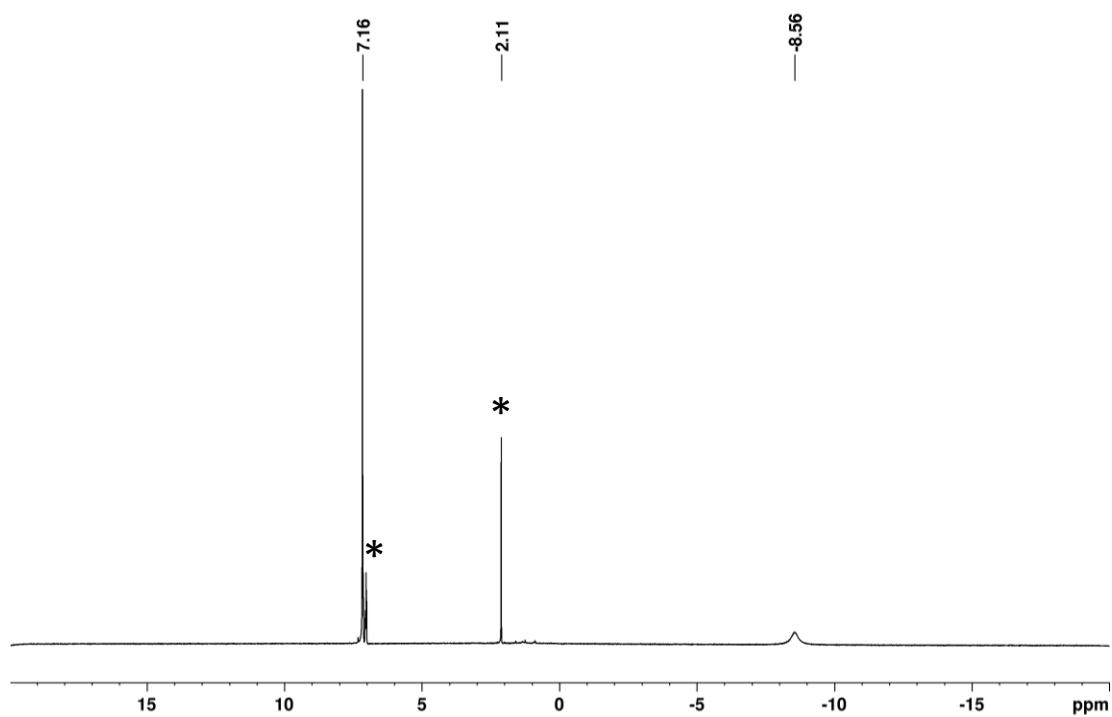


Fig. S10.

^1H NMR spectrum (298 K, 500 MHz, C_6D_6) of $(\text{thiolfan}^*)\text{YbCl}(\text{THF})_2$ (*residual toluene).

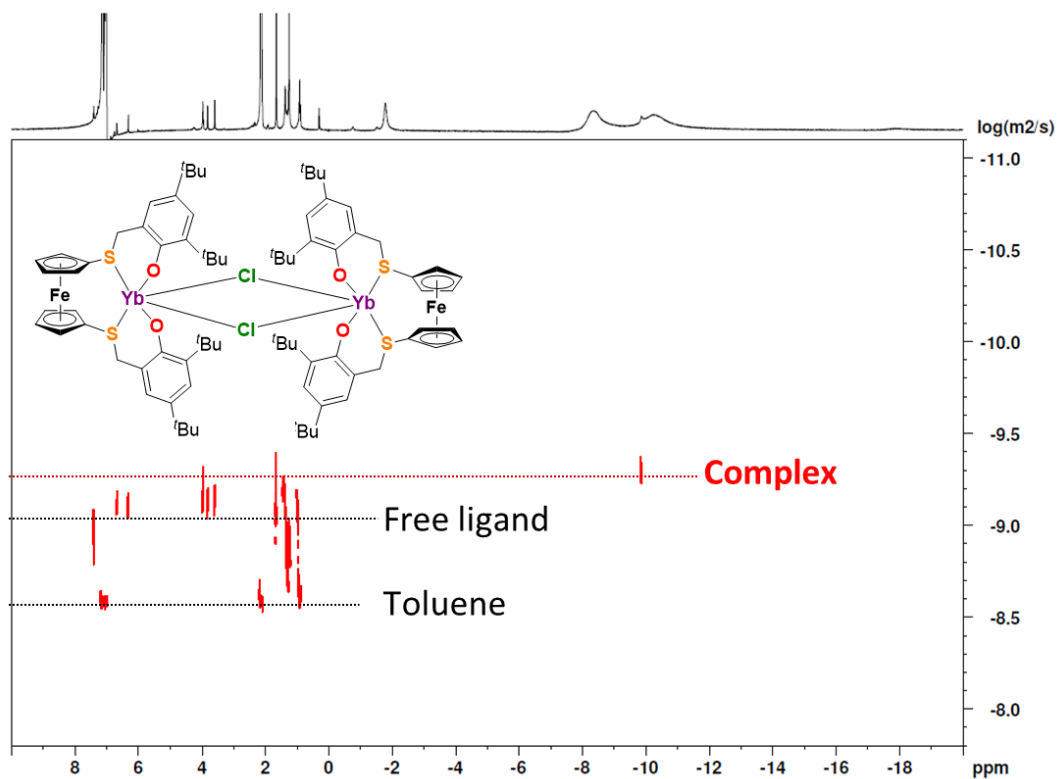


Fig. S11.

DOSY spectrum of **1'** [(thiolfan)YbCl] $_2$ in toluene- d_8 at 25 °C.

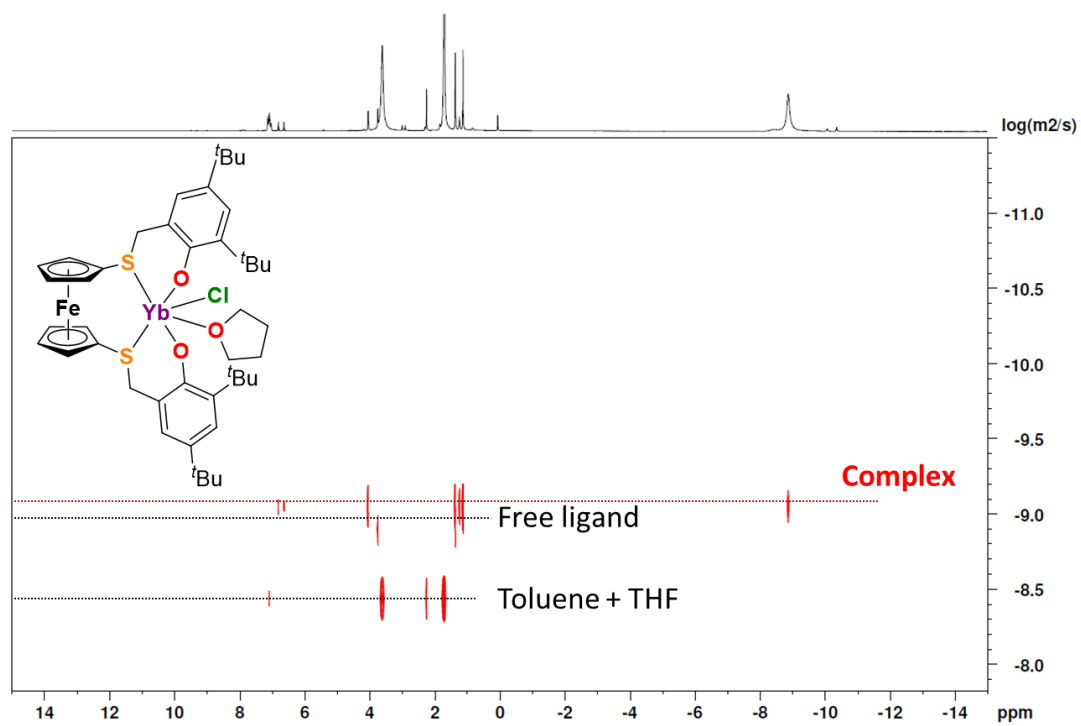


Fig. S12.

DOSY spectrum of **1** (thiolfan)YbCl(THF) in THF-d₈ at 25 °C.

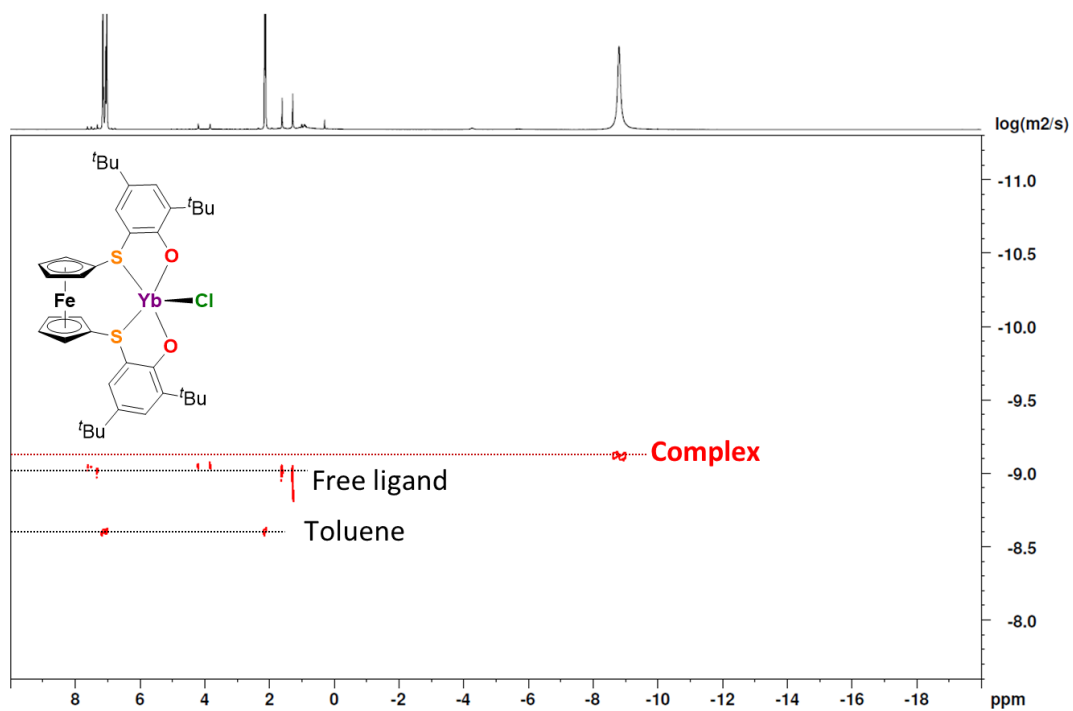


Fig. S13.

DOSY spectrum of **1** (thiolfan*)YbCl in toluene-d₈ at 25 °C.

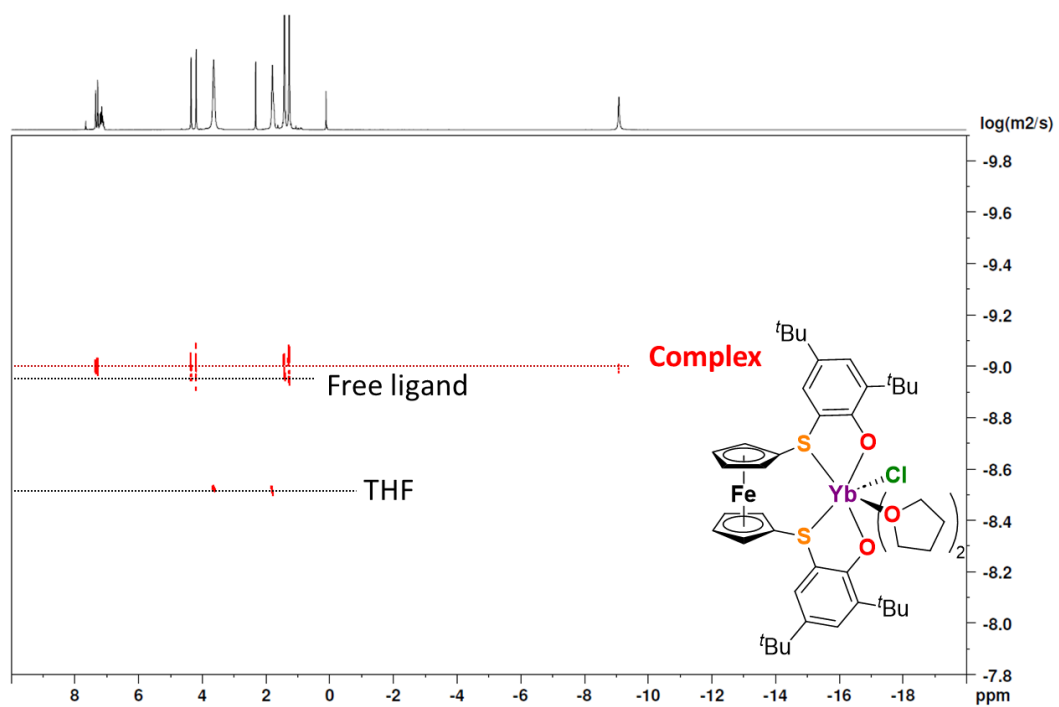


Fig. S14.

DOSY spectrum of **1** (thiolfan*)YbCl(THF)₂ in THF-d₈ at 25 °C.

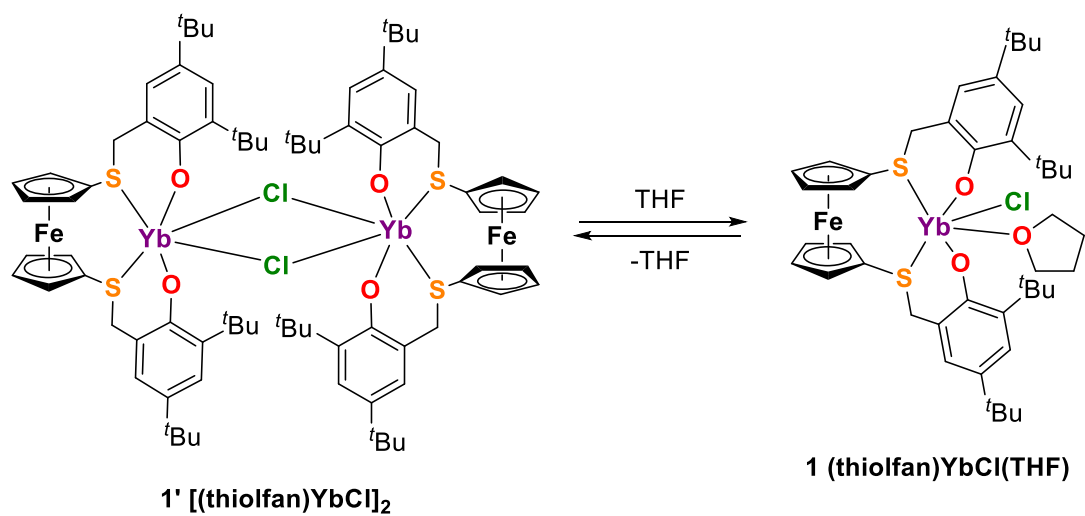


Fig. S15.

Fluxional behavior of (thiolfan)YbCl complexes in presence and absence of THF.

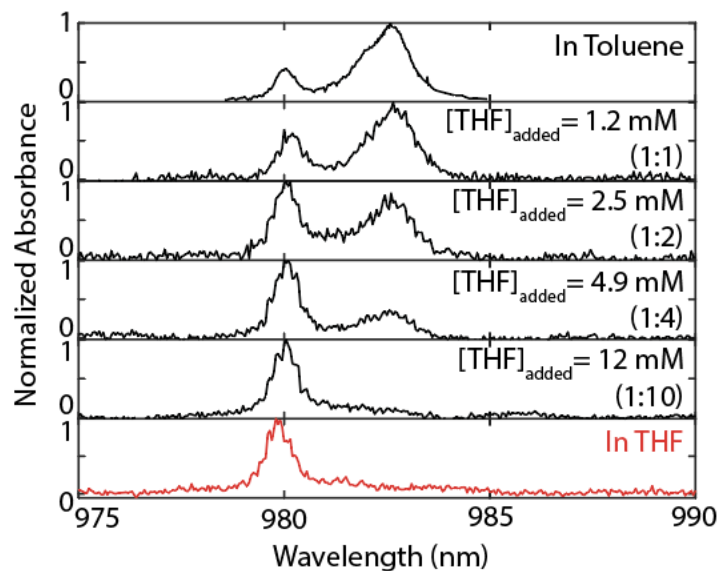


Fig. S16.

Dilution of [(thiolfan)YbCl]₂ in toluene with increasing amounts of THF, showing a gradual shift from the bimodal absorbance feature in toluene to the unimodal feature in THF. The concentration of Yb species is 1.3 mM, which accounts for monomers and dimers. The ratios of the Yb to THF concentrations are shown in brackets. The absorption spectra in toluene and in THF are shown on the top (black) and bottom (red) for comparison.

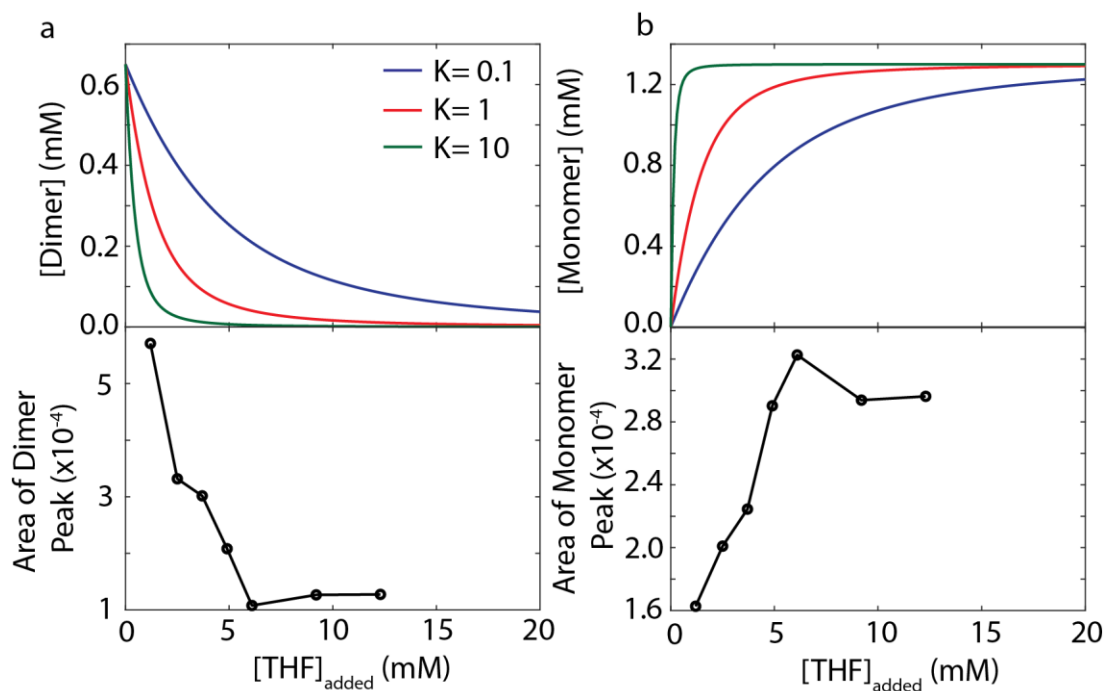


Fig. S17.

a) Top: calculated $[\text{Dimer}]$ concentrations, corresponding to $[A_2]$ in the mathematical derivations, for a range of equilibrium constants (K). Bottom: integrated area of the absorption feature at around 983 nm, which shows up in the sample in toluene environment, corresponding to the dimer form.

b) Top: calculated $[\text{Monomer}]$ concentrations, corresponding to $[A(\text{THF})]$ in the mathematical derivations, for a range of equilibrium constants (K). Bottom: integrated area of the absorption feature at around 980 nm, which dominates when the sample is in THF environment, corresponding to the monomer form.

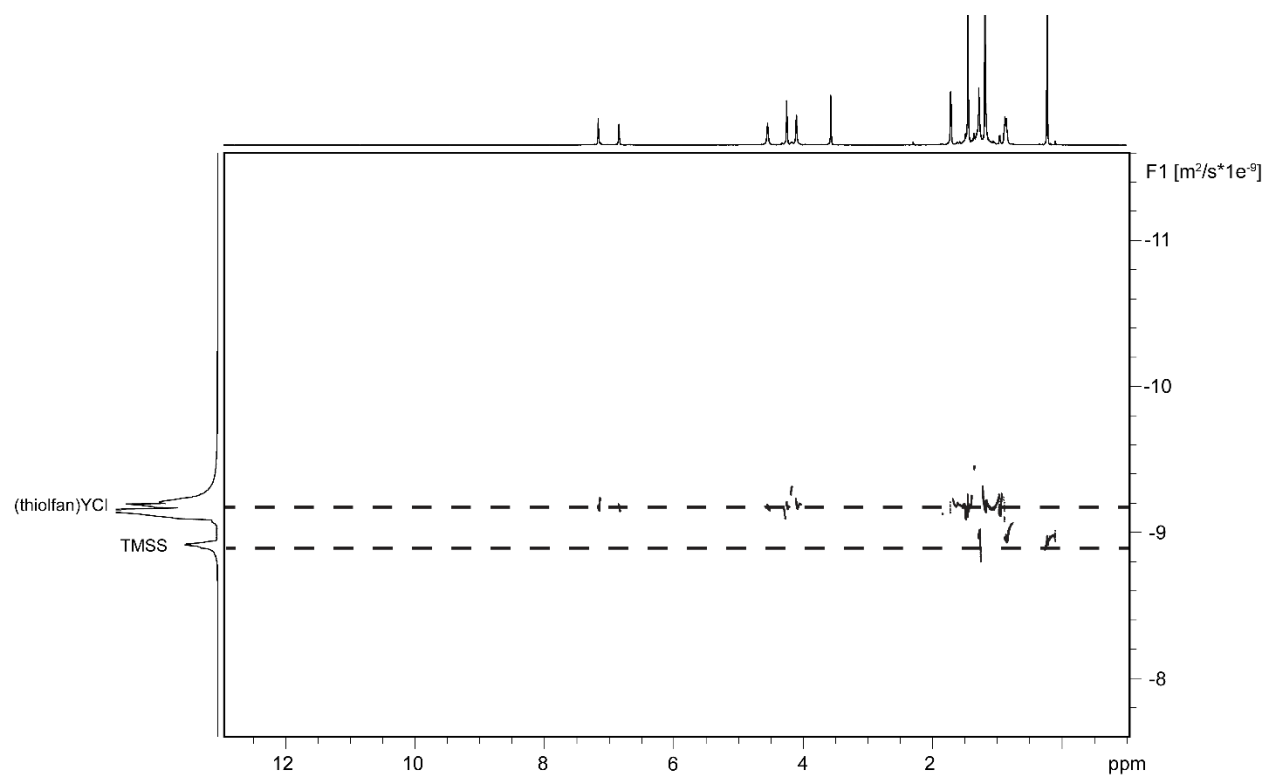


Fig. S18.

DOSY (298 K, 500 MHz, THF-d₈) of (thiolfan)YCl(THF) with TMSS as an internal standard.

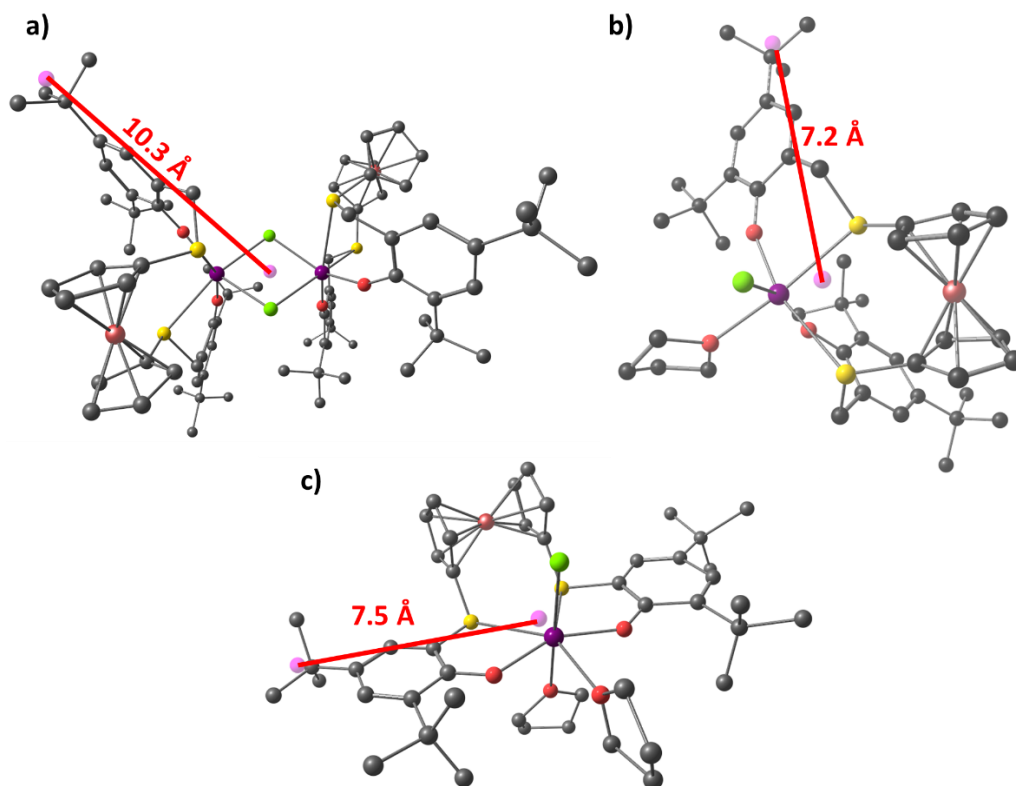


Fig. S19.

Isotropic representation of the solid-state structures of **1'** (a), **1** (b), and **2** (c). The pink dots represent the center of mass and the furthest point from the center of mass.

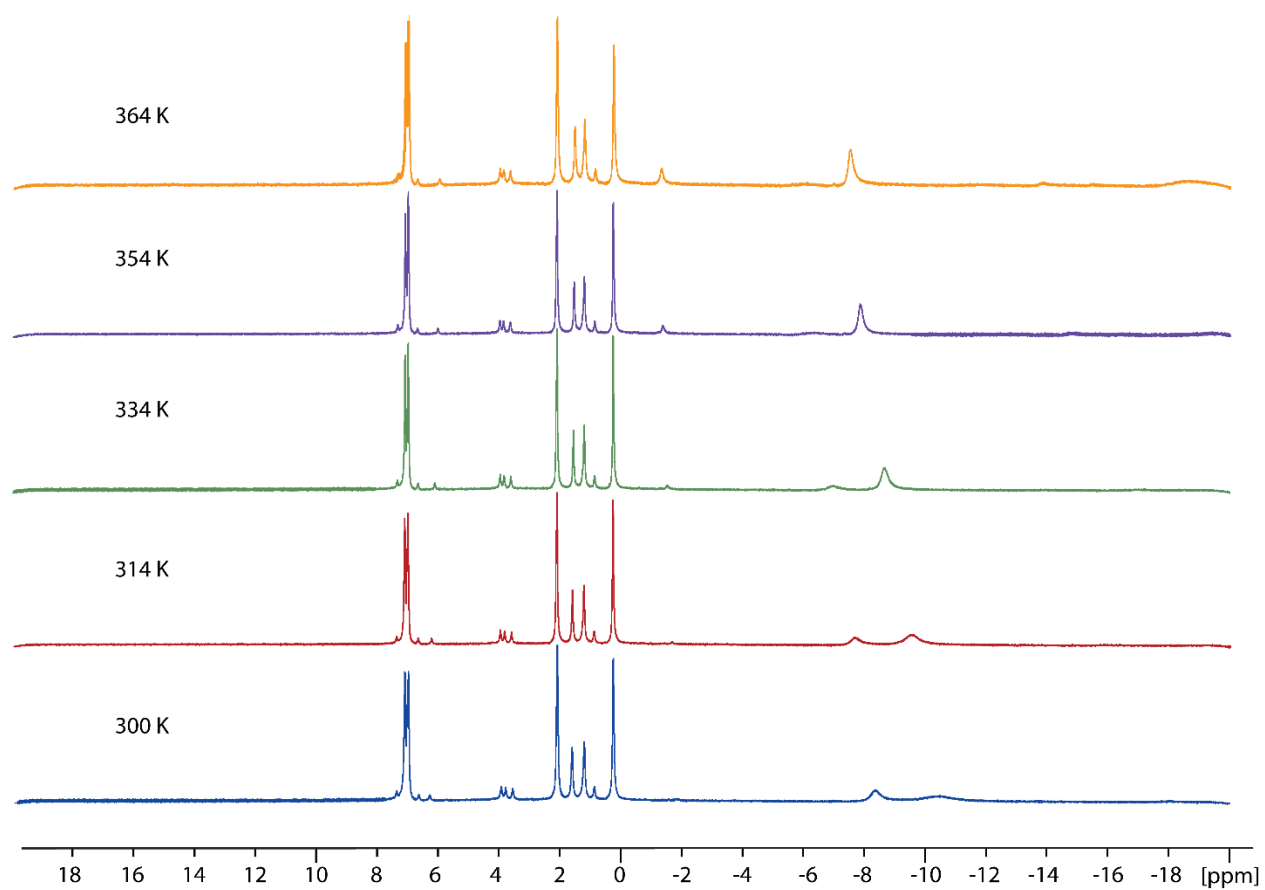


Fig. S20.

Variable temperature ¹H NMR study (500 MHz, toluene-d₈) of [(thiolfan)YbCl]₂.

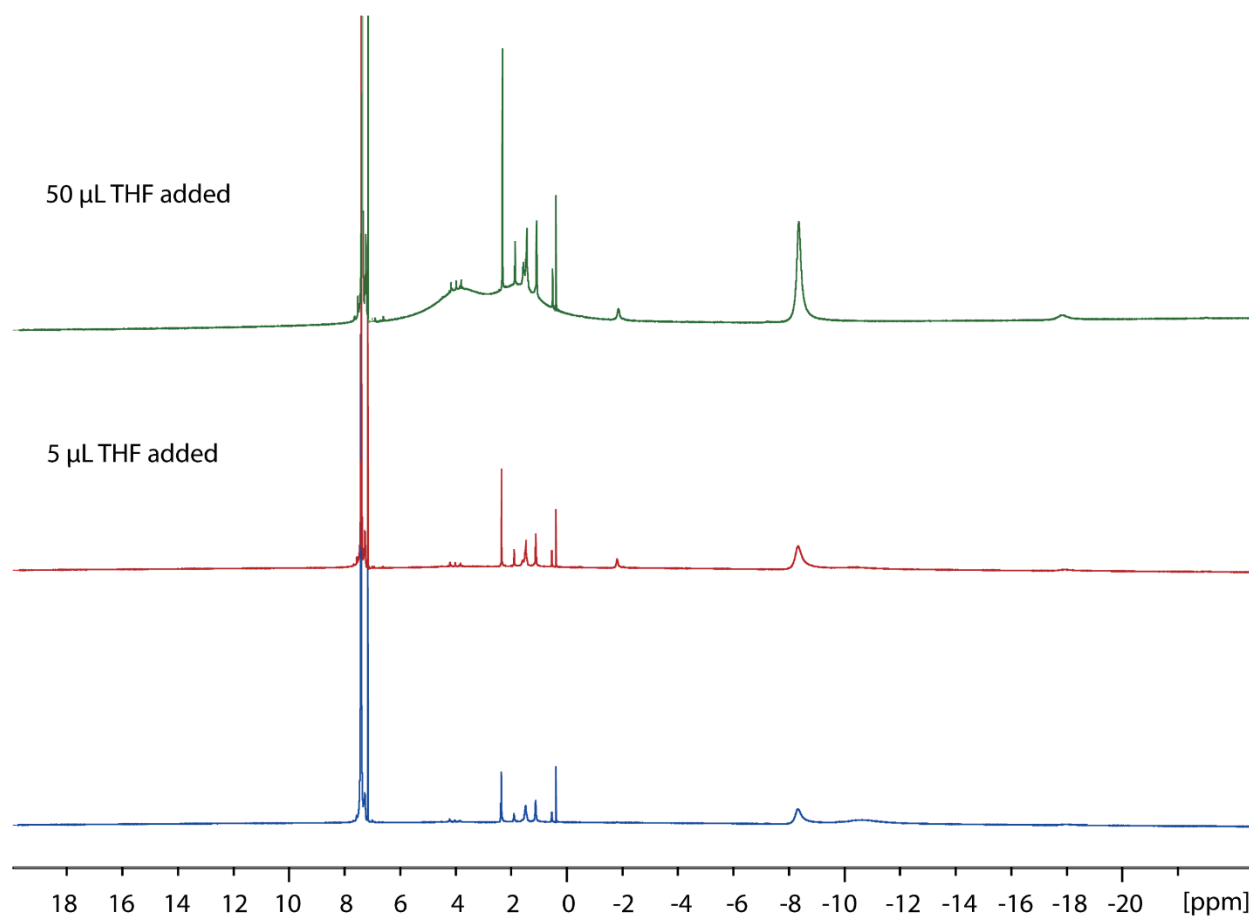


Fig. S21.

^1H NMR spectra (298 K, 500 MHz, C_6D_6) of $[(\text{thiolfan})\text{YbCl}]_2$ before and after the addition of THF.

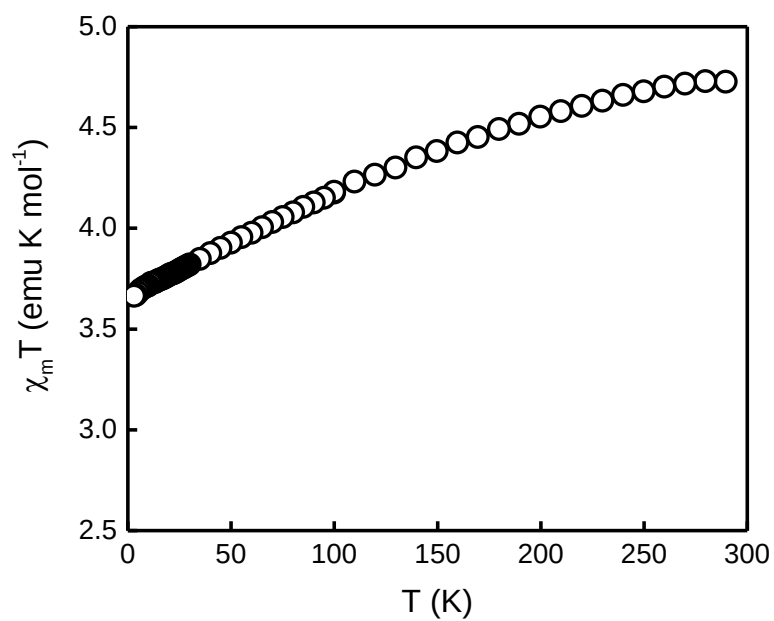


Fig. S22.

Plot of $\chi_m T$ versus T for [(thiolfan)YbCl]₂ under a 1000 Oe dc field in the temperature range 2-290 K.

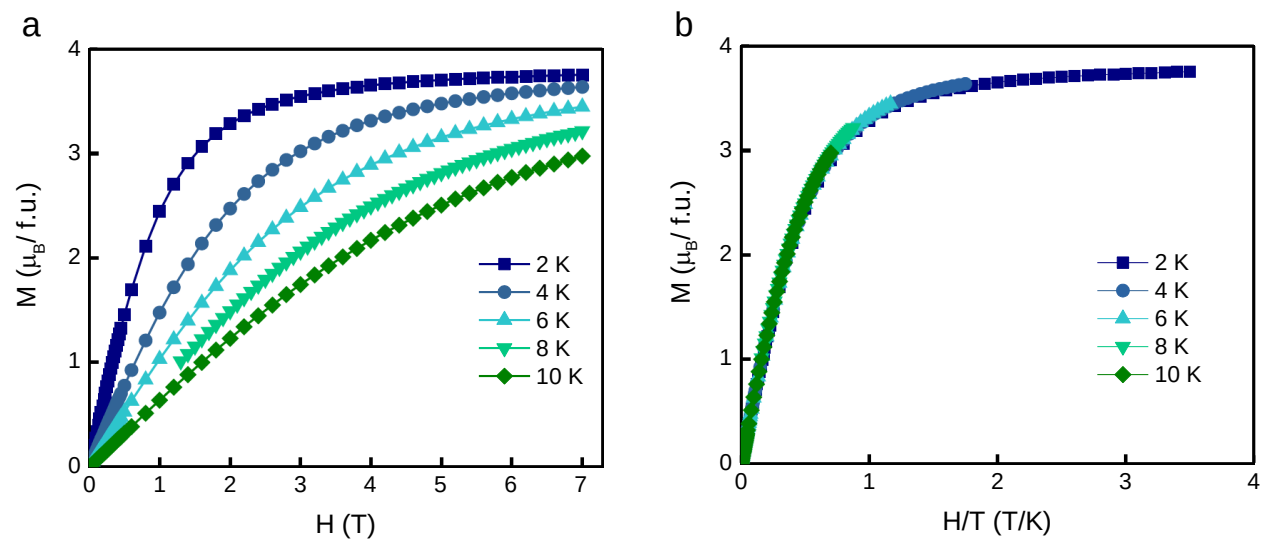


Fig. S23.

Isothermal M vs. H plots at 2, 4, 6, 8, and 10 K (a). M vs. H/T plots at 2, 4, 6, 8, and 10 K (b).

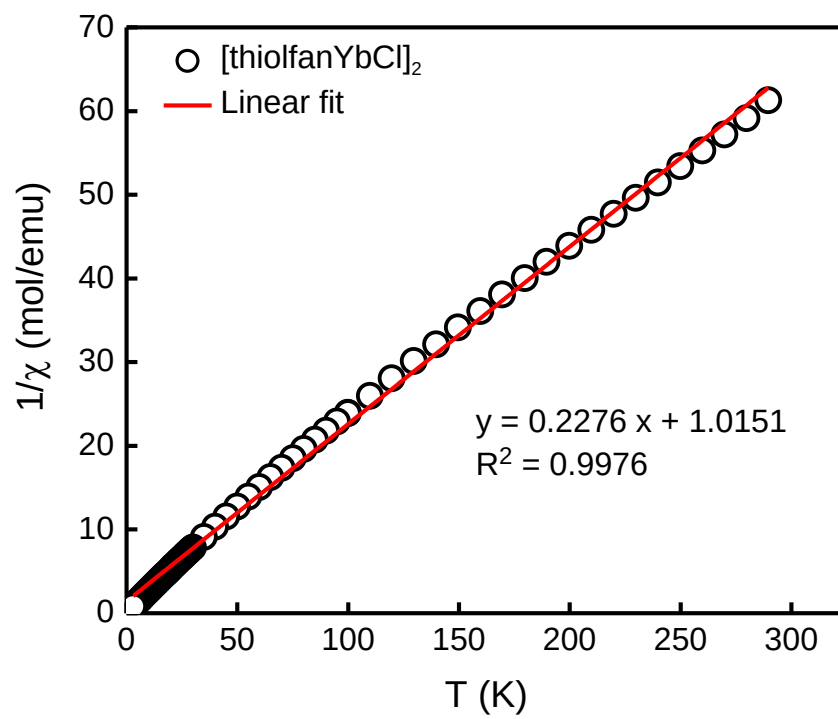


Fig. S24.

Plot of $1/\chi$ versus T for $[(\text{thiolfan})\text{YbCl}]_2$.

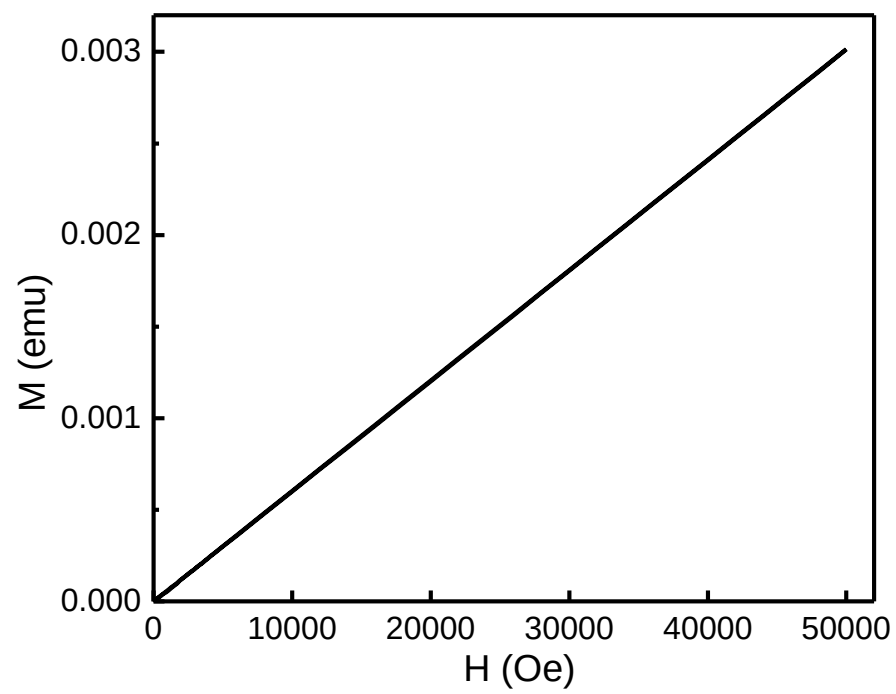


Fig. S25.
Plot of M versus H at 300 K for $[(\text{thiolfan})\text{YbCl}]_2$.

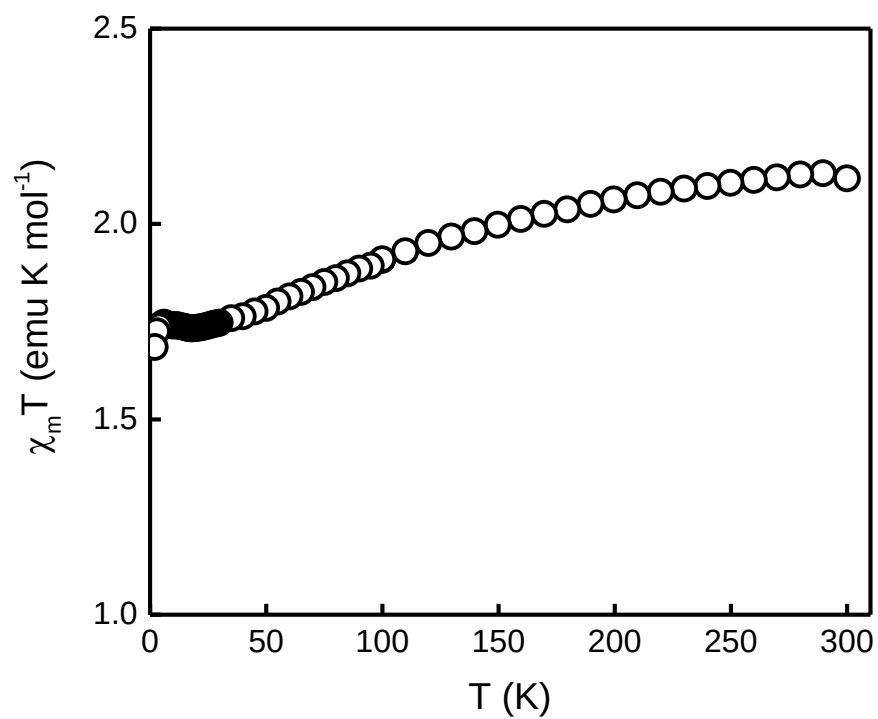


Fig. S26.

Plot of $\chi_m T$ versus T for (thiolfan*)YbCl(THF)₂ under a 1000 Oe dc field in the temperature range 2-300 K.

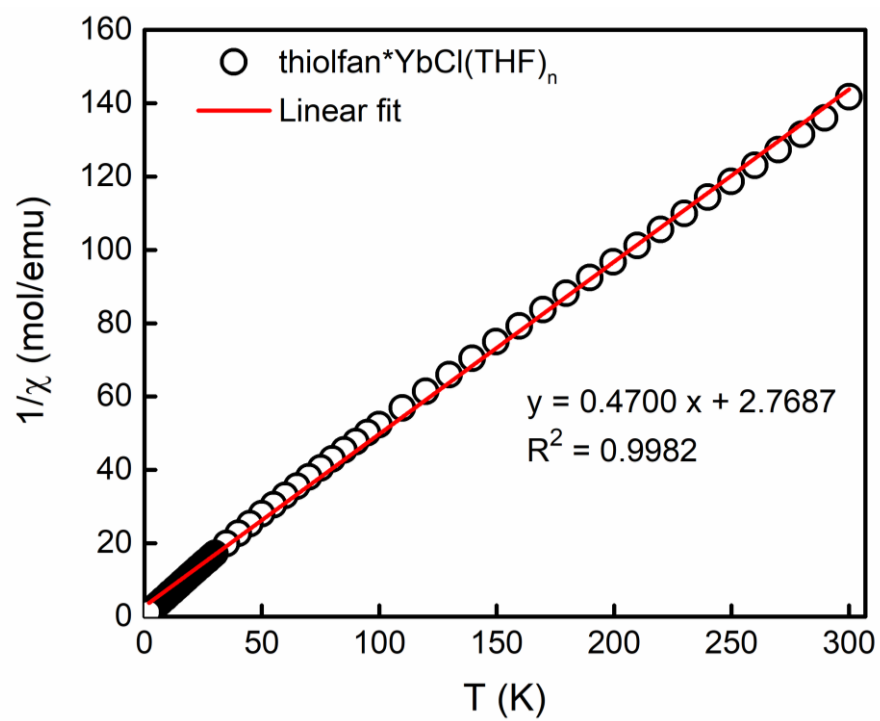


Fig. S27.

Plot of $1/\chi$ versus T for (thiolfan*)YbCl(THF)₂.

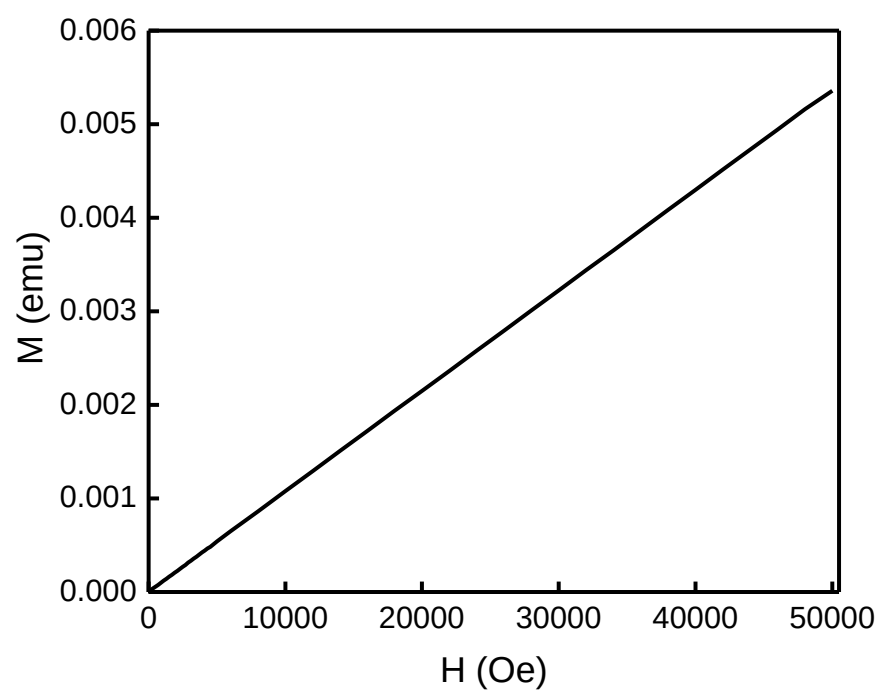


Fig. S28.

Plot of M versus H at 300 K for (thiolfan*)YbCl(THF)₂.

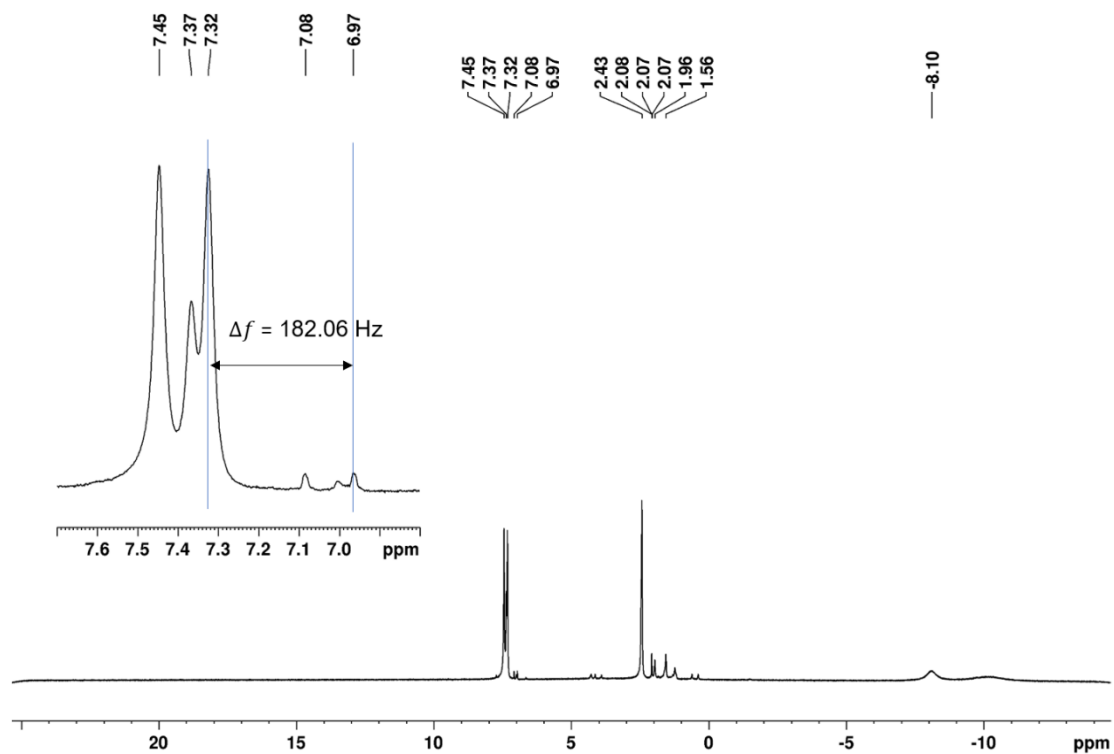


Fig. S29.

^1H NMR spectrum (25 °C, 500 MHz, Tol-d_8) of $[(\text{thiolfan})\text{YbCl}]_2$ in Tol-d_8 , external standard for the Evans method (chemical shift of $\text{THF-d}_8 = 2.08, 6.97, 7.01, 7.09 \text{ ppm}$).

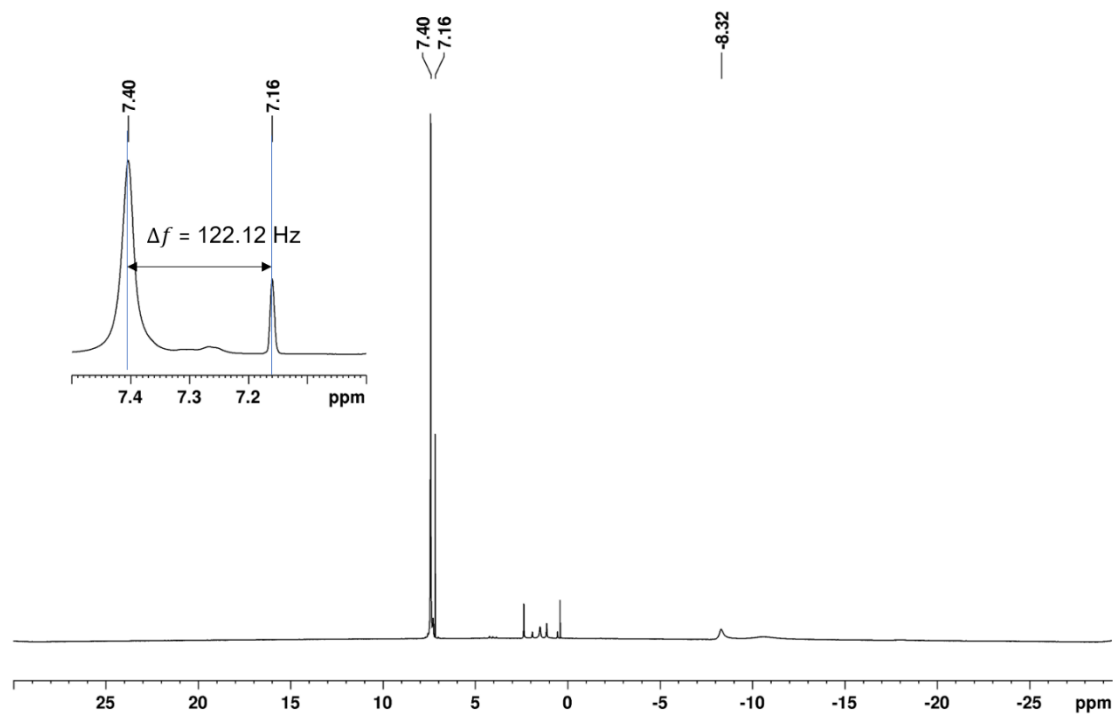


Fig. S30.

^1H NMR spectrum (25 °C, 500 MHz, C_6D_6) of (thiolfan)YbCl(THF) in C_6D_6 , external standard for the Evans method (chemical shift of $\text{C}_6\text{D}_6 = 7.16 \text{ ppm}$).

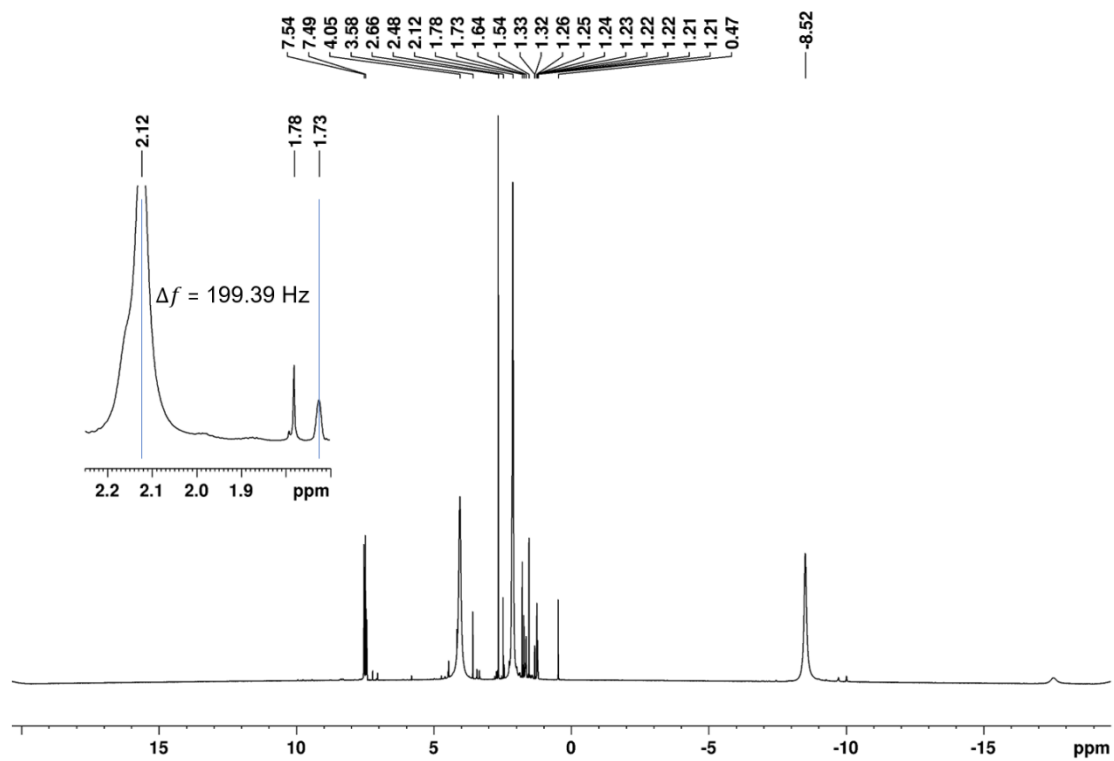


Fig. S31.

^1H NMR spectrum (23 °C, 500 MHz, THF-d_8) of (thiolfan) YbCl(THF) in THF-d_8 , external standard for the Evans method (chemical shift of $\text{THF-d}_8 = 1.72, 3.58 \text{ ppm}$).

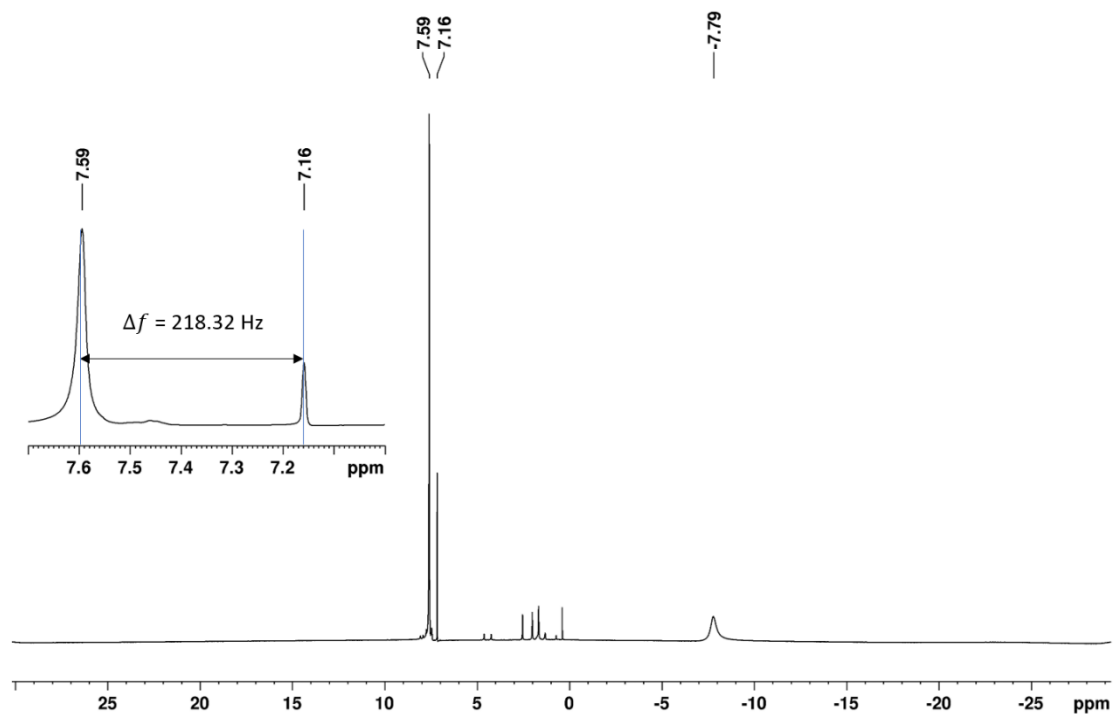


Fig. S32.

^1H NMR spectrum (25 °C, 500 MHz, C_6D_6) of (thiolfan*)YbCl(THF)₂ in C_6D_6 , external standard for the Evans method (chemical shift of $\text{C}_6\text{D}_6 = 7.16 \text{ ppm}$).

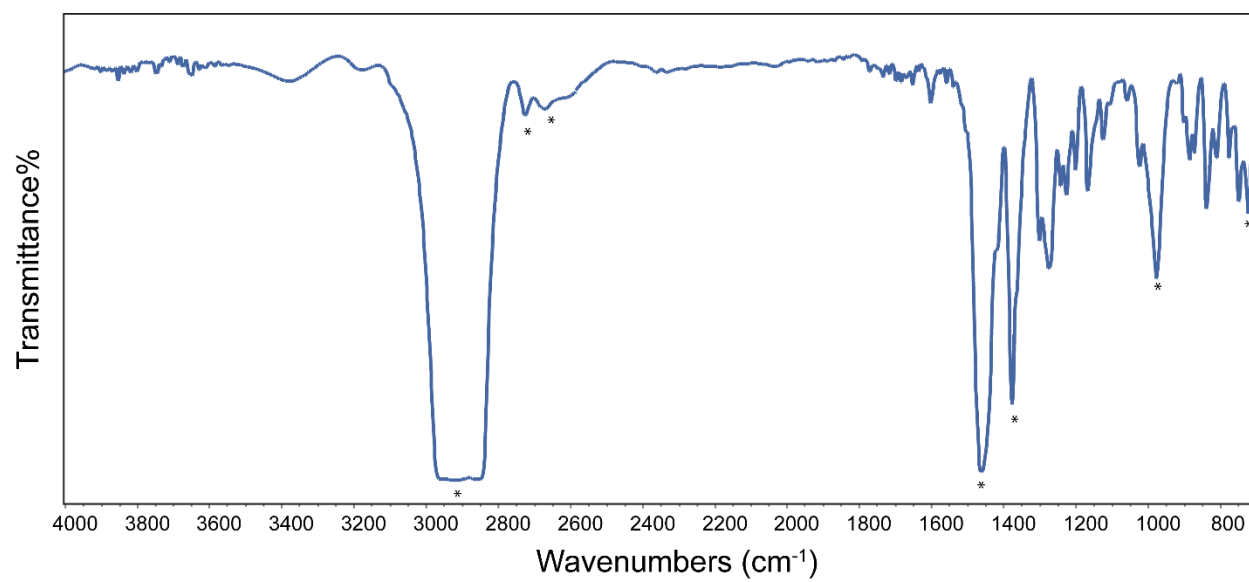


Fig. S33.

IR (Nujol) spectrum of [(thiolfan)YbCl]₂ (*: Nujol).

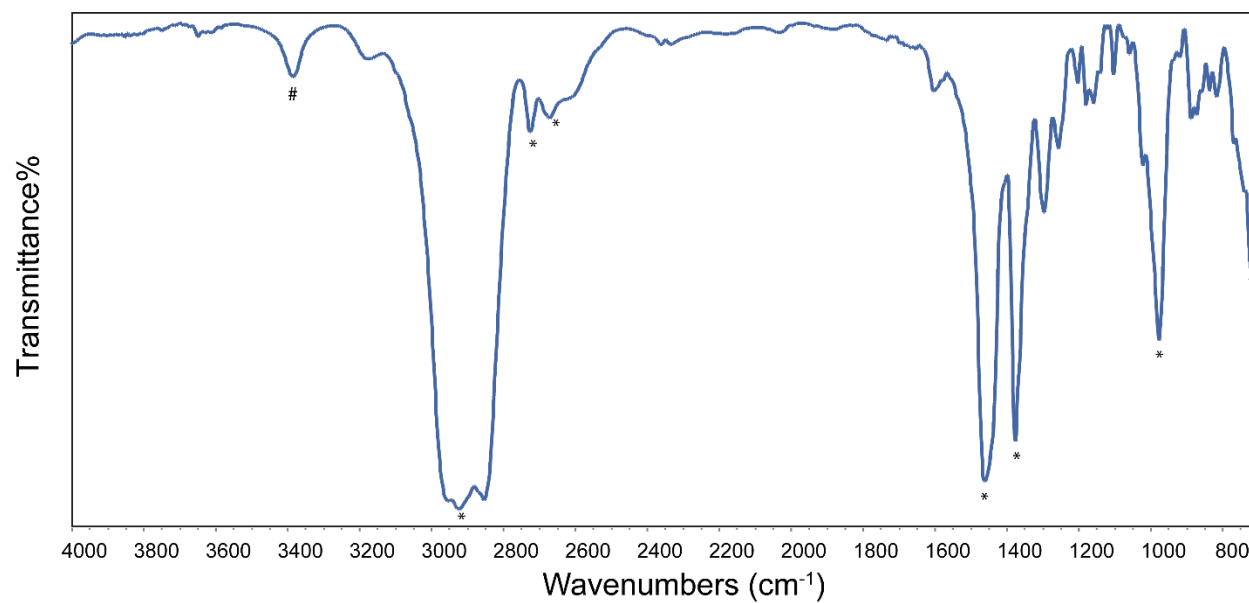


Fig. S34.

IR (Nujol) spectrum of (thiolfan*)YbCl(THF)₂ (*: Nujol; #: trace OH due to minor decomposition of the compound during the measurement).

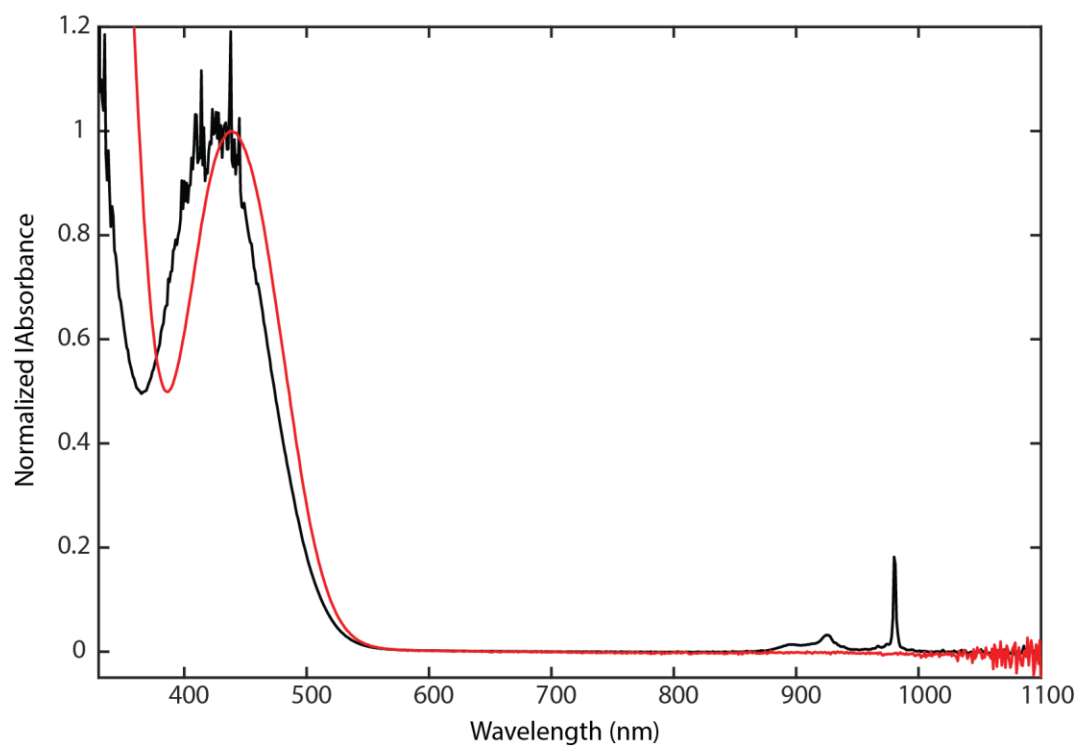


Fig. S35.

Absorbance of (thiolfan)YbCl(THF) in black and H₂(thiolfan) in red.

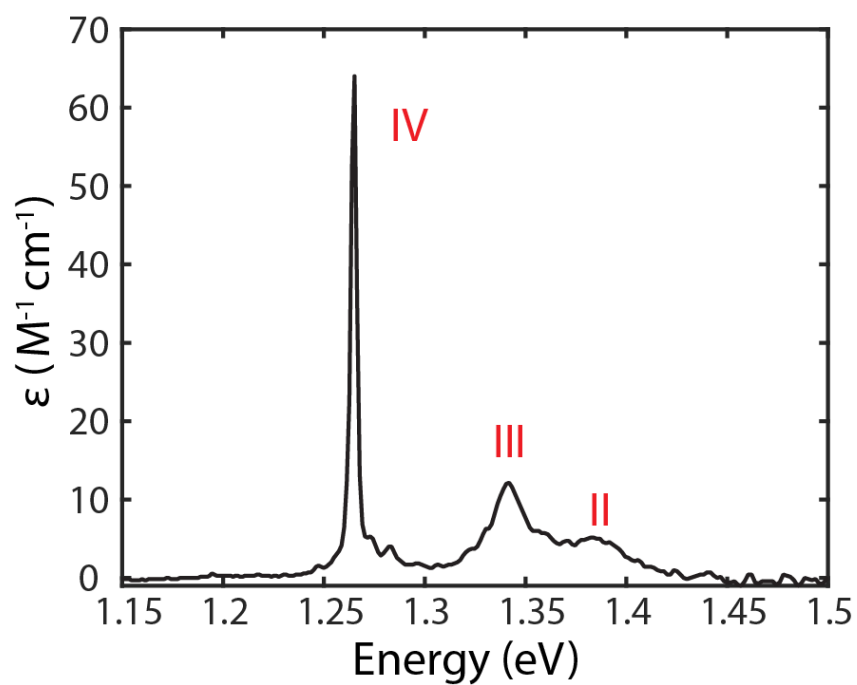


Fig. S36.

Molar absorptivity of (thiolfan)YbCl(THF) from the wide-field absorption measurement. The peak value is 5 times less than the one shown in fig. 3b, because the linewidth here is broader due to instrument limitations.

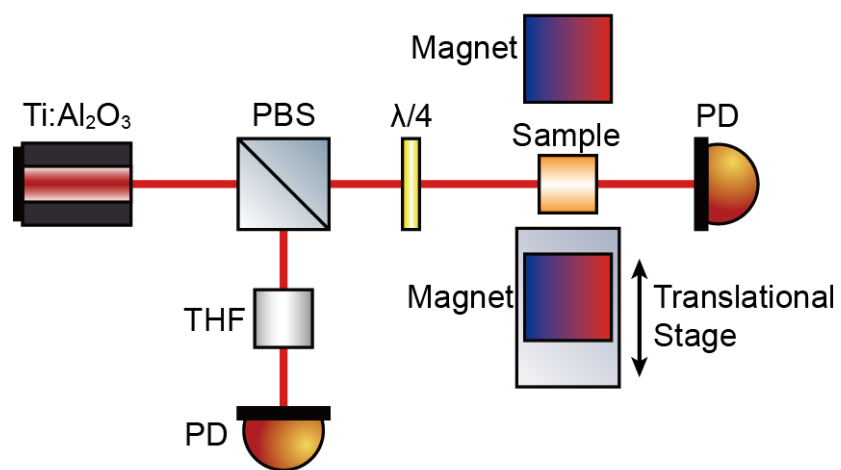


Fig. S37.

Optical setup of the high-resolution transmission/absorption spectrum measurement.

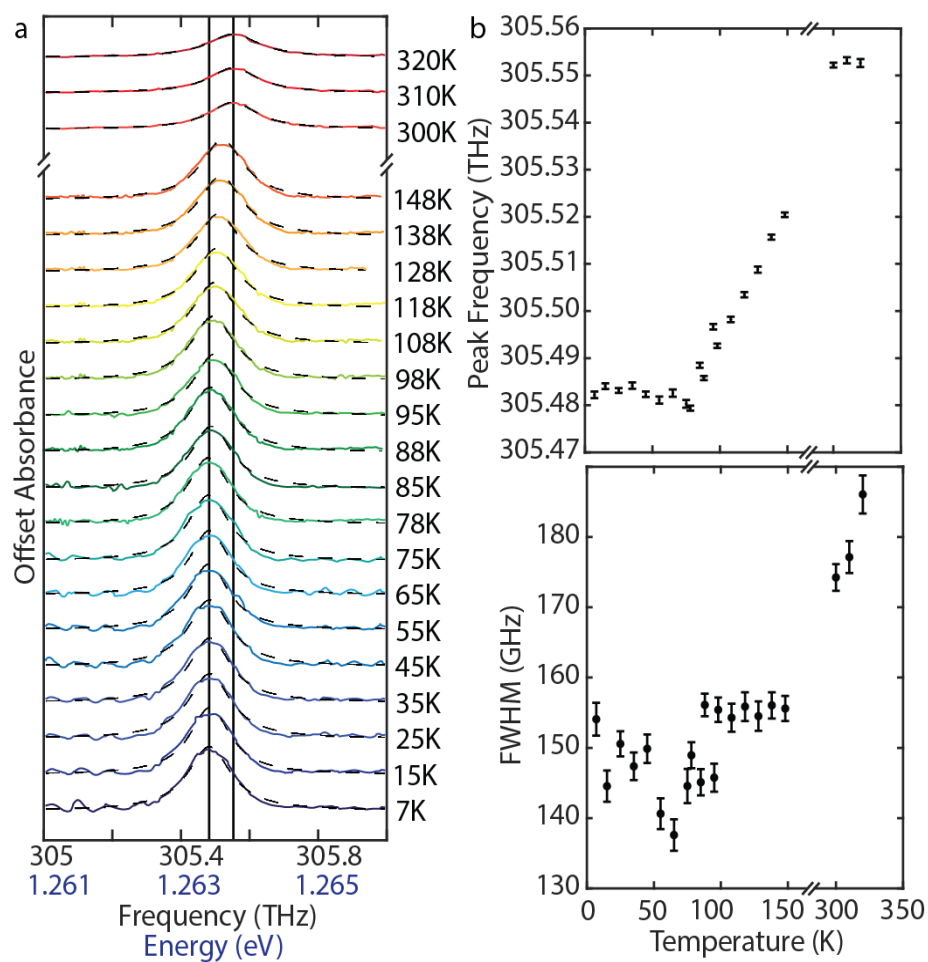


Fig. S38.

a) Temperature-dependent absorbance of (thiolfan)YbCl(2-MeTHF) and the corresponding Lorentzian fits. b) Fitted peak frequencies and linewidths. Error bars were extracted from Lorentzian fitting.

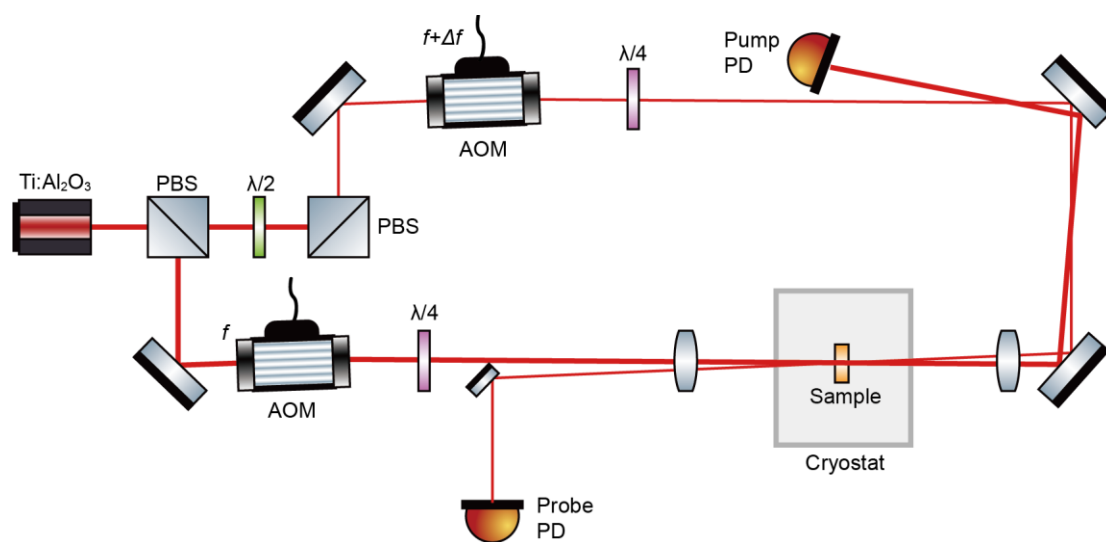


Fig. S39.
Optical setup for spectral hole burning measurement.

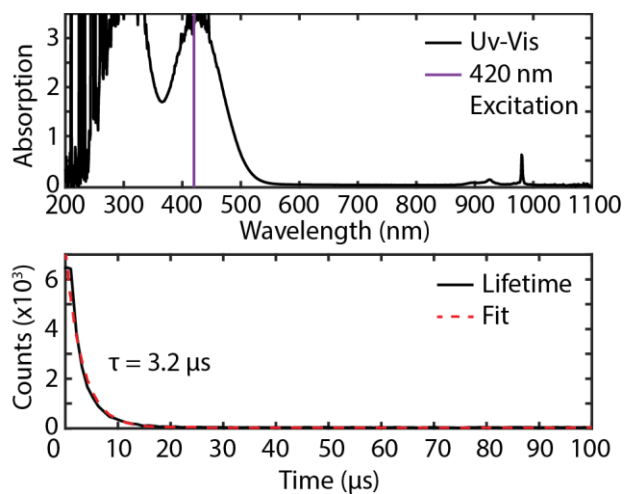


Fig. S40.

Top: broad absorption spectra of (thiolfan)YbCl(THF) in THF solution at room temperature. The excitation wavelength is indicated against the sample absorption. Bottom: lifetime measurement of the 980 nm emission and the corresponding fit.

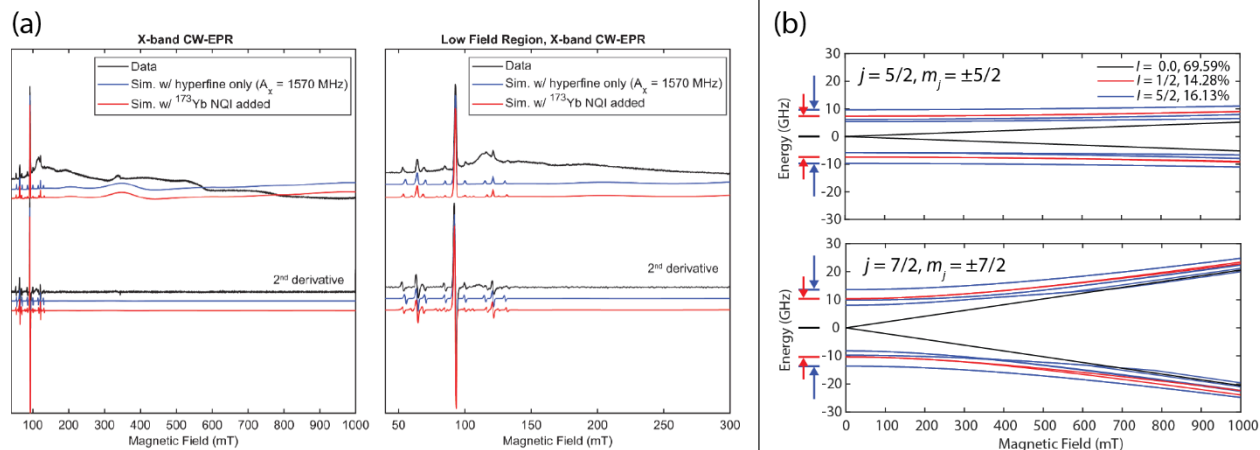


Fig. S41.

(a) X-band CW-EPR spectrum and 2nd derivative of (thiolfan)YbCl(THF) in frozen 2-MeTHF glass in the region from 0-1000 mT (left panel), and 0-300 mT (right panel) with spectral simulations offset underneath using the following parameters: $g = [7.41, 0.62, 0.42]$, $A(^{173}\text{Yb}) = [1553, 160, 160]$ MHz, $A(^{171}\text{Yb}) = [5915, 609, 609]$ MHz (magnitudes of A scale with respective ^{173}Yb , ^{171}Yb gyromagnetic ratios). Red traces are simulated using only g and A parameters, while the blue traces include an additional nuclear quadrupole interaction with the $I = 5/2$ nucleus, $Q(^{173}\text{Yb}) = [-105, -60, 165]$ MHz. Acquisition parameters: temperature = 5 K; microwave frequency = 9.638 GHz; MW power = 8.8 mW; modulation amplitude = 0.8 mT; conversion time = 10 ms. (b) Calculated hyperfine splitting as a function of the external magnetic field strength of the ground (bottom) and excited state (top) with g and A parameters from fitting and calculations.

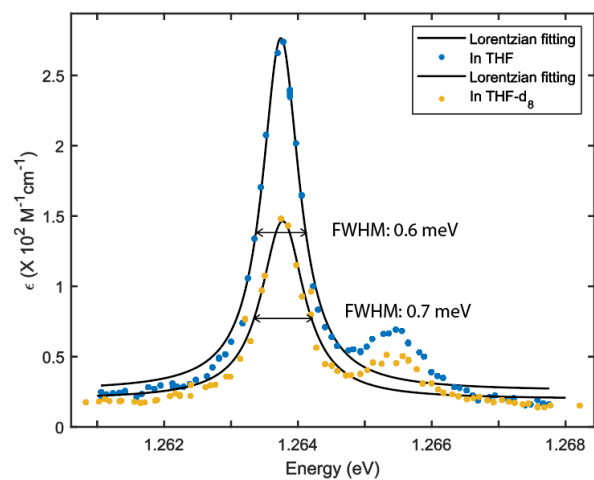


Fig. S42.

Absorption spectra of (thiolfan)YbCl(THF) in THF in blue and in THF-d₈ in yellow, showing an increase in inhomogeneous linewidth from 0.6 to 0.7 meV with solvent deuteration.

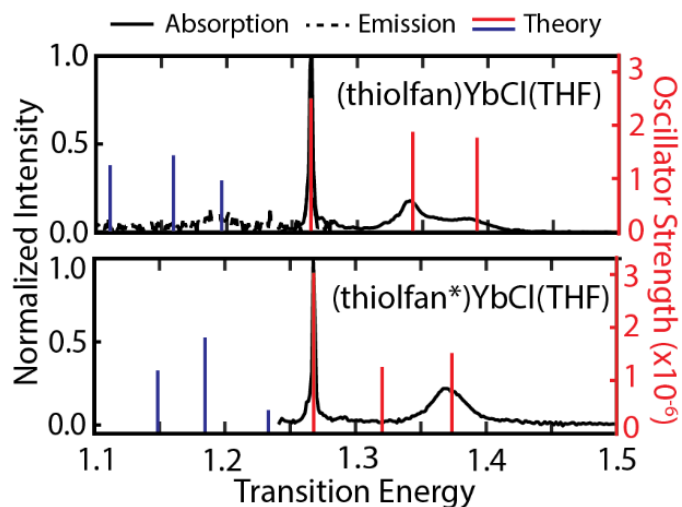


Fig. S43.

Theoretical and experimental spectra comparison. The absorption and emission spectra were normalized to the intensity of transition **IV**. The theoretical transition energies were shifted by 21.5 meV and 17.0 meV for (thiolfan)YbCl(THF) and (thiolfan*)YbCl(THF) to maximize overlap with experimental spectra, which are all within theoretical uncertainty.

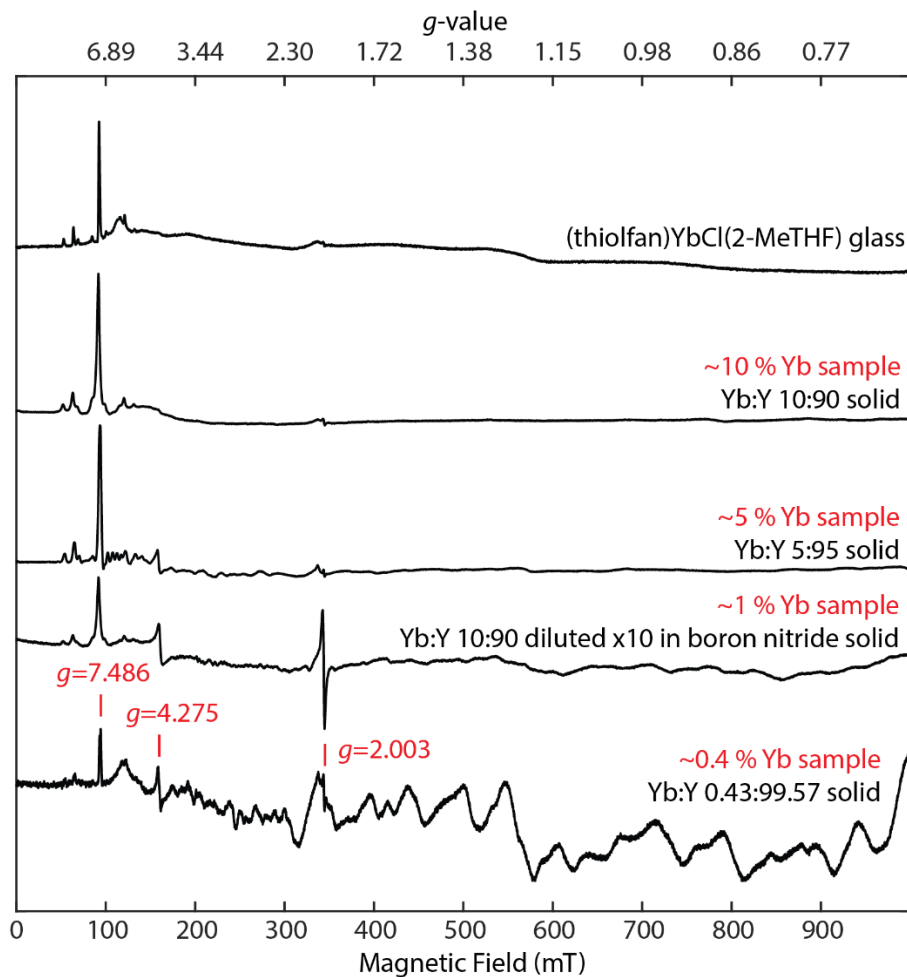


Fig. S44.

X-band CW-EPR spectra of (thiolfan)YbCl(THF) in frozen 2-MeTHF glass, Yb:Y 10:90 solid sample, Yb:Y 5:95 solid sample, Yb:Y 10:90 solid sample diluted in boron nitride to obtain 1%Yb sample, and Yb:Y 0.43:99.57 solid sample to resolve EPR peaks. Acquisition parameters: temperature = 5 K; microwave frequency = 9.638 GHz; MW power = 8.8 mW; modulation amplitude = 0.8 mT; conversion time = 10 ms.

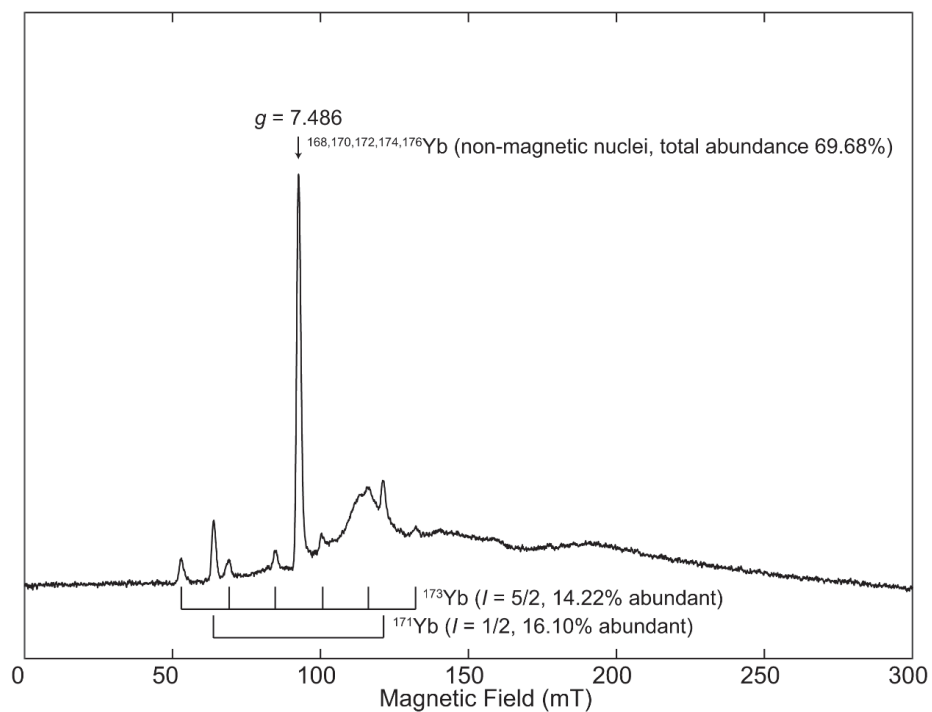


Fig. S45.

X-band CW-EPR spectrum of (thiolfan)YbCl(THF) in frozen 2-MeTHF glass in the region from 0-300 mT, with resolved features arising from hyperfine couplings to magnetic ^{171}Yb and ^{173}Yb nuclei indicated below. Acquisition parameters: temperature = 5 K; microwave frequency = 9.638 GHz; MW power = 8.8 mW; modulation amplitude = 0.8 mT; conversion time = 10 ms.

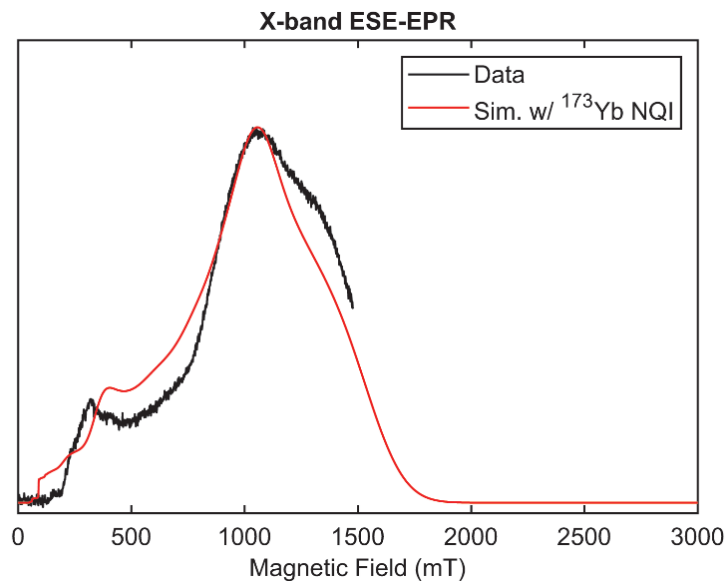


Fig. S46.

X-band ESE-EPR absorption spectrum of (thiolfan)YbCl(THF) in frozen 2-MeTHF glass (black trace) with spectral simulation using the following parameters: $g = [7.41, 0.62, 0.42]$, $A(^{173}\text{Yb}) = [1553, 160, 160]$ MHz, $A(^{171}\text{Yb}) = [5915, 609, 609]$ MHz (A magnitudes scale with respective ^{173}Yb , ^{171}Yb gyromagnetic ratios) $Q = [-105, -60, 165]$. Acquisition parameters: temperature = 5.6 K; microwave frequency = 9.373 GHz; $\tau = 300$ ns; $\pi/2$, π pulse lengths = 40, 80 ns; shot repetition time (srt) = 500 μs .

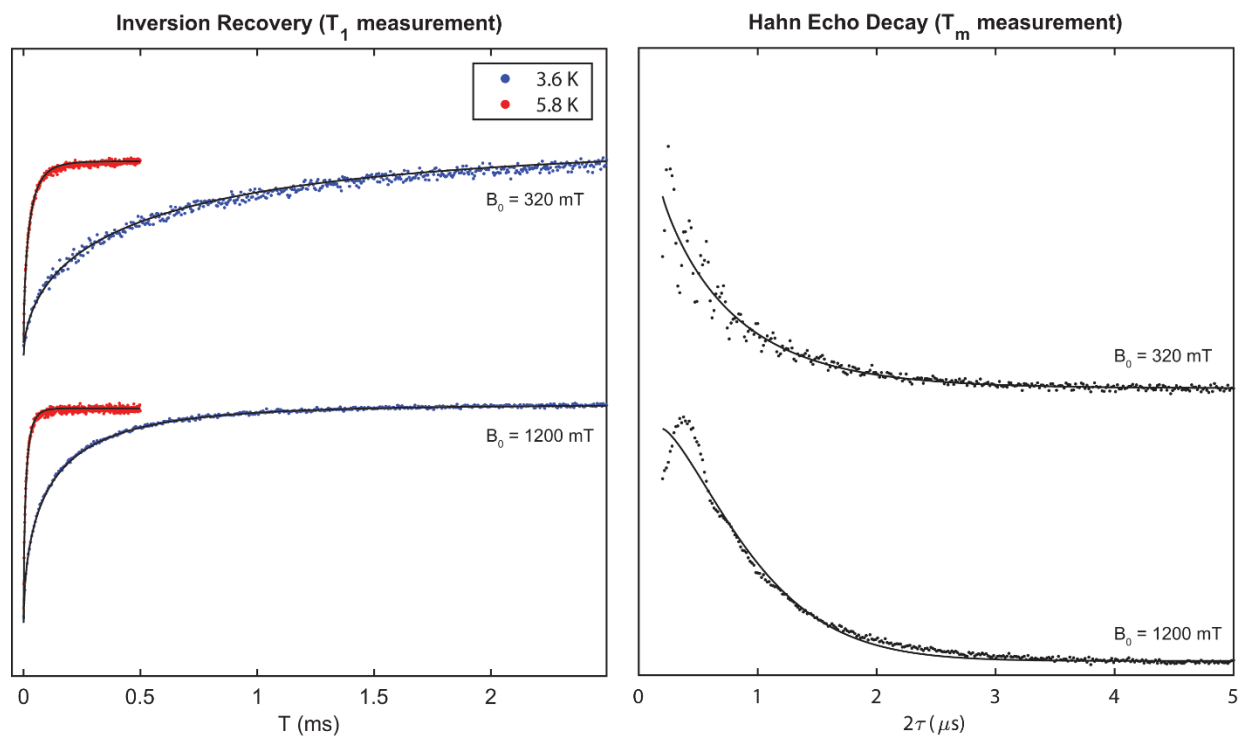


Fig. S47.

Left panel: X-band inversion recovery traces of (thiolfan)YbCl(2-MeTHF) in frozen 2-MeTHF glass at 3.6 (blue) and 5.8 K (red), at fields of 320 mT and 1200 mT. The time axis is truncated for display purposes, but all four curves presented reach saturation at longer times. At 3.6 K, T_1 is 518 μ s (320 mT, $\delta = 0.55$) and 116 μ s (1200 mT, $\delta = 0.56$), and at 5.8 K, T_1 is 23.5 μ s (320 mT, $\delta = 0.69$) and 10.4 μ s (1200 mT, $\delta = 0.69$). Right panel: X-band Hahn Echo decay traces of (thiolfan)YbCl(2-MeTHF) in frozen 2-MeTHF glass at 3.6 K, at fields of 320 mT and 1200 mT. T_m is 0.82 μ s (320 mT, $\delta = 0.92$) and 1.09 μ s (1200 mT, $\delta = 1.4$). T_1 and T_m decay constants were extracted through fits of data with a stretched exponential decay function of the form $I = -A(e^{-(\frac{T}{T_1})^\sigma} - I_0 - 1)$ and $I = -A(e^{-(\frac{2\tau}{T_m})^\sigma} - I_0)$, respectively, where σ is a stretch function.

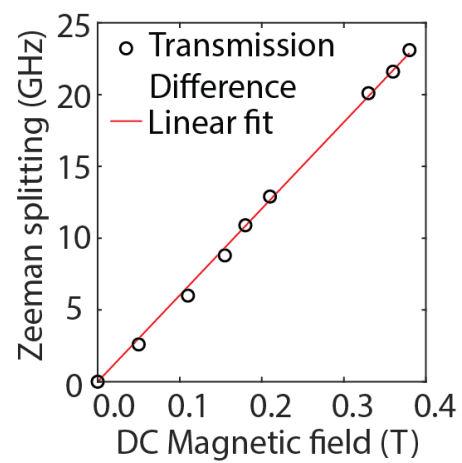


Fig. S48.

Expected linear relationship between Zeeman splitting and magnetic field strength.

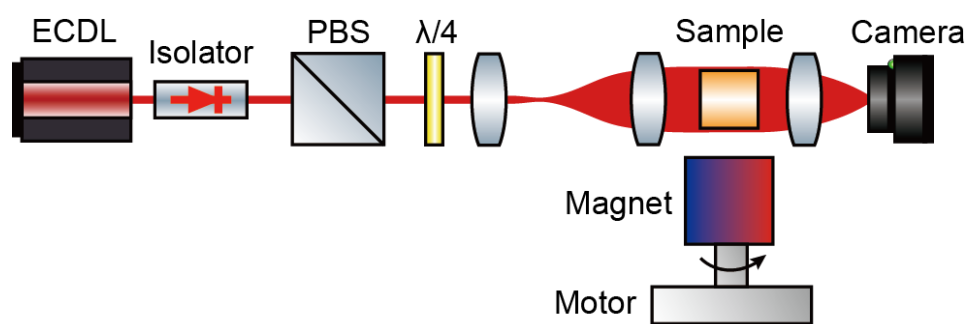


Fig. S49.
Optical setup of MCD imaging.

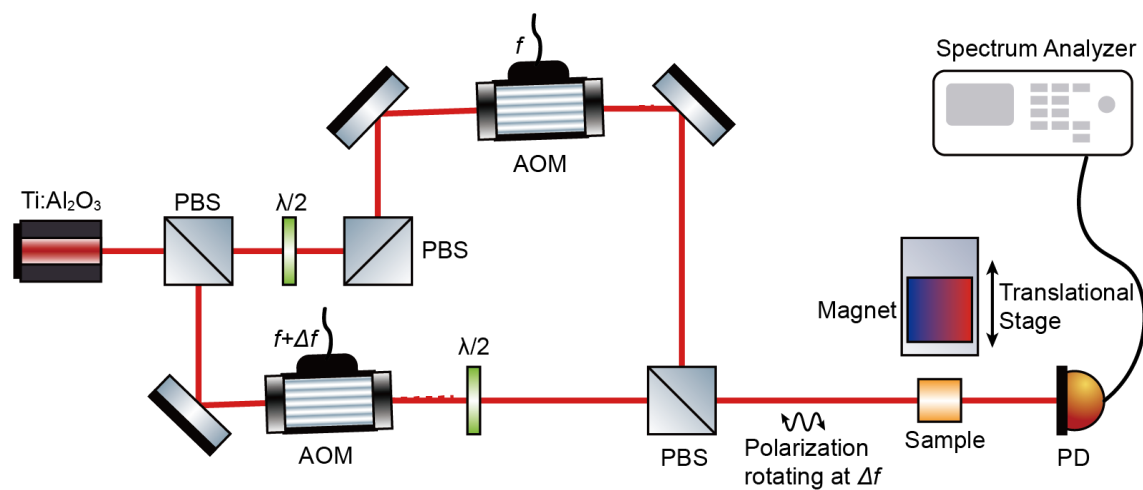


Fig. S50.

Optical setup for the direct measurement of the magnetic strength of a DC magnet using the MCD shift of the (thiolfan)YbCl(THF) sample.

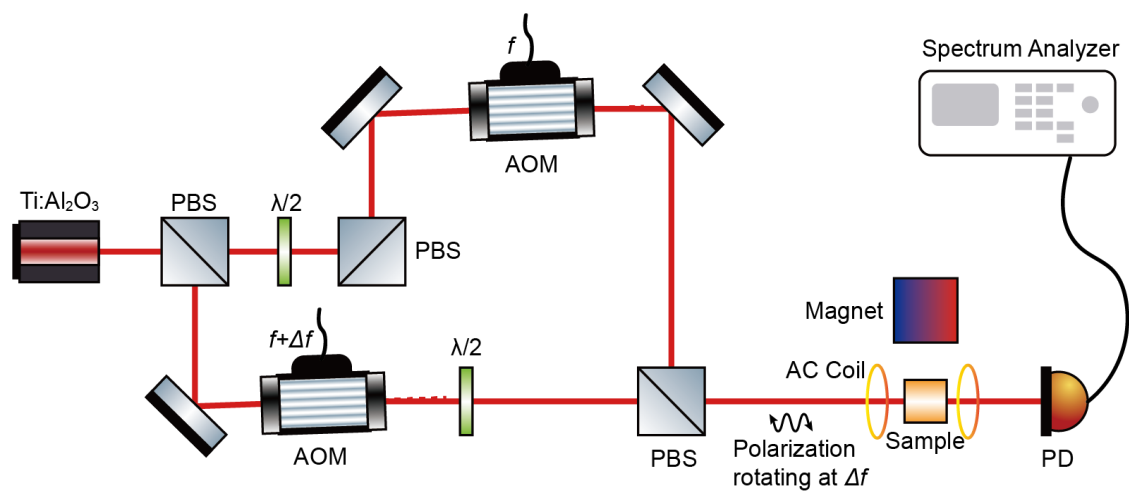


Fig. S51.

Optical setup of the direct measurement of the magnetic strength of an AC magnet using the MCD shift of the (thiolfan)YbCl(THF) sample.

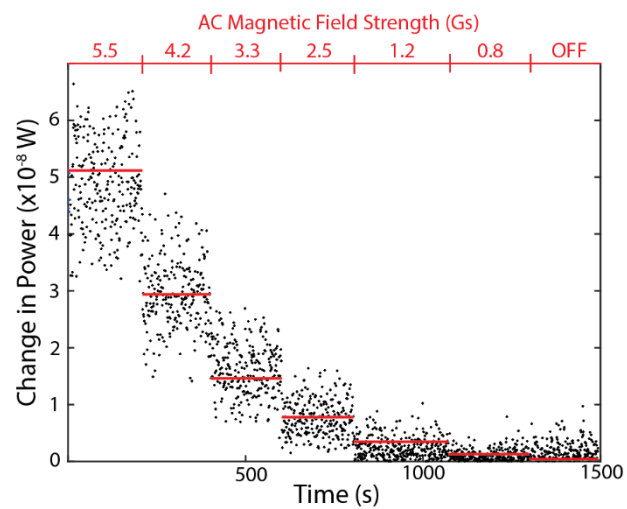


Fig. S52.

Raw data collected by a frequency analyzer as the magnitude of the AC field is changed.

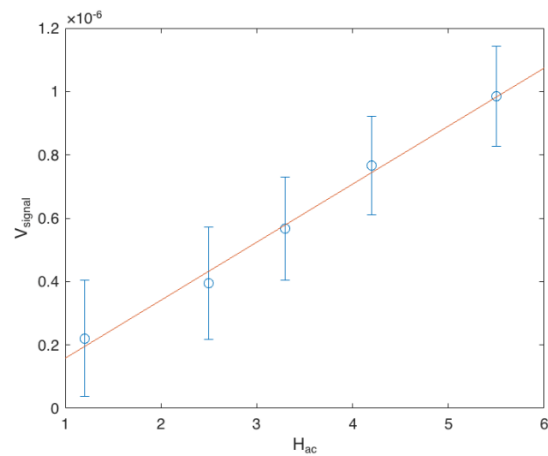


Fig. S53.

Voltage reading from the photodetector used for measuring transmission as a function of the AC field strength applied.

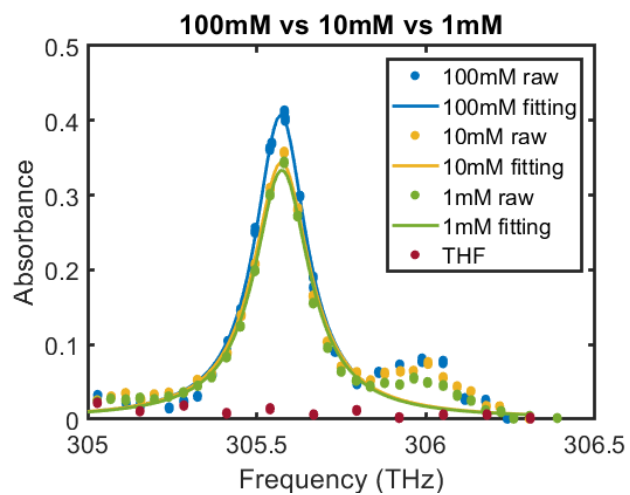


Fig. S54.

Absorption spectrum of transition IV of (thiolfan)YbCl(THF) in THF solution at 1 mM, 10 mM, and 100 mM concentrations, demonstrating consistent linewidth in 10 mm, 1 mm, and 0.1 mm cuvettes.

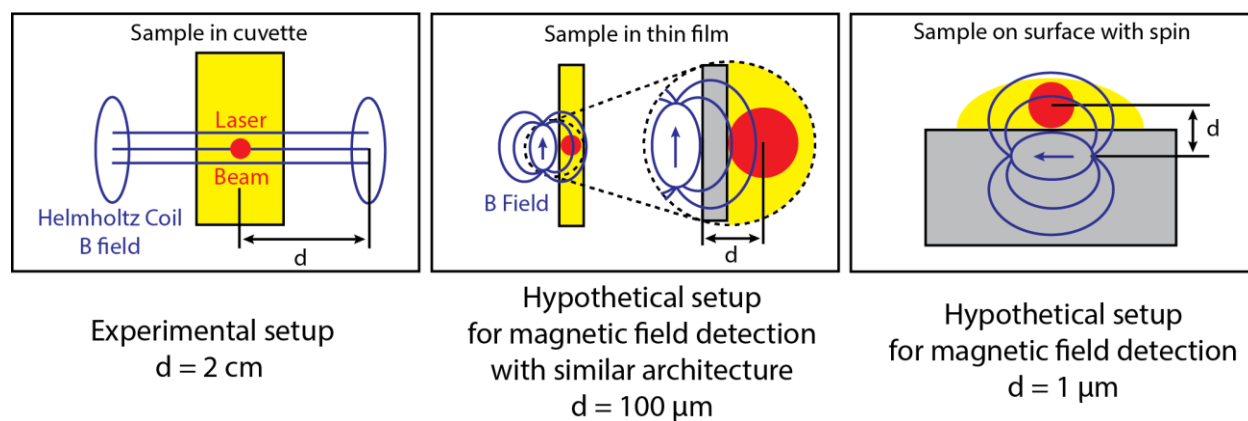


Fig. S55.

Diagrams of realized and proposed device architectures. Left: actual experimental setup used for AC magnetometry reported in this manuscript. Center: proposed device architecture for a thin film/cuvette format. Right: proposed device architecture for direct casting of ALMS onto surface.

	[(thiolfan)YbCl] ₂	(thiolfan)YbCl(THF)	(thiolfan*)YbCl(THF) ₂
Identification code	pld1905	pld2306b	pld2402
CCDC number	2280034	2279910	2335302
Empirical formula	C ₉₁ H ₁₂₂ Cl ₂ Fe ₂ O ₅ S ₄ Yb ₂	C ₄₄ H ₆₀ ClFeO ₃ S ₂ Yb	C ₄₆ H ₆₄ ClFeO ₄ S ₂ Yb
Formula weight [g/mol]	1952.80	965.38	1009.43
Temperature [K]	100 (2)	100 (2)	100 (2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
a [Å]	18.2162(18)	10.0390(2)	10.0773(6)
b [Å]	15.0982(15)	15.3323(3)	36.2320(18)
c [Å]	32.972(3)	15.4616(4)	15.7855(9)
α [°]	90	85.0770(10)	90
β [°]	102.091(2)	75.2870(10)	95.416(4)
γ [°]	90	87.8680(10)	90
Volume [Å³]	8867.2(15)	2293.04(9)	5737.9(6)
Z	4	2	4
ρ_{calc} [g/cm³]	1.463	1.398	1.169
μ [mm⁻¹]	2.614	7.857	6.314
F(000)	3992	986	2068
Crystal size [mm³]	0.090×0.080×0.070	0.1×0.1×0.05	0.20×0.100×0.050
Crystal color	yellow and green)	clear light yellow	clear light yellow
Crystal shape	block	plate	Plate
Radiation	MoK _α (λ=0.71073 Å)	CuK _α (λ=1.54178 Å)	CuK _α (λ=1.54178 Å)
2θ range for data collection [°]	2.29 to 56.76 (0.75 Å)	5.93 to 136.85 (0.83 Å)	6.13 to 137.10 (0.83 Å)
Index ranges	-24 ≤ h ≤ 24 -20 ≤ k ≤ 20 -43 ≤ l ≤ 44	-11 ≤ h ≤ 12 -18 ≤ k ≤ 18 -18 ≤ l ≤ 18	-12 ≤ h ≤ 11 -43 ≤ k ≤ 42 -19 ≤ l ≤ 14
Reflections collected	130664	37470	46505
Independent reflections	22122 <i>R</i> _{int} = 0.0830 <i>R</i> _{sigma} = 0.0675	8103 <i>R</i> _{int} = 0.0421 <i>R</i> _{sigma} = 0.0340	10499 <i>R</i> _{int} = 0.1568 <i>R</i> _{sigma} = 0.1100
Data/restraints /parameters	22122/0/724	8103/134/488	10499/6/486
Goodness-of-fit on F²	1.134	1.068	1.070
Final R indexes [I ≥ 2σ (I)]	<i>R</i> ₁ = 0.0724 <i>wR</i> ₂ = 0.1454	<i>R</i> ₁ = 0.0285 <i>wR</i> ₂ = 0.0703	0.1444
Final R indexes [all data]	<i>R</i> ₁ = 0.1176 <i>wR</i> ₂ = 0.1611	<i>R</i> ₁ = 0.0330 <i>wR</i> ₂ = 0.0720	<i>R</i> ₁ = 0.1745 <i>wR</i> ₂ = 0.3812
Largest diff. peak/hole [eÅ³]	4.14/-4.24	1.15/-1.05	2.66/-5.50

Table S1.

Selected crystal data for [(thiolfan)YbCl]₂, (thiolfan)YbCl(THF), and (thiolfan*)YbCl(THF)₂.

Entry	Complex	Calculated diffusion coefficient (m ² /s)	Calculated molecular radius
1	[(thiolfan)YbCl] ₂	3.826×10^{-10}	10.2 Å
2	(thiolfan*)YbCl	7.484×10^{-10}	5.2 Å

Table S2.

Calculated diffusion constants of Yb complexes in toluene-d₈ ($\eta = 5.60 \times 10^{-4} \frac{kg}{ms}$) and their calculated molecular radii based on DOSY experiments.

Entry	Complex	Calculated diffusion coefficient (m ² /s)	Calculated molecular radius
1	(thiolfan)YbCl(THF)	6.653×10^{-10}	7.1 Å
2	(thiolfan*)YbCl(THF) ₂	1.039×10^{-9}	4.6 Å

Table S3.

Calculated diffusion constants of Yb complexes in THF-d₈ ($\eta = 4.60 \times 10^{-4} \frac{kg}{ms}$) and their calculated molecular radii based on DOSY experiments.

Name	Ion Transition	FWHM (meV)	Phase	Temp.	Ref.	# in fig. 3a
(thiolfan)YbCl(THF)	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	0.6	Solution	RT		1
Yb^{3+} Helicene	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	3.6	Single Crystal	4 K	18	3
Yb Trensall	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	4.6	Single Crystal	RT	19	4
Yb^{3+} Methide Complex	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	5.1	Solution		20	5
$[\text{YbL}_2(\text{OTf})_2](\text{OTf})$	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	25.3	Solution	4 K	21	6
YbPO_4 :5% Er^{3+} Nanocrystals	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	32.8	Colloidal Nanocrystal	RT	60	
Yb^{3+} doped phosphate photonic crystal fiber	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	8	Crystal	RT	61	
Yb^{3+} doped silica glass	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	10	Glass	RT	62	
Yb^{3+} :YAG Crystal	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	3.4	Crystal	RT	63	
Yb(III) N,O-chelated Complex	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	8.4	Crystal	RT	64	
Yb^{3+} : Y_2SiO_5	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	0.4	Crystal	12 K	65	
Yb^{3+} :YVO	$\text{Yb}^{3+} \ ^2\text{F}_{7/2} - \ ^2\text{F}_{5/2}$	1e-5	Crystal	40 mK	66	
$\text{Eu}(\text{BA})_4(\text{pip})$	$\text{Eu}^{3+} \ ^7\text{F}_0 - \ ^5\text{D}_0$	0.027	Crystal	10 K	67	
$\text{Eu}(\text{trensall})$	$\text{Eu}^{3+} \ ^7\text{F}_0 - \ ^5\text{D}_0$	0.372	Crystal	4.2 K	68	
Pr^{3+} in HClO_4	$\text{Pr}^{3+} \ ^3\text{H}_4 - \ ^3\text{P}_0$	26	Solution	RT	69	
Nd^{3+} in HClO_4	$\text{Nd}^{3+} \ ^4\text{I}_{9/2} - \ ^3\text{G}_{1/2}$	10	Solution	RT	69	
Pm^{3+} in HClO_4	$\text{Pm}^{3+} \ ^5\text{I}_4 - \ ^5\text{I}_8$	22	Solution	RT	69	
Eu^{3+} in HClO_4	$\text{Eu}^{3+} \ ^7\text{F}_0 - \ ^5\text{D}_1$	11	Solution	RT	69	
Er^{3+} in HClO_4	$\text{Er}^{3+} \ ^4\text{I}_{15/2} - \ ^2\text{K}_{15/2}$	17	Solution	RT	69	
Er^{3+} :YVO ₄	$\text{Er}^{3+} \ ^4\text{I}_{15/2} - \ ^4\text{I}_{14/2}$	6.7e-4	Crystal	1 K	70	
Er^{3+} : Y_2SiO_5	$\text{Er}^{3+} \ ^4\text{I}_{15/2} - \ ^4\text{I}_{14/2}$	3.02e-10	Crystal	2 K	71	

Table S4.

Expanded linewidth comparison, including ones shown in Fig. 3a in the manuscript (18-21, 60-71).

Initial State	Final State	Transition Energy (eV)	Oscillator Strength
1	9	1.2647	1.4E-10
	10		2.7E-08
	11	1.3455	1.5E-10
	12		3.6E-09
	13	1.3834	2.3E-10
	14		2.3E-10
2	9	1.2647	2.5E-08
	10		6.0E-11
	11	1.3455	3.6E-09
	12		1.4E-10
	13	1.3834	6.0E-11
	14		3.2E-10

Table S5.

Optical absorption transition energies with corresponding M1 oscillator strengths calculated from an atomic model.

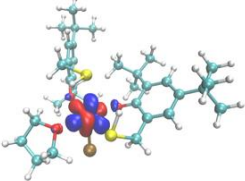
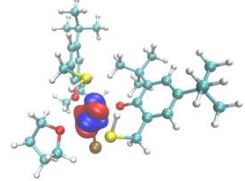
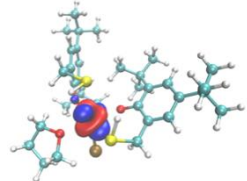
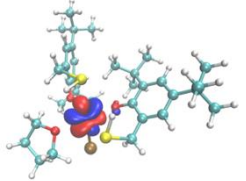
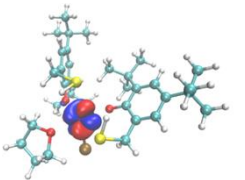
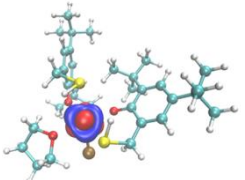
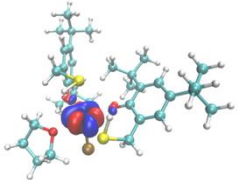
			
Orbital 1	Orbital 2	Orbital 3	Orbital 4
			

Table S6.
CAS 7 4f orbitals involved in the CASSCF calculation.

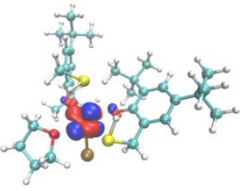
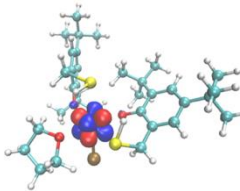
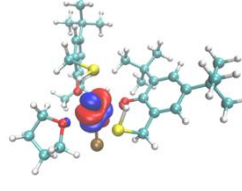
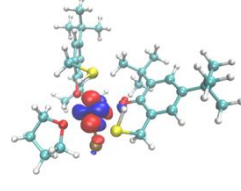
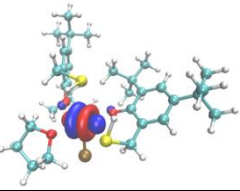
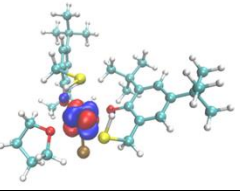
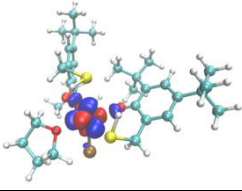
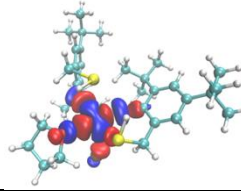
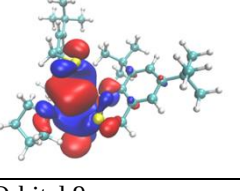
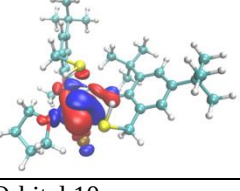
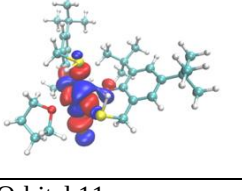
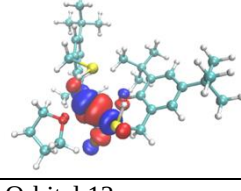
			
Orbital 1	Orbital 2	Orbital 3	Orbital 4
			
Orbital 5	Orbital 6	Orbital 7	Orbital 8
			
Orbital 9	Orbital 10	Orbital 11	Orbital 12

Table S7.

CAS 12 orbitals involved in the CASSCF calculation, 7 4f orbitals and a mixture of virtual 5d/6d orbitals.

Initial State	Final State	Transition Number	Transition Energy (eV)	Length Oscillator	Dipole Strength	Velocity Oscillator	Dipole Strength
	only 4f orbitals in active space						
1	9	IV	1.288	2.05E-07		2.33E-07	
	10	IV		3.5E-08		2.36E-06	
	11	III	1.338	1.31E-07		3.60E-06	
	12	III		1.37E-07		1.95E-06	
	13	II	1.373	1.81E-07		1.15E-06	
	14	II		2.60E-07		3.99E-06	
2	9	IV	1.288	3.5E-08		2.36E-06	
	10	IV		2.05E-07		2.33E-07	
	11	III	1.338	1.37E-07		1.95E-06	
	12	III		1.31E-07		3.6E-06	
	13	II	1.373	2.60E-07		3.99E-06	
	14	II		1.81E-07		1.15E-06	
3	9	V	1.238	1.95E-08		2.30E-06	
	10	V		1.10E-07		2.49E-06	
4	9	V	1.238	1.10E-07		2.49E-06	
	10	V		1.95E-08		2.30E-06	
	4f + 5d orbitals in active space						
1	9	IV	1.286	5.17E-07		3.29E-05	
	10	IV		7.35E-07		1.76E-05	
	11	III	1.364	6.13E-07		1.445E-04	
	12	III		3.25E-07		5.84E-05	
	13	II	1.413	4.76E-07		9.07E-05	
	14	II		4.07E-07		1.20E-04	
2	9	IV	1.286	7.35E-07		1.76E-05	
	10	IV		5.17E-07		3.29E-05	
	11	III	1.364	3.25E-07		5.84E-05	
	12	III		6.13E-07		1.45E-04	
	13	II	1.413	4.07E-07		1.20E-04	
	14	II		4.76E-07		9.07E-05	
3	9	V	1.218	4.81E-07		8.26E-05	
	10	V		6.79E-08		1.25E-05	
4	9	V	1.218	6.79E-08		1.25E-05	
	10	V		4.81E-07		8.26E-05	

Table S8.

Transition energies and electric velocity dipole oscillator strengths computed with the RASSI-SOC module between CAS(13,7) and CAS(13,12) active spaces. Length dipole and velocity dipole oscillator strengths are tabulated.

State	Orbital # (Weight)	AO %
only 4f orbitals in active space, Table S6		
1,2	7 (0.291)	7: 99.9% 4f
	1 (0.592)	1: 99.85% 4f
9,10	2 (0.263)	2: 99.3% 4f
	5 (0.600)	5: 99.6% 4f
4f + 5d orbitals in active space, Table S7		
1,2	2 (0.432)	2: 99.4% 4f
	5 (0.323)	5: 99.6% 4f
9,10	6 (0.434)	6: 99.9% 4f

Table S9.

Most dominant orbitals involved in the electronic transition from CASSCF and RASSI-SOC calculations. Orbital numbers are from orbitals listed in tabs. S6, S7, respectively.

Bra State	Ket State	Transition Number	SOC Element	Matrix
only 4f orbitals in active space				
9	1	IV	455.20	
	2	IV	375.17	
	3	V	740.96	
	4	V	121.04	
10	1	IV	375.17	
	2	IV	455.20	
	3	V	121.04	
	4	V	740.96	
11	1	III	102.91	
	2	III	161.75	
12	1	III	161.75	
	2	III	102.91	
13	1	II	205.49	
	2	II	462.18	
14	1	II	462.18	
	2	II	205.49	
4f + 5d orbitals in active space				
9	1	IV	82.37	
	2	IV	439.82	
	3	V	715.64	
	4	V	128.45	
10	1	IV	439.82	
	2	IV	82.37	
	3	V	128.45	
	4	V	715.64	
11	1	III	404.37	
	2	III	451.46	
12	1	III	451.46	
	2	III	404.37	
13	1	II	121.41	
	2	II	520.11	
14	1	II	520.11	
	2	II	121.41	

Table S10.

Spin-orbit coupling matrix elements between different RASSI-SOC states for CAS(13,7) and CAS(13,12) active spaces.

Bra State	Ket State	Transition Number	SOC Matrix Element
SA-7-CASSCF			
9	1	IV	477.31
	2	IV	294.13
	3	V	627.16
	4	V	168.35
10	1	IV	294.13
	2	IV	477.31
	3	V	168.35
	4	V	627.16
11	1	III	218.96
	2	III	192.36
12	1	III	192.36
	2	III	218.96
13	1	II	5.67
	2	II	515.29
14	1	II	515.29
	2	II	5.67
SA-7-CASCI			
9	1	IV	82.37
	2	IV	439.82
	3	V	715.64
	4	V	128.45
10	1	IV	439.82
	2	IV	82.37
	3	V	128.45
	4	V	715.64
11	1	III	404.37
	2	III	451.46
12	1	III	451.46
	2	III	404.37
13	1	II	121.41
	2	II	520.11
14	1	II	520.11
	2	II	121.41

Table S11.

Spin-orbit coupling matrix elements between different RASSI-SOC states for SA-7-CASCI vs. SA-7-CASSCF using CAS(13,12) active spaces.

	$ m_j = 7/2$	$ m_j = 5/2$
Measured from EPR (fig. S44)	7.486 ± 0.008	-
Derived from EPR and MCD	-	3.2 ± 0.2
Calculated	$g_x = 7.49$ $g_y = 0.34$ $g_z = 0.38$	$g_x = 4.27$ $g_y = 0.17$ $g_z = 0.15$
Landé g factor for Yb^{3+}	8	4.28

Table S12.

Comparison of measured and calculated g factors for the ground and excited states of transition **IV** in (thiolfan)YbCl(THF), both lower than the theoretical gas phase limits. The g factor calculations were done using the EPRG (RASSI module for EPR g-factor calculations).

Movie S1.

Dynamic MCD imaging of (thiolfan)YbCl(THF) transmission under static magnetic field. The intensity and relative direction of the magnetic field to the laser propagation is indicated by the color map (red: parallel, blue: anti-parallel). The intensity fades with increasing distance from the magnet (maximum strength 0.3 T), which is at the bottom out of view in the video. The interference pattern is most likely from scattering off the cuvette and magnet.

References and Notes

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