Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: *Near-Infrared Circular Dichroism of Chiral Ytterbium Complexes: An Ab-initio Investigation*

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Experimental CD Spectra for [Yb(DOTMA)]$^-$

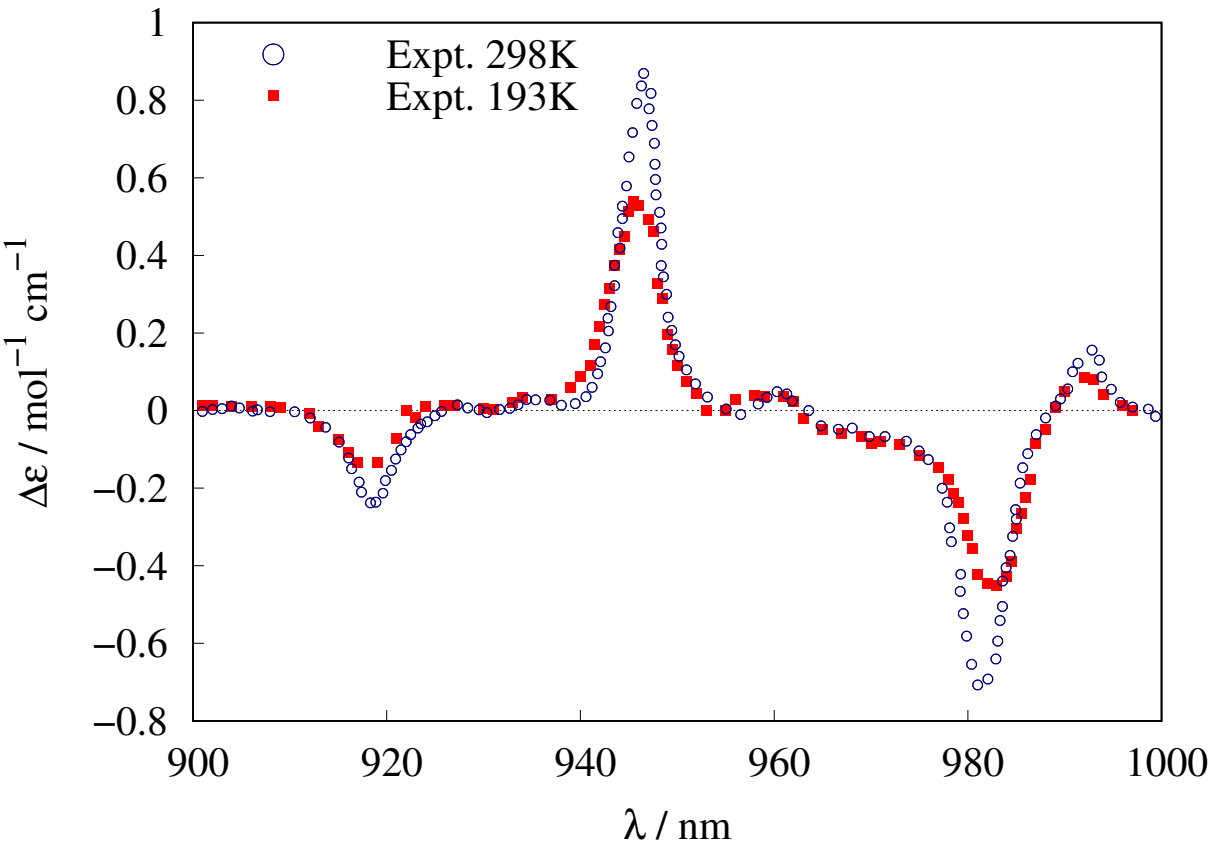

Figure S1: Experimental CD spectra of [Yb(DOTMA)]$^-$ at 193K (red squares) and 298 K (blue circles) in methanol. The two spectra were generated using data extracted from Reference 1

Additional Calculated CD Spectra for [Yb(DOTMA)]$^-$ with the NMR Structure

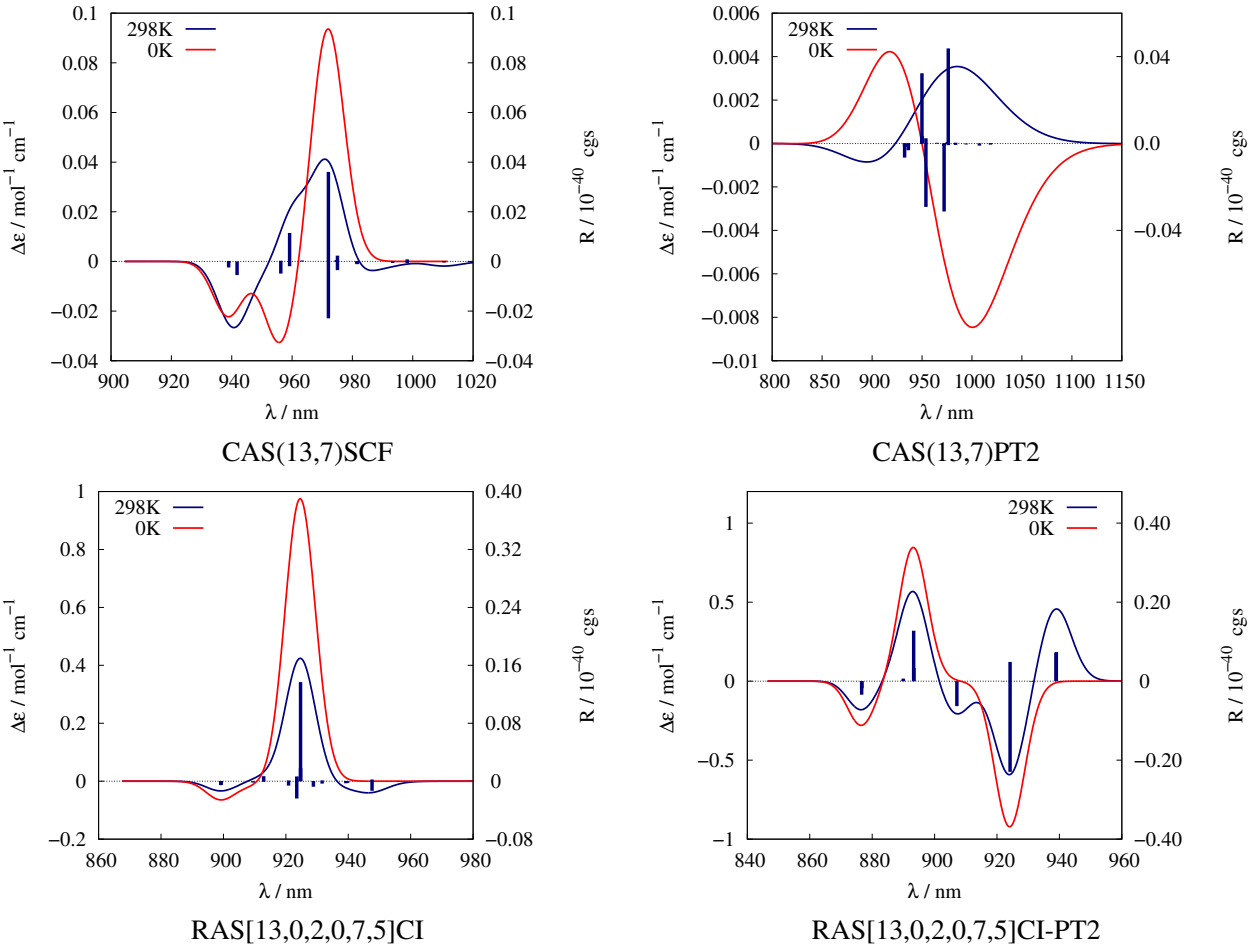

Figure S2: Comparison of the calculated CD spectra ($\Delta\epsilon$, in mol^{-1}) at 0K (red line) and 298K (blue line) for [Yb(DOTMA)]$^-$ using the NMR Structure and obtained at the CAS(13,7)SCF, CAS(13,7)PT2, RAS[13,0,2,0,7,5]CI and RAS[13,0,2,0,7,5]CI-PT2 levels of theory. The blue sticks added on the spectra represent the corresponding calculated rotatory strengths (10^{-40} cgs) at 298 K. Mind the change of scale between the different level of theory. The scale of both $\Delta\epsilon$ and R have been chosen to present clear spectra.

Additional Calculated CD Spectra for [Yb(DOTMA)]$^-$ with the PBE Optimized Structure

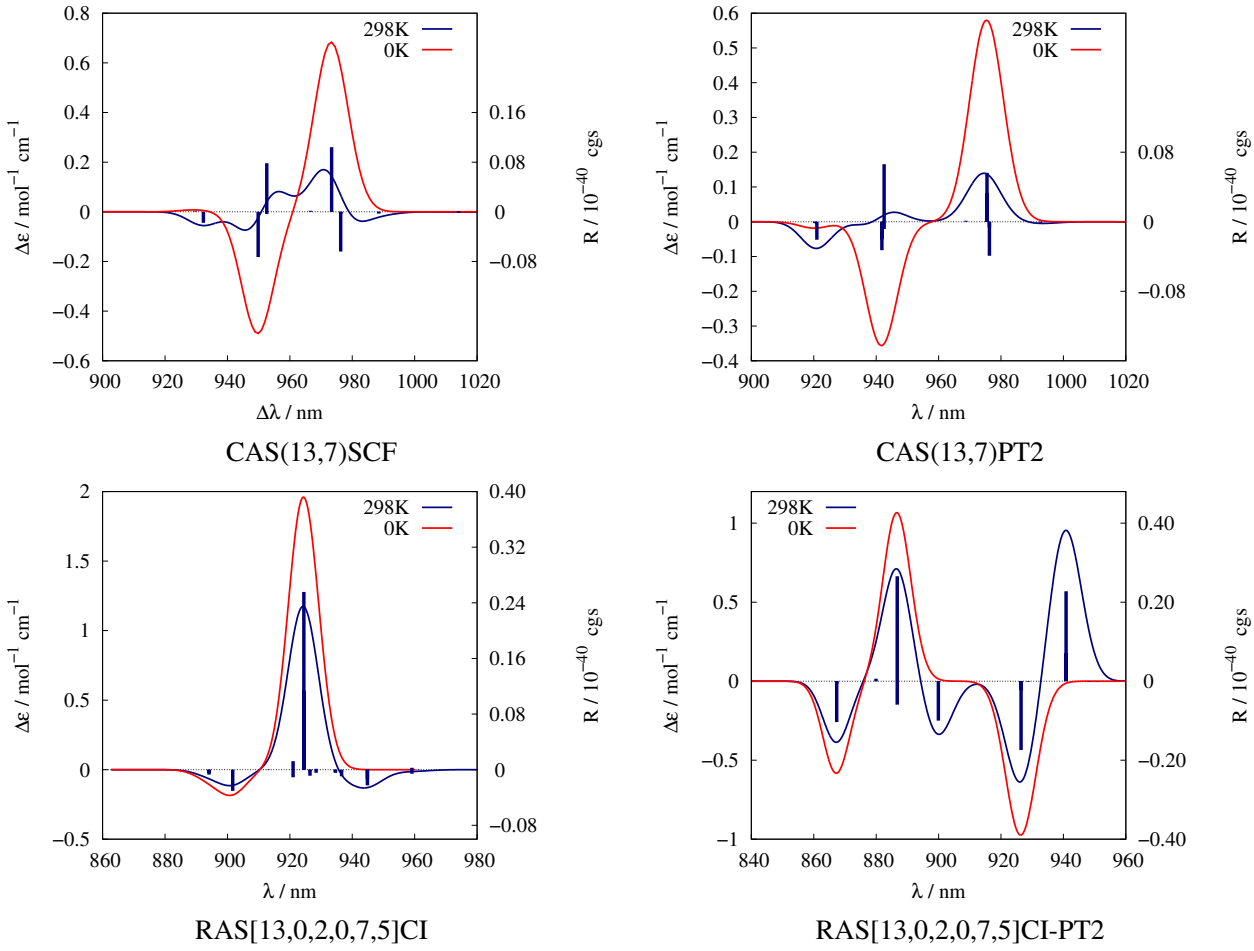

Figure S3: Comparison of the calculated CD spectra ($\Delta\epsilon$, in mol^{-1}) at 0K (red line) and 298K (blue line) for [Yb(DOTMA)]$^-$ using the PBE Structure and obtained at the CAS(13,7)SCF, CAS(13,7)PT2, RAS[13,0,2,0,7,5]CI and RAS[13,0,2,0,7,5]CI-PT2 levels of theory. The blue sticks added on the spectra represent the corresponding calculated rotatory strengths (10^{-40} cgs) at 298 K. Mind the change of scale between the different level of theory. The scale of both $\Delta\epsilon$ and R have been chosen to present clear spectra.

Additional Calculated CD Spectra for [Yb(DOTMA)]$^-$ with the PBE0 Optimized Structure

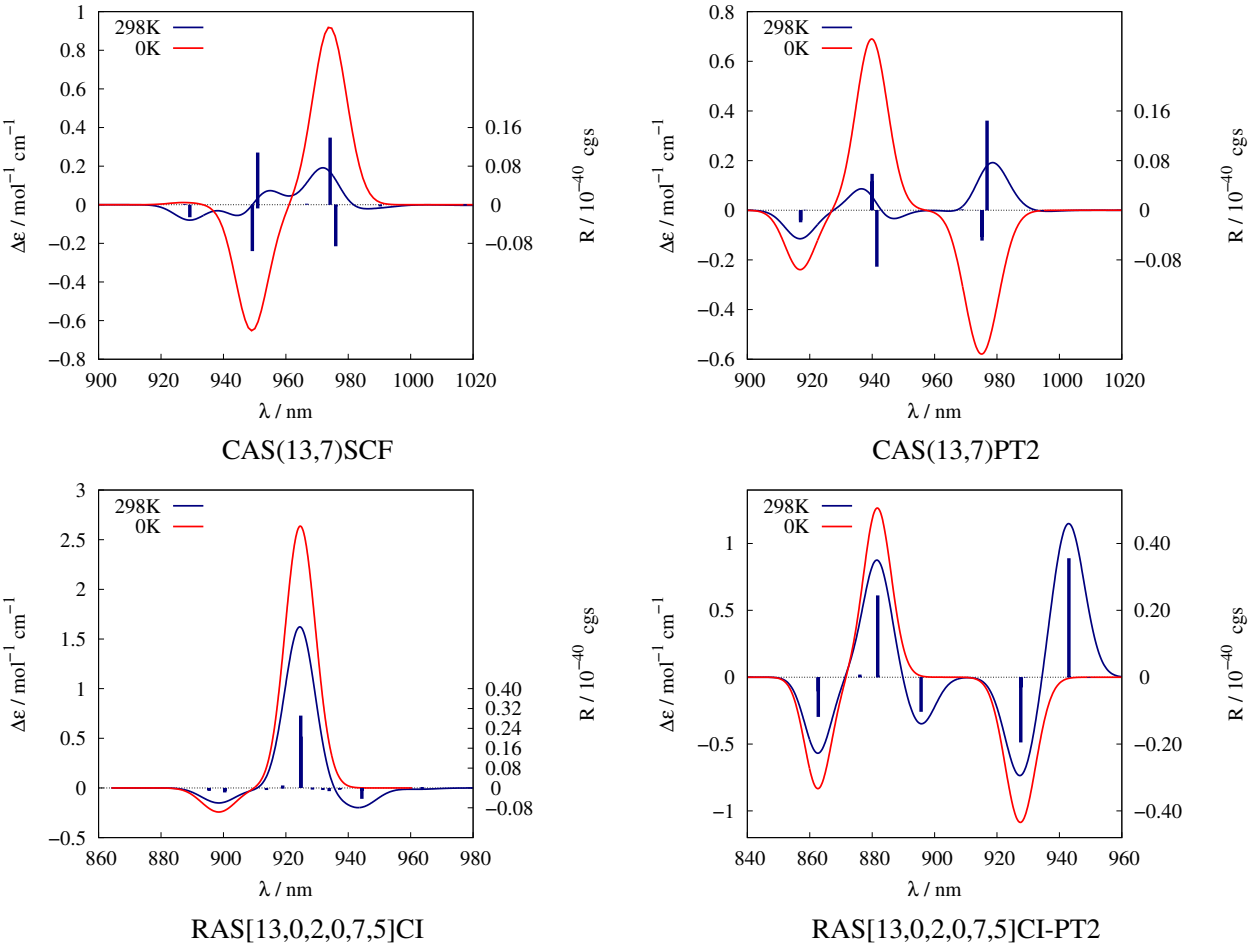

Figure S4: Comparison of the calculated CD spectra ($\Delta\epsilon$, in mol^{-1}) at 0K (red line) and 298K (blue line) for [Yb(DOTMA)]$^-$ using the PBE0 Structure and obtained at the CAS(13,7)SCF, CAS(13,7)PT2, RAS[13,0,2,0,7,5]CI and RAS[13,0,2,0,7,5]CI-PT2 levels of theory. The blue sticks added on the spectra represent the corresponding calculated rotatory strengths (10^{-40} cgs) at 298 K. Mind the change of scale between the different level of theory. The scale of both $\Delta\epsilon$ and R have been chosen to present clear spectra.

Structural Comparison of the Different Structures of [Yb(DOTMA)]$^-$

Table S1: Principal bond lengths (in Å) and angle (°) of the first coordination sphere of the Yb(III) ion in [Yb(DOTMA)]$^-$.

	Yb–O	Yb–N	O–Yb–O
NMR	2.485	2.661	131.1
PBE	2.312	2.622	124.2
PBE0	2.257	2.554	124.9

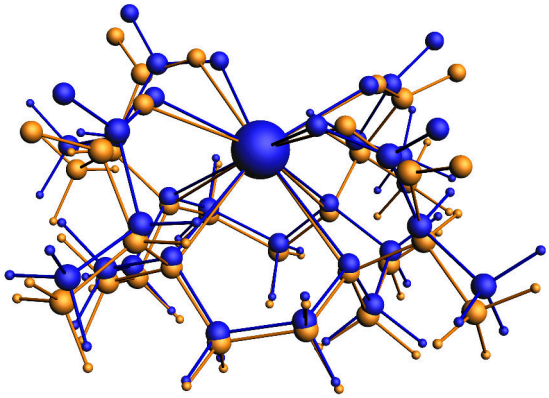

Figure S5: Overlay of the NMR (orange) and PBE0 (blue) structures.

Calculated Electronic Structures in [Yb(DOTMA)]$^-$

Table S2: Calculated relative energies (cm^{-1}) of the lowest Kramers doublets in [Yb(DOTMA)]$^-$ as a function of the structure used in the calculations.

	CAS(13,7)SCF			CAS(13,7)PT2			RAS[13,0,2,0,7,5]CI			RAS[13,0,2,0,7,5]CI-PT2		
	NMR	PBE	PBE0	NMR	PBE	PBE0	NMR	PBE	PBE0	NMR	PBE	PBE0
1	0	0	0	0	0	0	0	0	0	0	0	0
2	31	31	19	43	8	17	167	233	224	165	165	176
3	269	412	436	360	544	583	261	390	398	574	731	808
4	390	481	508	468	591	634	354	413	437	678	761	828
1’	10289	10275	10266	10288	10252	10255	10815	10818	10815	10818	10795	10781
2’	10458	10529	10535	10528	10618	10639	10996	11091	11107	11198	11278	11342
3’	10651	10758	10781	10724	10867	10905	11122	11186	11169	11423	11531	11592

Gauge-origin Dependence of the Calculations

Table S3: Calculated energies (cm^{-1}), squared electric dipole (μ, $\times 10^{-40}$ cgs), squared magnetic dipole (m, $\times 10^{-40}$ cgs) and rotatory strengths (R, $\times 10^{-40}$ cgs) as a function of the position of the gauge origin using the NMR structure at the RAS13,0,2,0,7,5]CI-PT2 level.

Gauge-Origin	Center of Mass (0.0,0.0,0.0)				Not Center of Mass (3.0,4.0,5.0)		
	ΔE	$\|\mu\|^2$	$\|m\|^2$	R	$\|\mu\|^2$	$\|m\|^2$	R
1 → 1'	10818	4.871940	0.155390	-0.260298	4.871970	0.157000	-0.267753
1 → 2'	11198	1.776884	0.088406	0.240431	1.776883	0.095586	0.253626
1 → 3'	11423	0.337334	0.046620	-0.083184	0.3373340	0.045037	-0.081906

Details of the Boltzmann distribution calculations

According to the Boltzmann distribution, the probability to find a particule in quantum state i of an energy E_i at temperature T over n states is :

$$\frac{N_i}{N_{tot}} = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{j=1}^{n} e^{-\frac{E_j}{k_B T}}}$$

Consequently, it is possible to estimate the relative population of the four cristal field states of the $^2F_{7/2}$ ground state of the Yb(III), depending of the temperature. Indeed, the distribution can be obtained by solving the following four-equations system where k_B corresponds to the Boltzmann constant and E_i the energy of the M_J states ($i = 1 - 4$):

$$\begin{cases} \frac{N_2}{N_1} = e^{\frac{E_1 - E_2}{k_B T}} \\ \frac{N_3}{N_1} = e^{\frac{E_1 - E_3}{k_B T}} \\ \frac{N_4}{N_1} = e^{\frac{E_1 - E_4}{k_B T}} \\ N_{tot} = N_1 + N_2 + N_3 + N_4 \end{cases}$$

References

[1] L. Di Bari, G. Pintacuda, P. Salvadori, *J. Am. Chem. Soc.*, 2000, **122**, 5557–5562.