Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

A Rare Earth Metallocene Containing a 2,2’-Azopyridyl Radical Anion

Francis Delano IV, Ernesto Castellanos,
John McCracken, and Selvan Demir*

Department of Chemistry, Michigan State University, 578 South Shaw Lane, East Lansing, Michigan 48824, USA

*Correspondence to: sdemir@chemistry.msu.edu (S.D.)

Chem. Sci.

Table of Contents

Table S1. Crystal data and structure refinement of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**.

Compound	$(Cp^{Me4H})_2Y(abpy^{\bullet})$	
Formula	$C_{28}H_{34}N_4Y$	
$D_{calc.}$/ g cm^{-3}	1.349	
μ/mm^{-1}	3.394	
Formula Weight / g mol^{-1}	515.50	
Color	dark violet	
Shape	plate	
Size/mm^3	0.16×0.15×0.09	
T/K	100.01(10)	
Crystal System	triclinic	
Space Group	P-1	
Unit Cell Dimensions	a = 9.27977(15) Å	α = 88.3450(12)°
	b = 15.8832(2) Å	β = 82.9269(13)°
	c = 17.3902(3) Å	γ = 86.1875(12)°
V/Å^3	2537.50(7)	
Z	4	
Z'	2	
Wavelength/Å	1.54184	
Radiation type	Cu K_{α}	
Θ_{min}/°	2.561	
Θ_{max}/°	77.278	
Measured Refl's.	33611	
Indep't Refl's	10316	
Refl's I≥2 σ(I)	9356	
R_{int}	0.0386	
Parameters	989	
Restraints	1264	
Largest Peak	1.291	
Deepest Hole	-1.347	
GooF	1.082	
wR_2 (all data)	0.1137	
wR_2	0.1110	
R_1 (all data)	0.0474	
R_1	0.0440	

Table S2. Metrical data from the crystal structure of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**. Bond distances are given in Angstroms (Å) for disordered parts A, B, C, and D respectively. Atom labels correspond to those shown in Fig. S1.

$(Cp^{Me4H})_2Y(abpy^{\bullet})$		A	B	C	D
Y-C ($Cp^{Me4H}{}_1$)	C_{11}	2.6110(3)		2.615(4)	
	C_{12}	2.642(3)		2.650(3)	
	C_{13}	2.695(3)		2.701(3)	
	C_{14}	2.703(3)		2.705(3)	
	C_{15}	2.661(3)		2.660(4)	
Y-C ($Cp^{Me4H}{}_2$)	C_{20}	2.622(5)	2.55(3)	2.67(1)	2.676(8)
	C_{21}	2.66(3)	2.67(3)	2.62(2)	2.667(8)
	C_{22}	2.665(7)	2.70(3)	2.54(1)	2.709(6)
	C_{23}	2.680(7)	2.72(3)	2.62(1)	2.722(7)
	C_{24}	2.653(6)	2.71(3)	2.70(1)	2.669(1)
Y-N_{azo}	N_1	2.348(8)	2.300(2)	2.312(4)	2.300(8)
	N_2	3.65(8)	3.35(3)	3.61(4)	3.350(8)
Y-N_{ppy}	N_3	2.743(1)	2.634(5)	2.514(9)	2.62(1)
	N_4	2.438(1)	2.453(5)	2.534(7)	2.59(1)
N-N		1.333(1)	1.329(4)	1.322(5)	1.32(1)

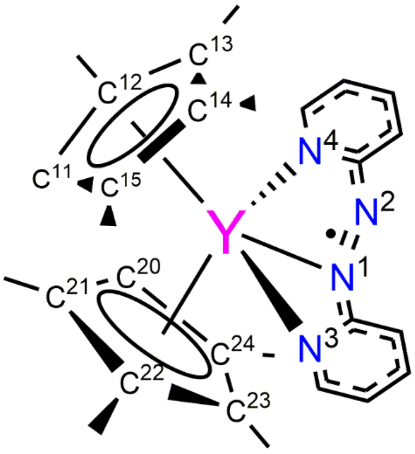

Figure S1. Structure of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, with corresponding atom labels.

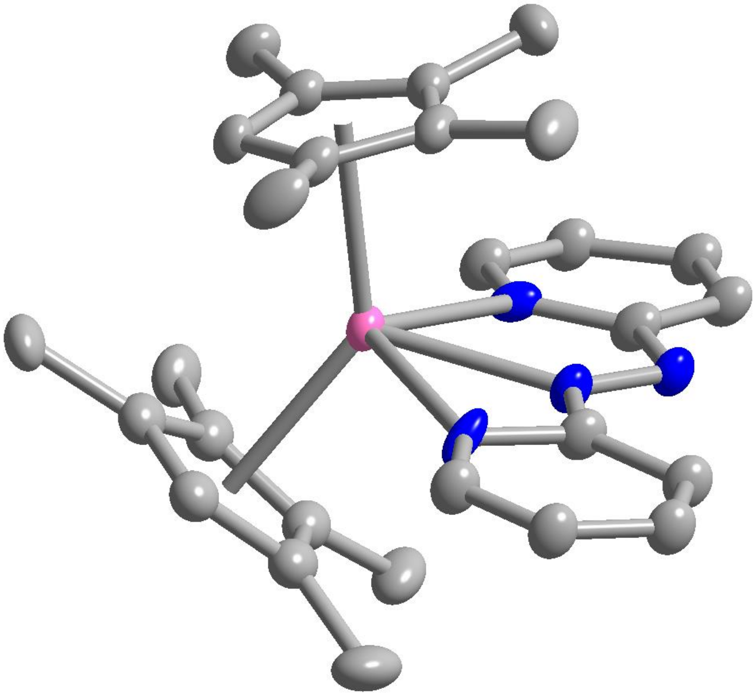

Figure S2. Structure of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms have been removed for clarity.

^{1}H-NMR Spectroscopy

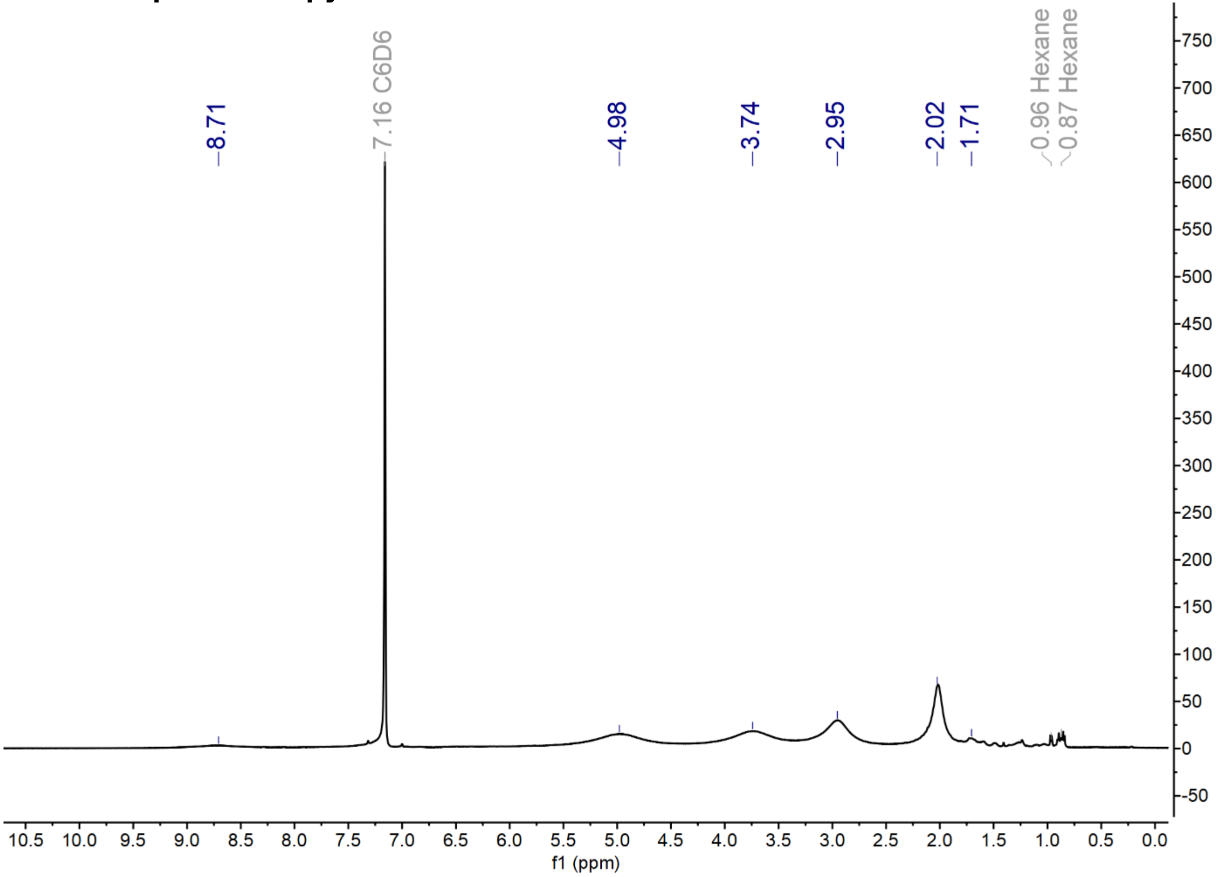

Figure S3. ^{1}H-NMR spectrum of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, at 25 °C in benzene-d_6.

UV-Vis-NIR Spectroscopy

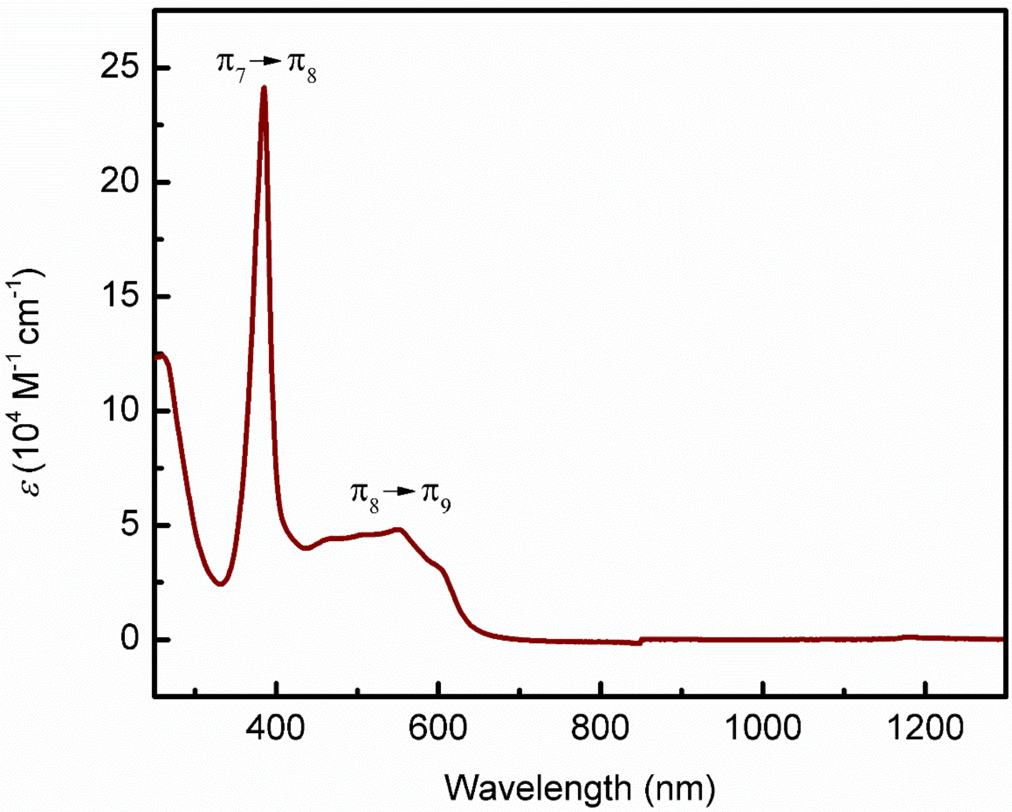

Figure S4. UV-Vis-NIR spectrum of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, in THF at a concentration of 17.2 μM. Molar absorptivities calculated for one concentration. Significant absorptions occur at λ = 260, 385, and 551 nm.

IR Spectroscopy

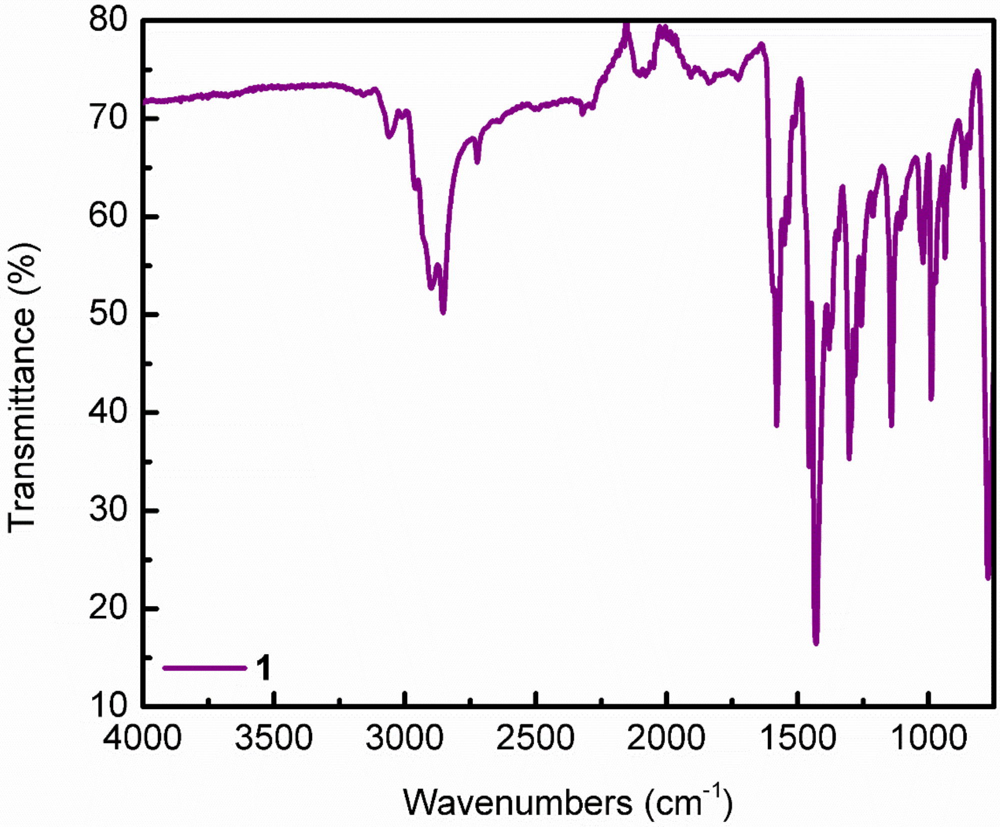

Figure S5. FTIR spectrum of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**.

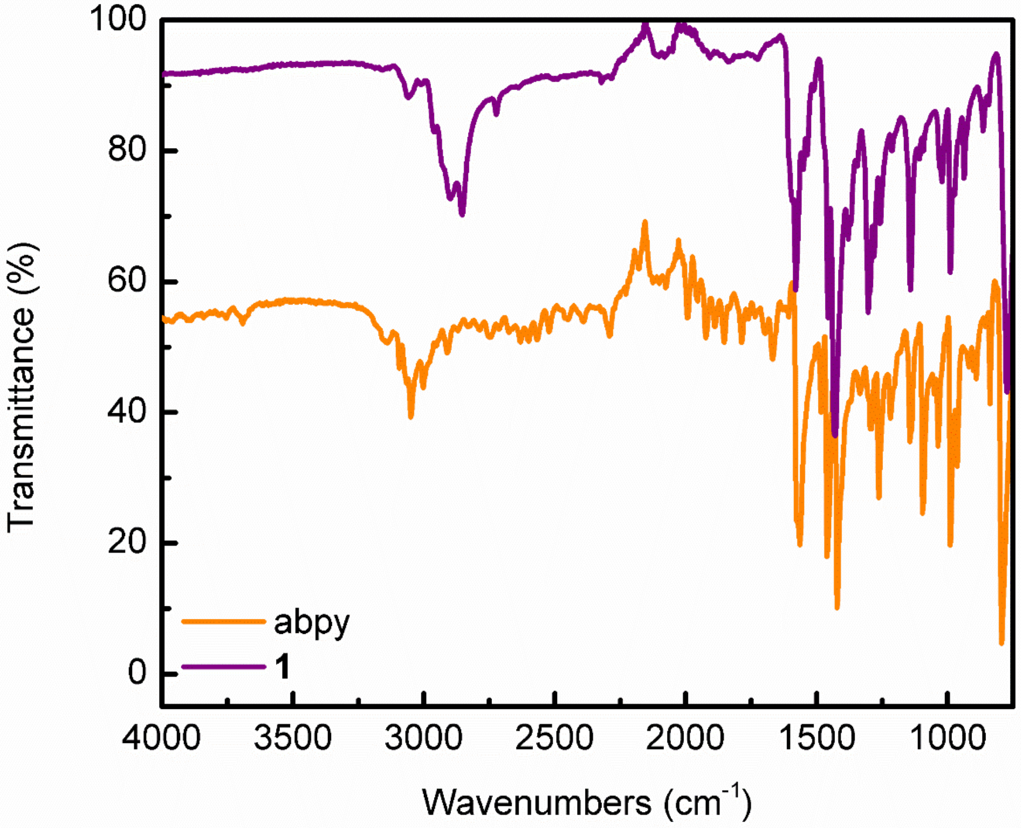

Figure S6. FTIR spectrum of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, (purple) in comparison to the free 2,2'-azobispyridine ligand, abpy, (orange).

Evans Method

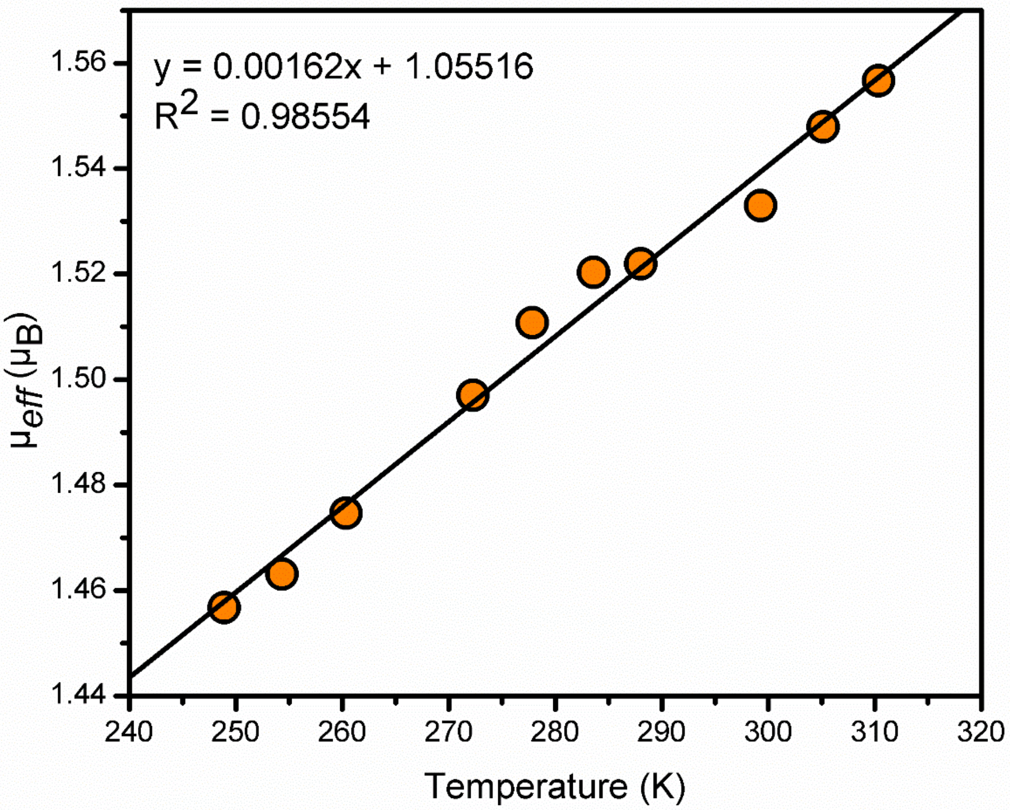

Figure S7. Temperature dependence of solution state effective magnetic moment (μ_{eff}) for $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**.

Comparison of Experimental and Computed IR Spectra

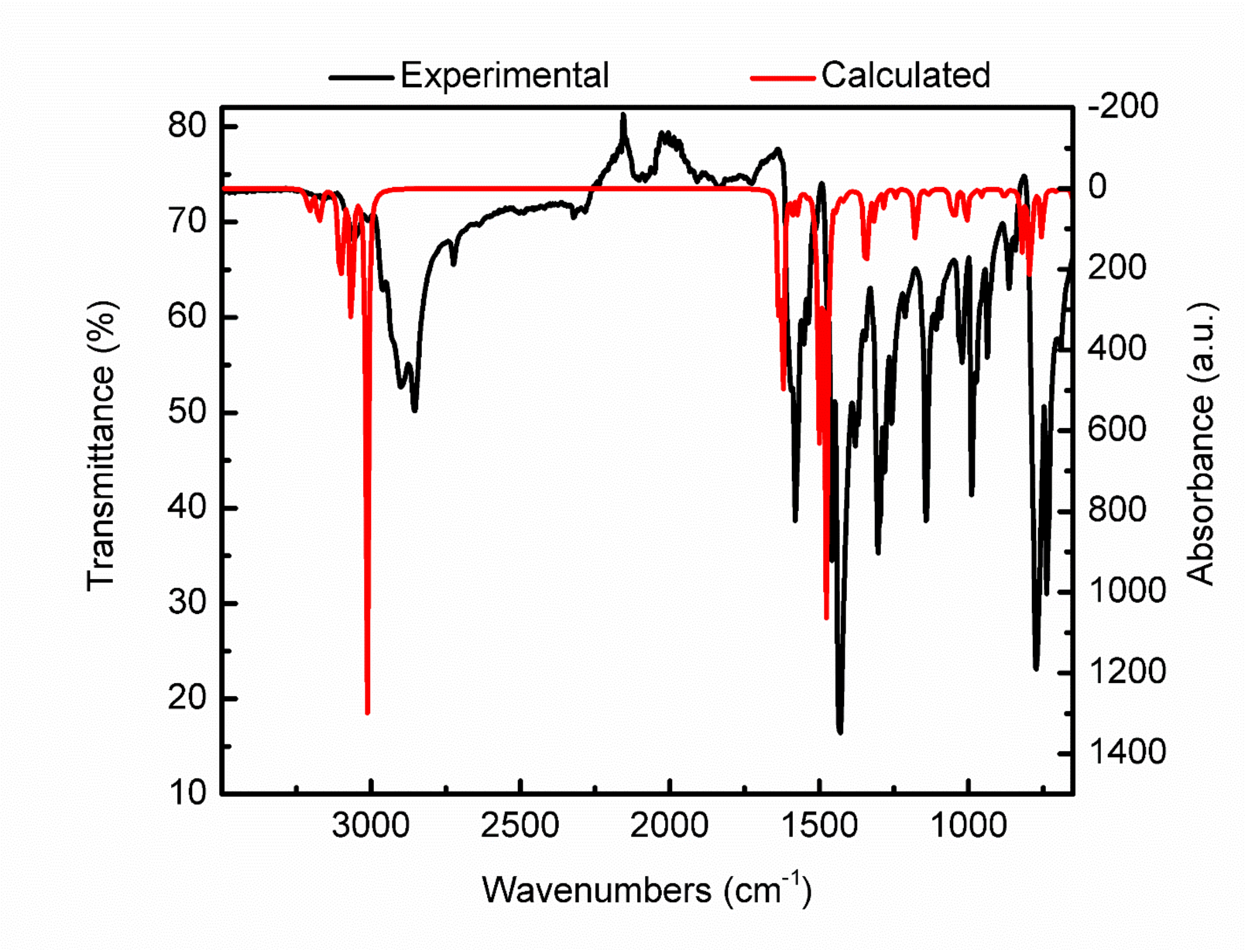

Figure S8. Comparison of experimental FTIR spectrum (black) and calculated stretching frequencies (red) of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**.

Table S3: Computed and average experimental bond metrics of the four parts (A–D) in (Cp^{Me4H})$_2$Y(abpy$^{\bullet}$), **1**, with six different unrestricted functionals using the def2-TZVP basis set for Y, including a 28 electron ECP, and the def2-SV(P) basis set for N, C, and H atoms.

Experimental (Å)		**Calculated**					
		B3LYP	**CAM**	**M06**	**PBE0**	**TPSSh**	**TPSS**
		Distances (Å)					
Y-C$^{*}_{avg}$	2.6646	2.6758	2.6596	2.6572	2.6550	2.6692	2.6634
Y-C$^{\ddagger}_{avg}$	2.6637	2.6766	2.6604	2.6546	2.6546	2.6682	2.6640
Y-N$_{N1}$	2.3071	2.3350	2.3260	2.3310	2.3270	2.3330	2.3290
Y-N$_{N2}$	3.4523	3.3490	3.3370	3.3410	3.3350	3.3520	3.3570
Y-N$_{N3}$	2.63	2.6180	2.6210	2.6200	2.6110	2.5900	2.5820
Y-N$_{N4}$	2.52	2.5250	2.5250	2.5190	2.5110	2.5050	2.5060
N-N	1.327	1.3130	1.3070	1.3060	1.3040	1.3150	1.3220
	MD	**-0.010**	-0.018	-0.019	-0.024	-0.019	-0.020
	MSE	**0.0017**	0.0020	0.0019	0.0022	0.0018	0.0017
	RMSE	**0.042**	0.045	0.044	0.047	0.043	0.042
	MAPE	**0.313%**	0.640%	0.687%	0.864%	0.637%	0.657%

C$^{*}_{avg}$ = Average Y-C (Cp^{Me4H}$_1$) distances.
C$^{\ddagger}_{avg}$ = Average Y-C (Cp^{Me4H}$_2$) distances.

Table S4: Computed and average experimental bond metrics of the four parts (A–D) in $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**, with the unrestricted hybrid B3LYP functional and def2-TZVP basis set on all atoms with a fully relativistic ECP for Y.

	Exp	B3LYP
Distances (Å)		
Y-C^{*}_{avg}	2.6646	2.6844
Y-$C^{‡}_{avg}$	2.6637	2.6836
Y-N_{N1}	2.3071	2.3430
Y-N_{N2}	3.4523	3.3590
Y-N_{N3}	2.63	2.6390
Y-N_{N4}	2.52	2.5300
N-N	1.327	1.3150
	MD	**-0.002**
	MSE	**0.0016**
	RMSE	**0.040**
	MAPE	**0.025%**

C^{*}_{avg} = Average Y-C ($Cp^{Me4H}{}_1$) distances.
$C^{‡}_{avg}$ = Average Y-C ($Cp^{Me4H}{}_2$) distances.

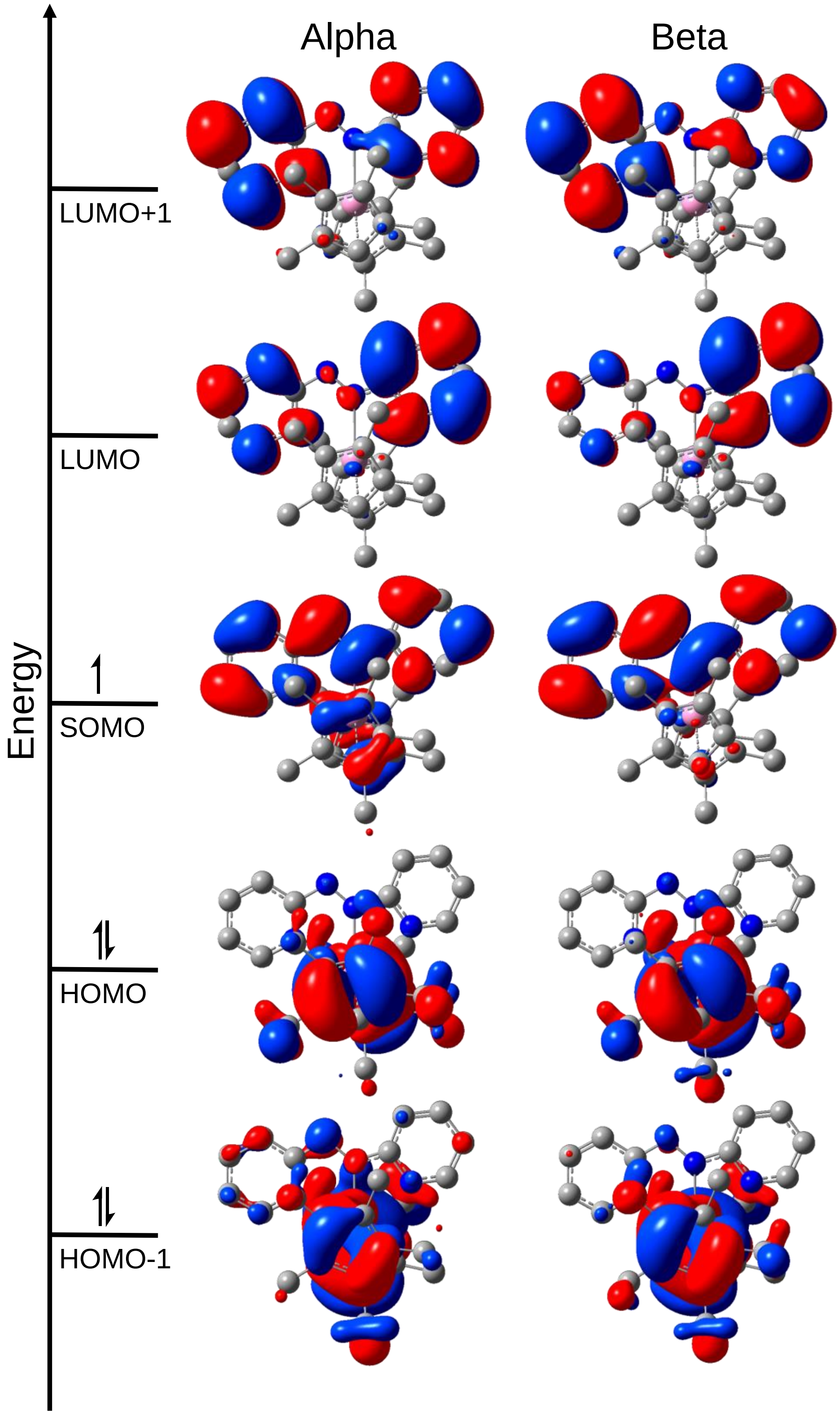

Figure S9. Calculated frontier orbitals of $(Cp^{Me4H})_2Y(abpy^{\bullet})$, **1**.

EPR Spectroscopy

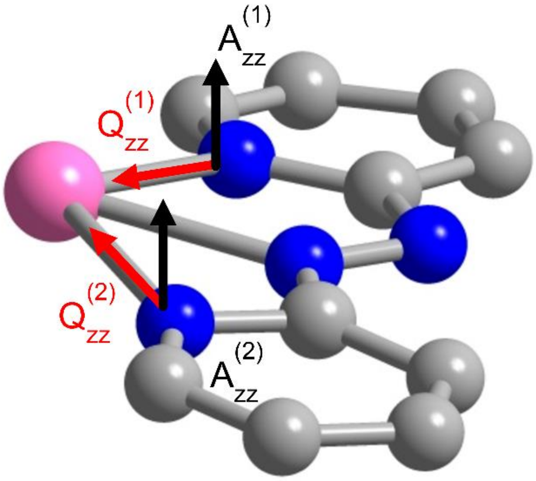

Figure S10. Fragment of the $(Cp^{Me4H})_2Y(abpy^{\bullet})$ molecule showing the relative orientations of hyperfine, $A_{zz}^{(\#)}$, and nuclear quadrupole, $Q_{zz}^{(\#)}$, principal axes for the pyridine nitrogen atoms considered in the HYSCORE simulation shown as red contours in Figure 6. The hyperfine couplings for both nitrogens were constrained to have axial symmetry with their principal axes being aligned with their respective p^{π} orbitals, and with each other. The principal axes of the nuclear quadrupole tensors were oriented along their respective N-Y bonds and separated in the N-Y-N plane by an angle of 60º.

Electrochemistry

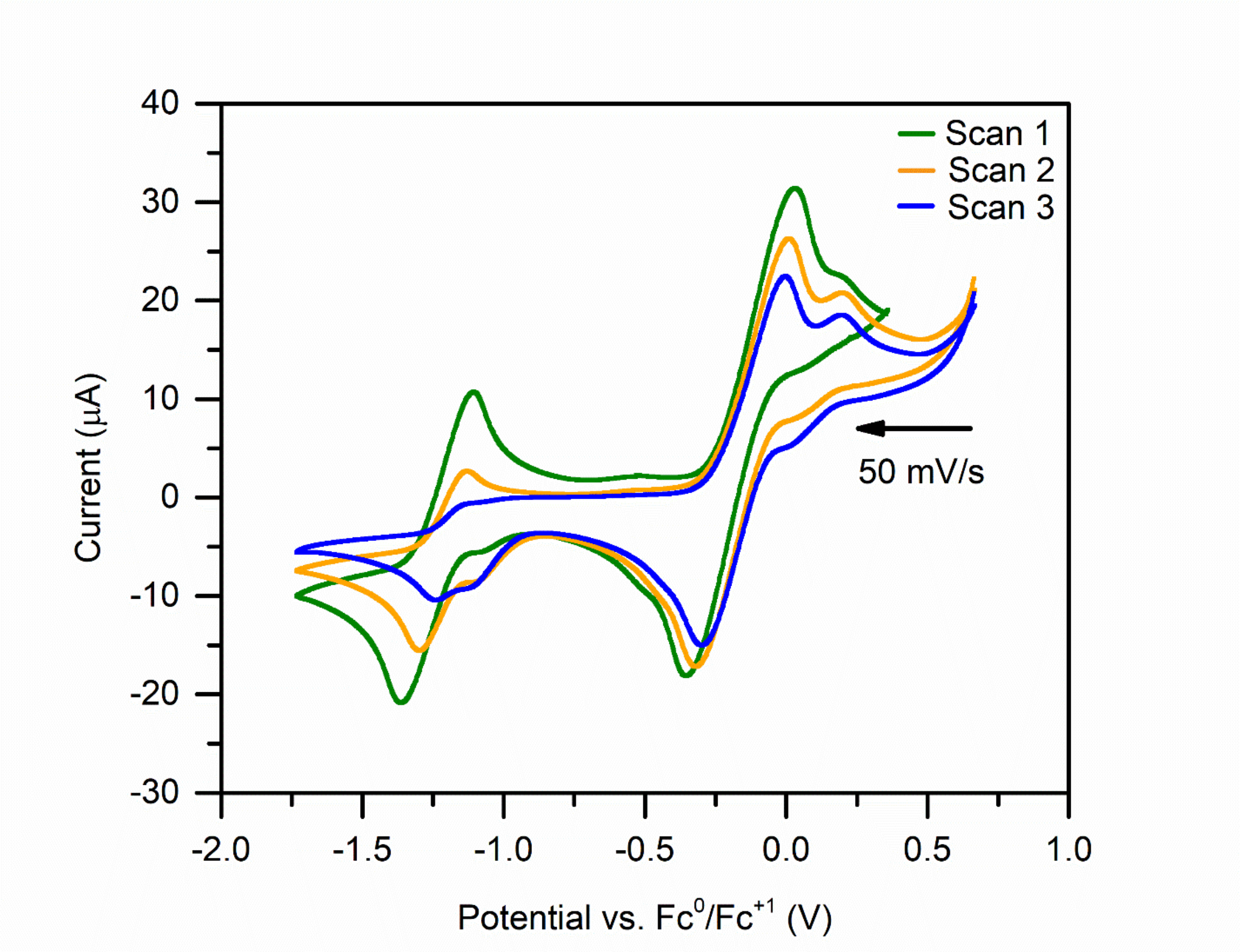

Figure S11. Cyclic voltammogram of (Cp^{Me4H})$_2$Y(abpy$^{\bullet}$), **1**, vs. Fc. 250 mM [N^{n}Bu$_4$][PF$_6$] in THF and 3 mM analyte over three scans. The appearance of a new redox feature during subsequent scans suggests an irreversible chemical change.