

# Large Polarization of Push-Pull “Cruciforms” via Coordination with Lanthanide Ions

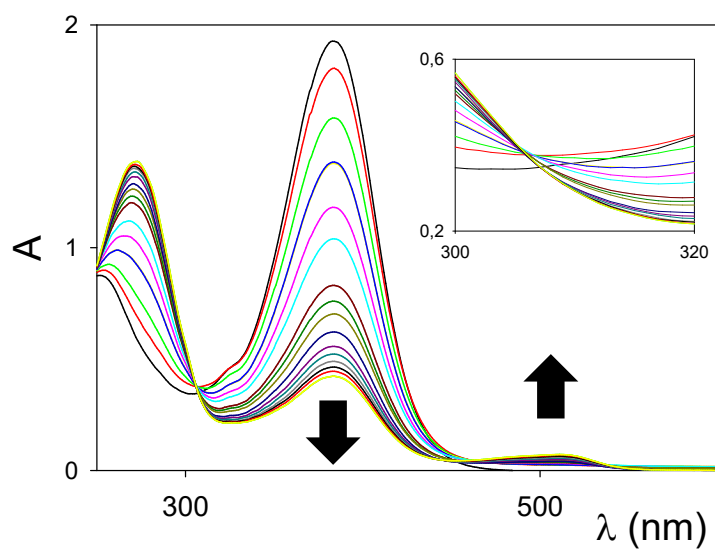
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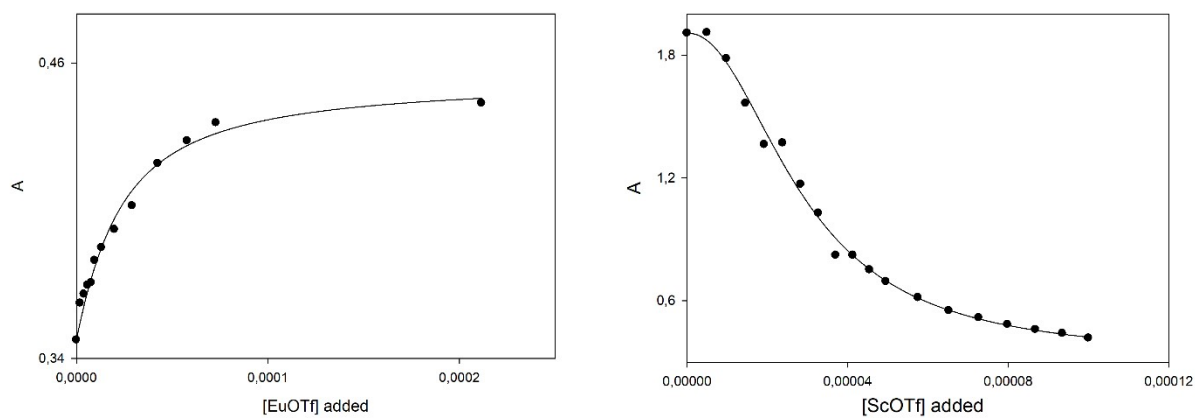
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Memorial Drive, Coral Gables, Florida 33146-0431 – USA

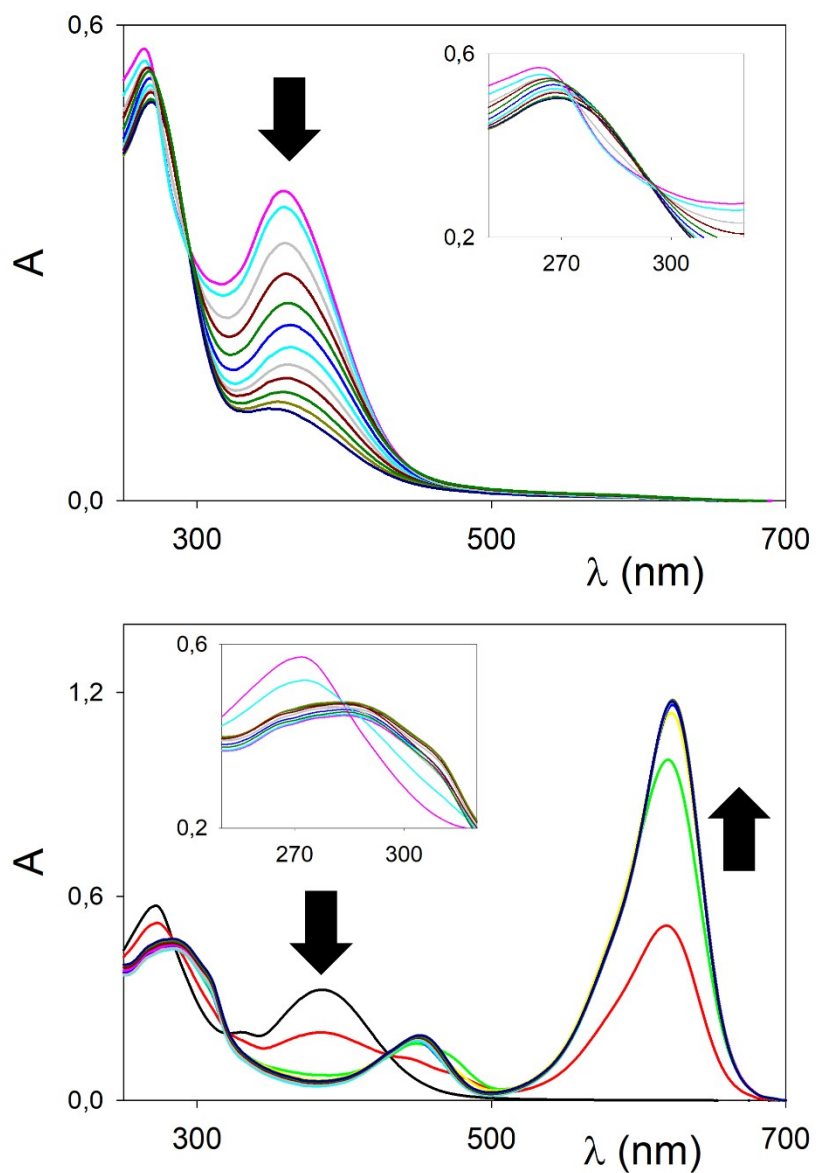
Email: [dario.pasini@unipv.it](mailto:dario.pasini@unipv.it)



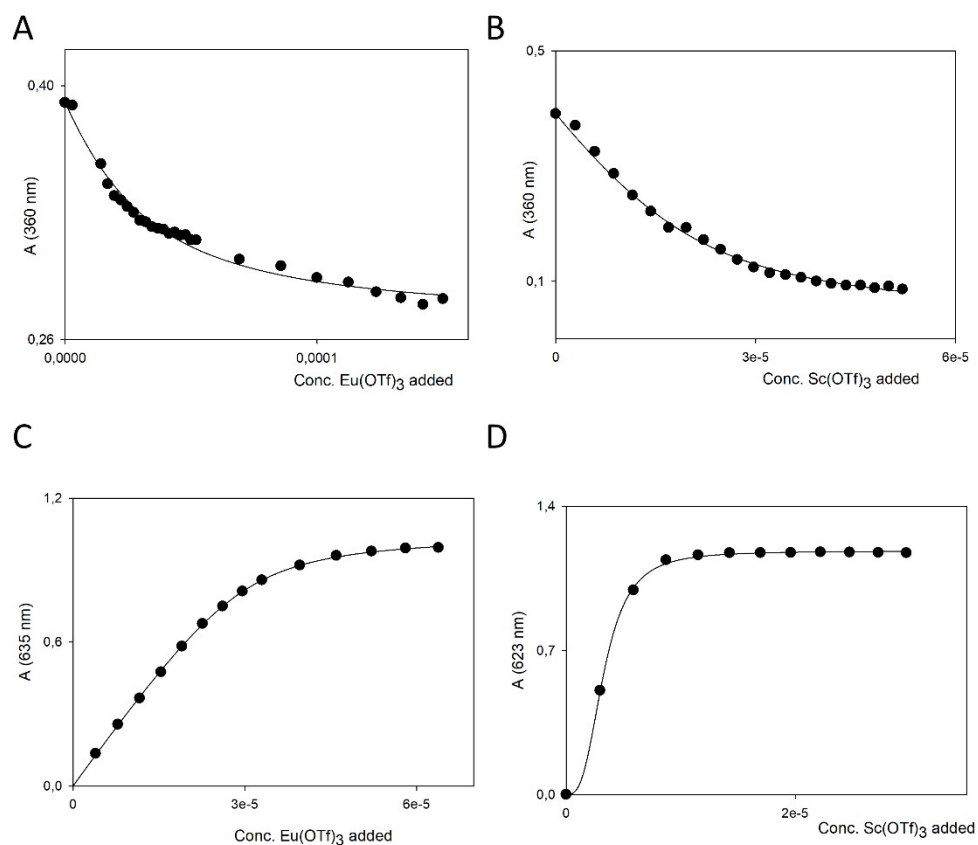
**Figure S1.** UV/VIS titration (MeCN, 298 K) of **1b** ( $10^{-5}$  M) with  $\text{Sc}(\text{OTf})_3$ .



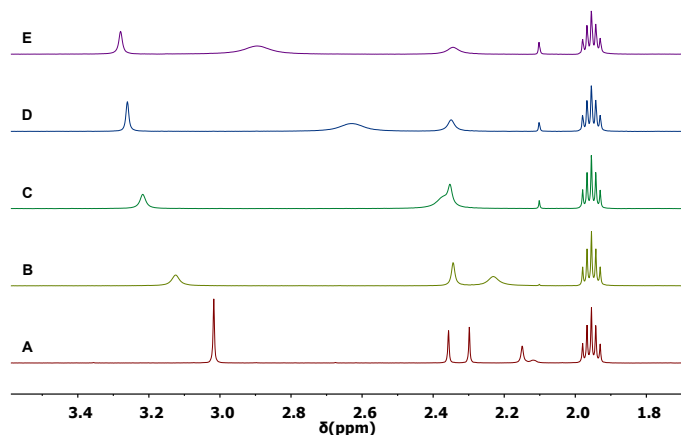
**Figure S2.** UV/VIS titration profiles and best fitting for titration of **1b** with  $\text{Eu}(\text{OTf})_3$  (left, fitting for a 1:1 binding) and  $\text{Sc}(\text{OTf})_3$  (right, fitting with the Hill equation).



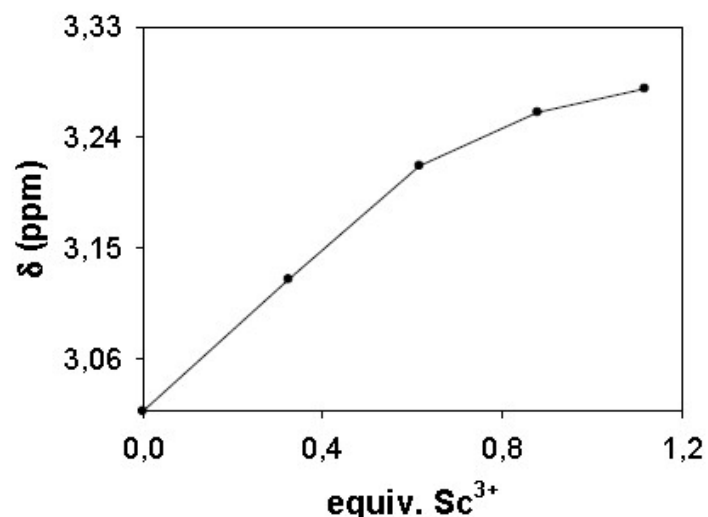
**Figure S3.** UV/VIS titration (MeCN, 298 K) of **2a** (top,  $10^{-5}$  M) and **2b** (bottom,  $10^{-5}$  M) with  $\text{Sc}(\text{OTf})_3$ .



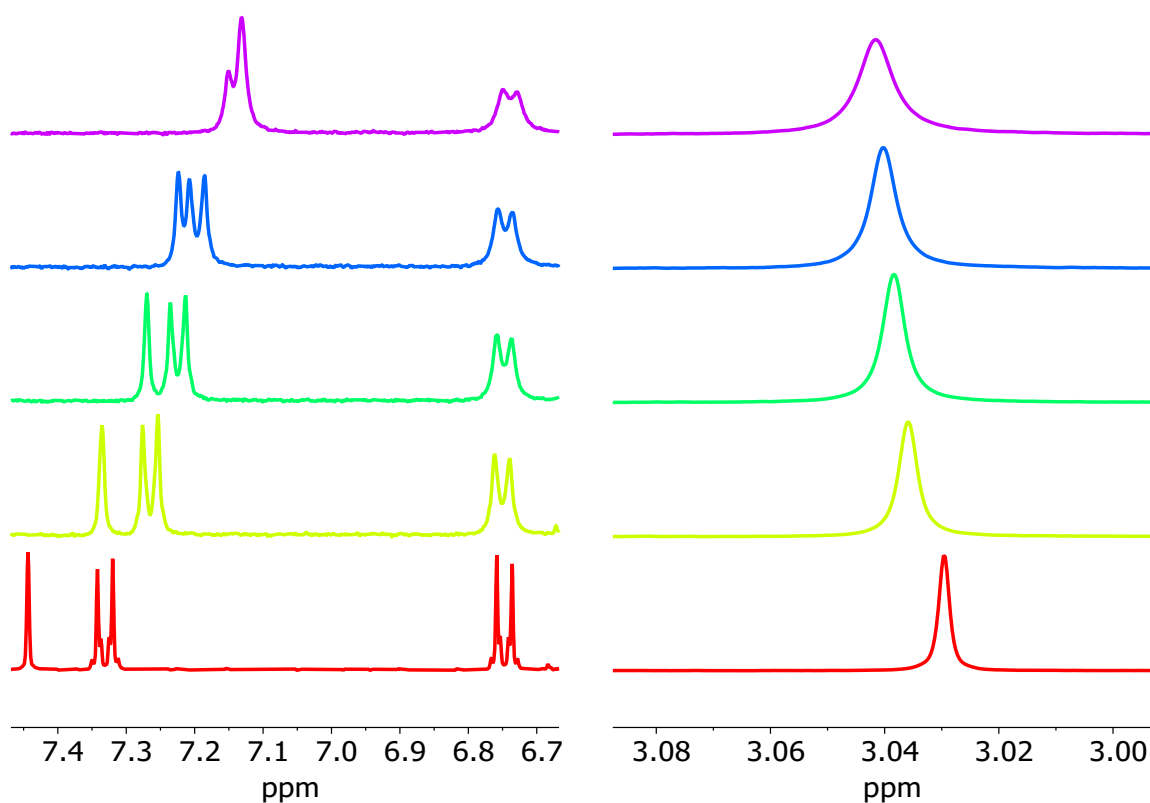
**Figure S4.** UV/VIS titration profiles and best fitting for titration of **2a** and **2b** with  $\text{Eu}(\text{OTf})_3$  (A and C) and  $\text{Sc}(\text{OTf})_3$  (B and D).



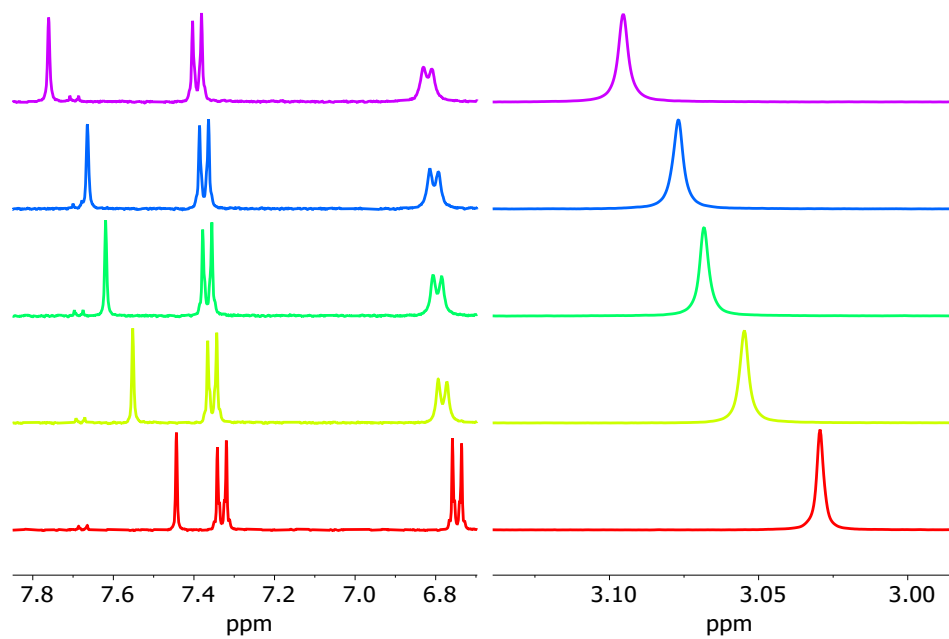
**Figure S5.** Partial  $^1\text{H}$  NMR spectra (300 MHz, 298 K) of: (A) ligand **1b** (0,005 M in  $\text{CD}_3\text{CN}$ ); (B) **1b** with 0,3 equivalents; (C) 0,6 equivalents; (D) 0,9 equivalents; (E) 1,1 equivalents of  $\text{Sc}(\text{OTf})_3$



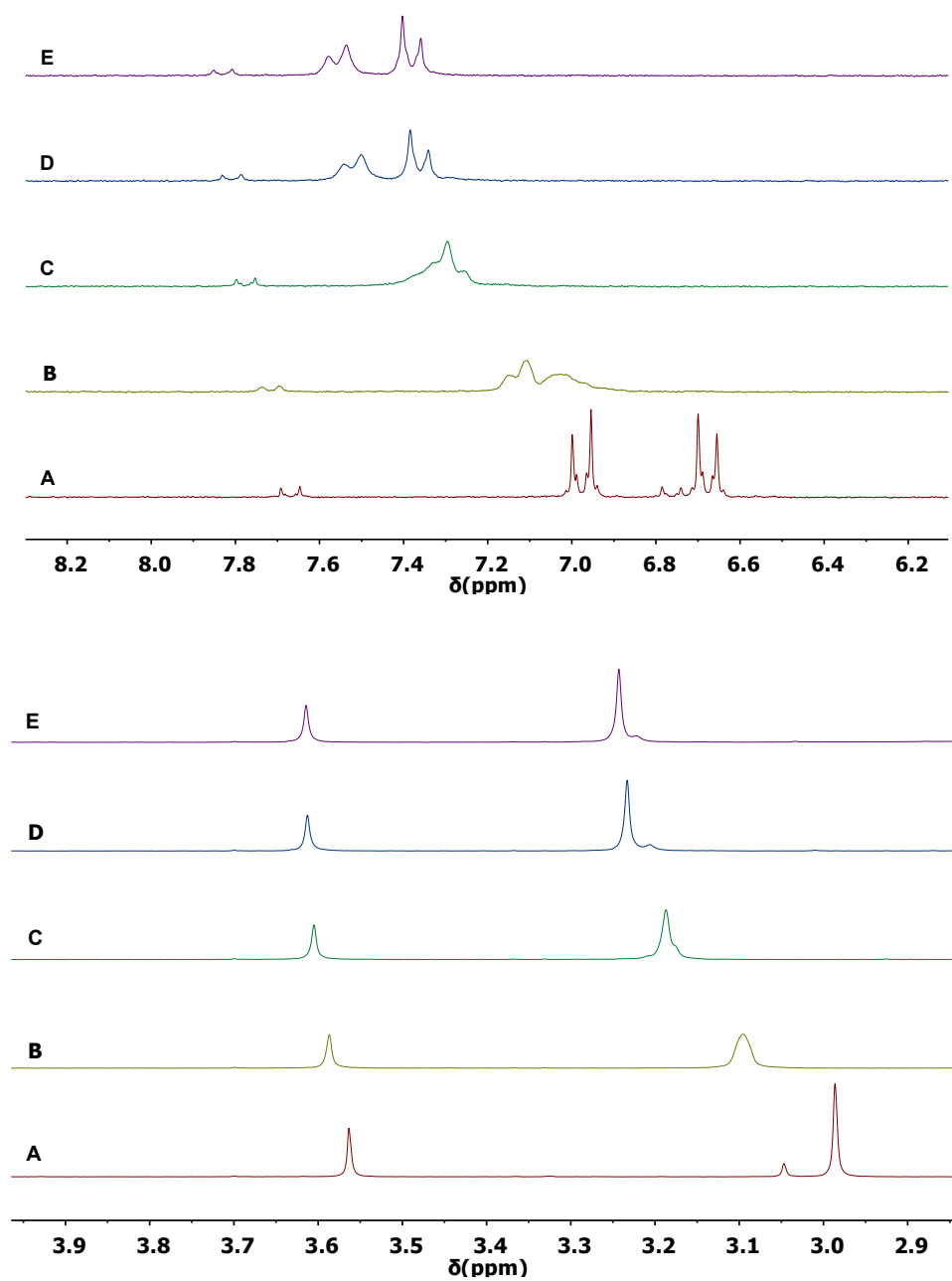
**Figure S6.** <sup>1</sup>H NMR titration profile for the proton resonances of the dimethylamino groups in the titration of chromophore **1b**.



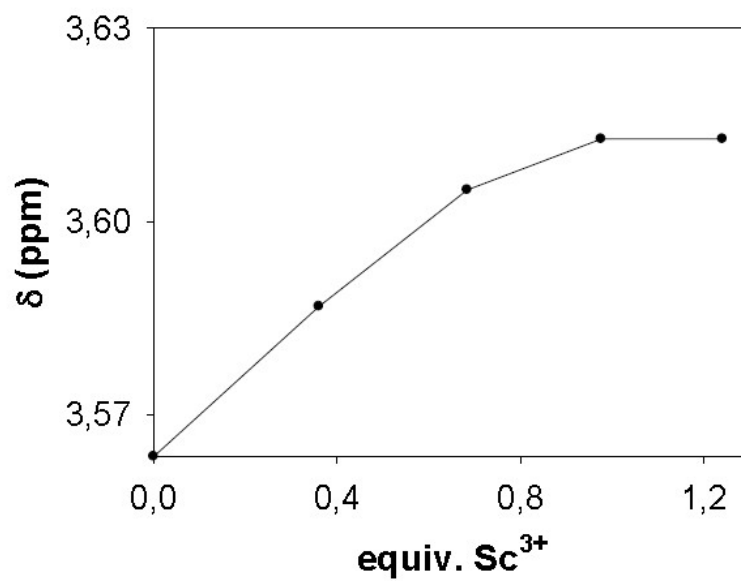
**Figure S7.** Partial <sup>1</sup>H NMR spectra (400 MHz, 298 K) of (from bottom to top): (red trace) ligand **1b** (0.0054 M in CD<sub>3</sub>CN); (yellow trace) **1b** with 0.14 equivalents of Eu(OTf)<sub>3</sub>; (green trace) 0.23 equivalents; (blue trace) 0.31 equivalents; (violet trace) 0.53 equivalents of Eu(OTf)<sub>3</sub>



**Figure S8.** Partial <sup>1</sup>H NMR spectra (400 MHz, 298 K) of (from bottom to top): (red trace) ligand **1b** (0.0054 M in CD<sub>3</sub>CN); (yellow trace) with 0.24 equivalents of Y(OTf)<sub>3</sub>; (green trace) 0.42 equivalents; (blue trace) 0.57 equivalents; (violet trace) 0.95 equivalents of Y(OTf)<sub>3</sub>

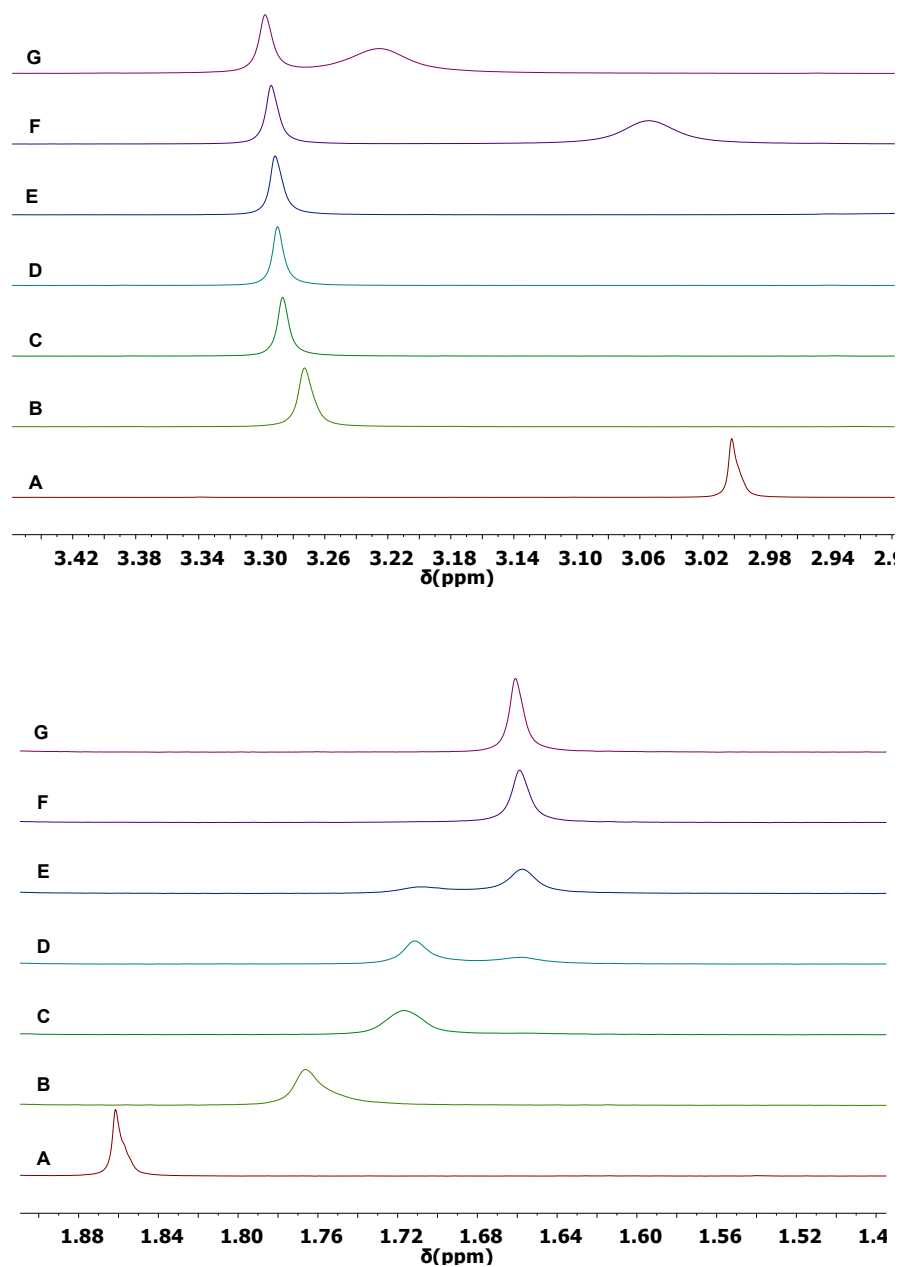


**Figure S9.** Partial  $^1\text{H}$  NMR spectra (300 MHz, 298 K) of: (A) ligand **2a** (0.005 M in  $\text{CD}_3\text{CN}$ ); (B) **2a** with 0.4 equivalents; (C) 0.7 equivalents; (D) 0.9 equivalents; (E) 1.2 equivalents of  $\text{Sc}(\text{OTf})_3$

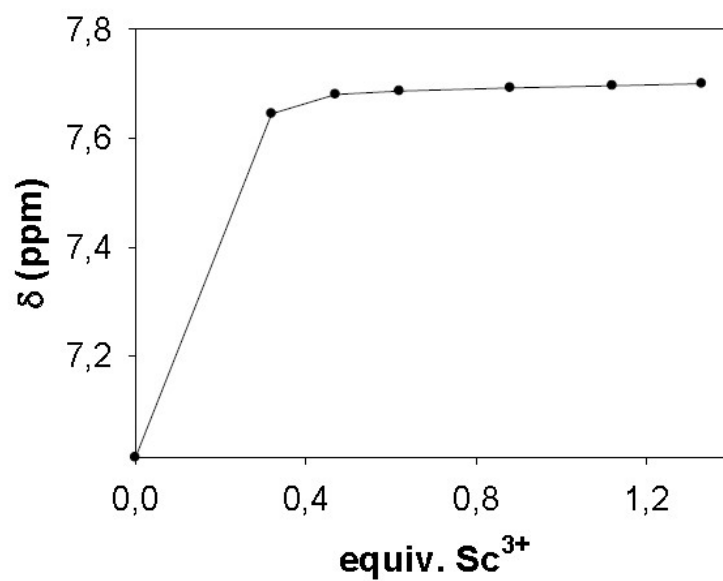


**Figure S10.**  $^1\text{H}$  NMR titration profile for the proton resonances of the dimethylamino groups in the titration of chromophore **2a**.

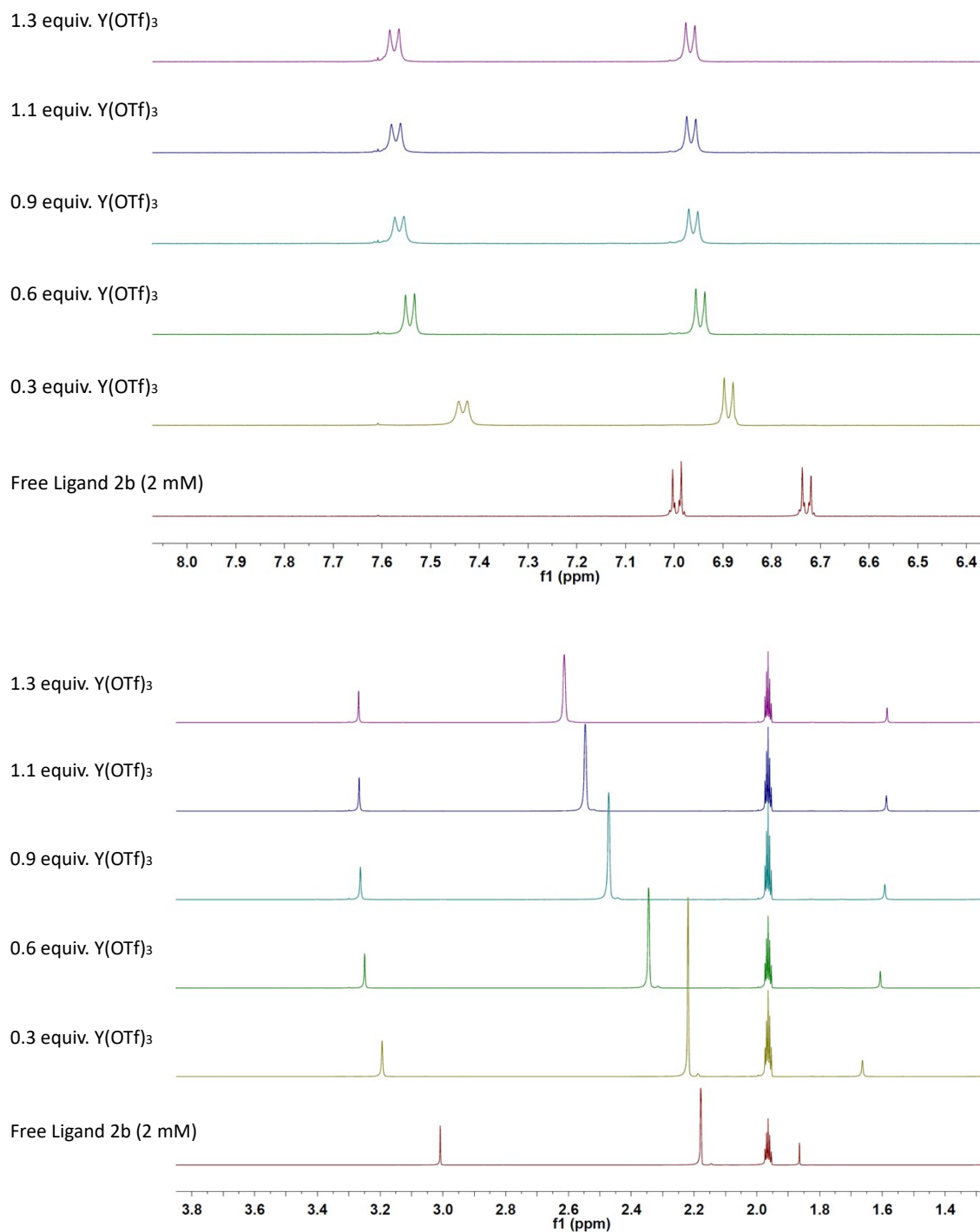




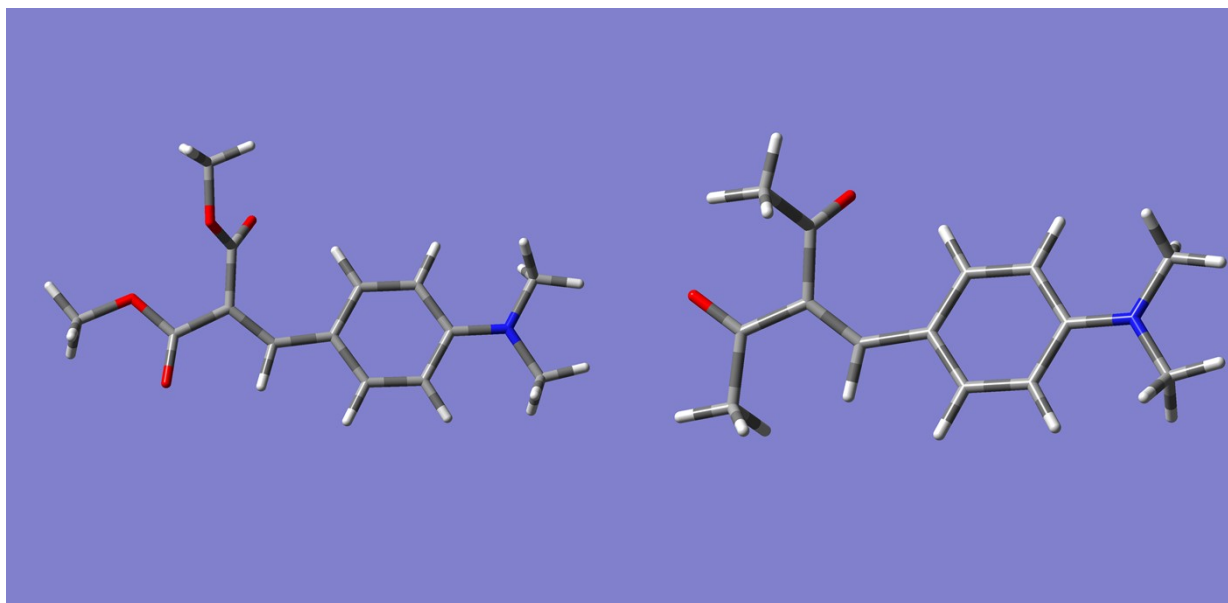
**Figure S11.** Partial  $^1\text{H}$  NMR spectra (300 MHz, 298 K) of (A) ligand **2b** (0.005 M in  $\text{CD}_3\text{CN}$ ); (B) **2b** with 0.3 equivalents; (C) 0.5 equivalents; (D) 0.6 equivalents; (E) 0.9 equivalents; (F) 1.1 equivalents; (G) 1.3 equivalents of  $\text{Sc}(\text{OTf})_3$



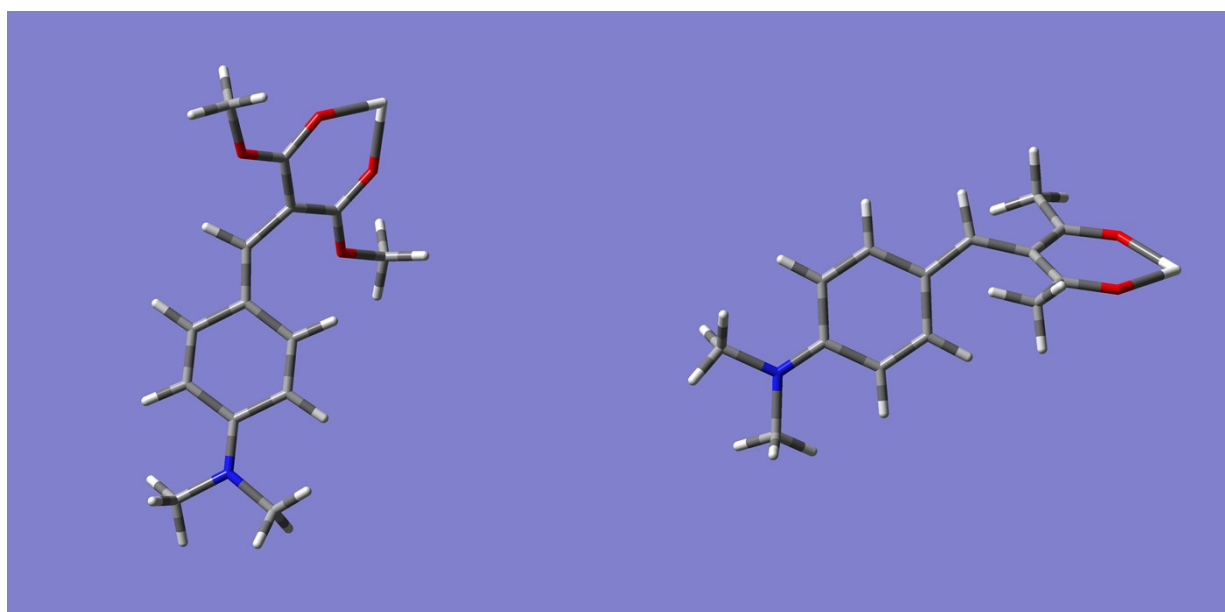
**Figure S12.**  $^1\text{H}$  NMR titration profile for the proton resonances of the aromatic  $\text{H}_\text{B}$  proton resonances in the titration of chromophore **2b**.



**Figure S13.** Partial  $^1\text{H}$  NMR spectra (500 MHz, 298 K) of (A) ligand **2b** (0.002 M in  $\text{CD}_3\text{CN}$ ); (B) **2b** with 0.3 equivalents; (C) 0.5 equivalents; (D) 0.6 equivalents; (E) 0.9 equivalents; (F) 1.1 equivalents; (G) 1.3 equivalents of  $\text{Sc}(\text{OTf})_3$



**Figure S14.** Minimized molecular structures for **1a** (left) and **1b** (right).



**Figure S15.** Minimized molecular structures for Minimized molecular structures for 1:1 complexes with scandium of ligands **1a** (left) and **1b** (right).

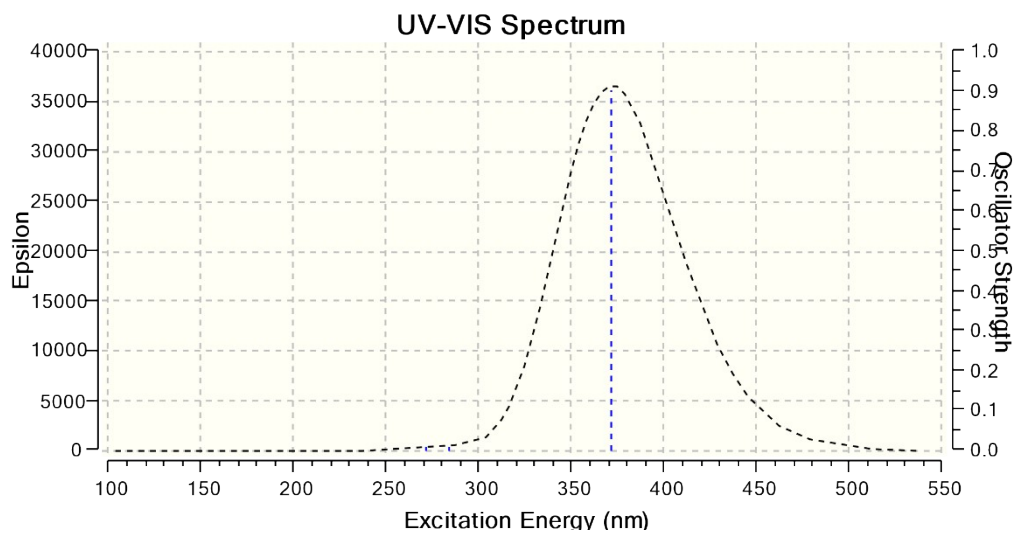


Figure S16. Calculated UV-Vis spectrum of 1a.

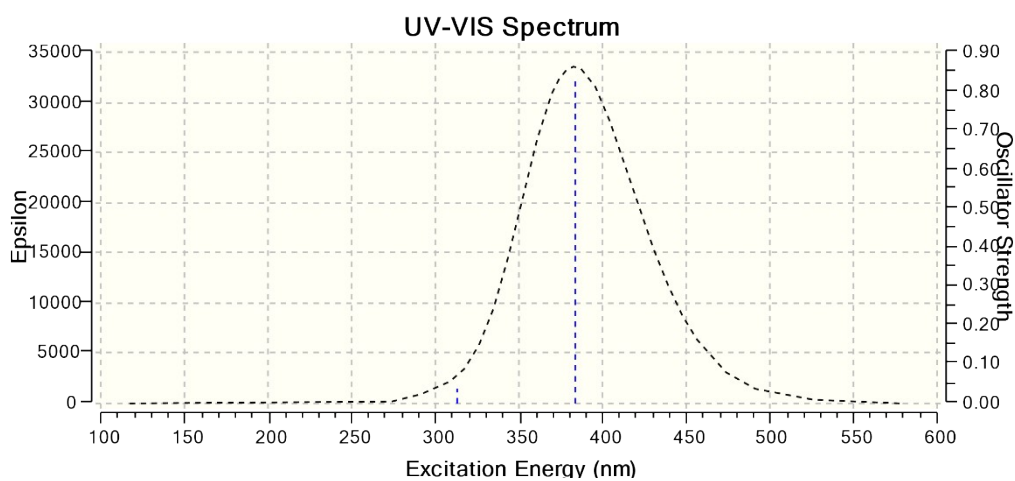


Figure S17. Calculated UV-Vis spectrum of 1b.

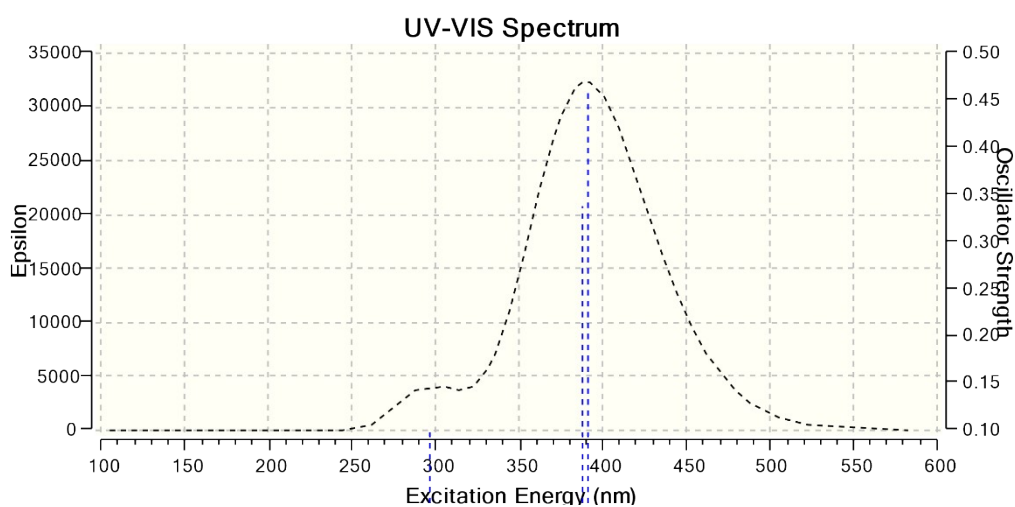
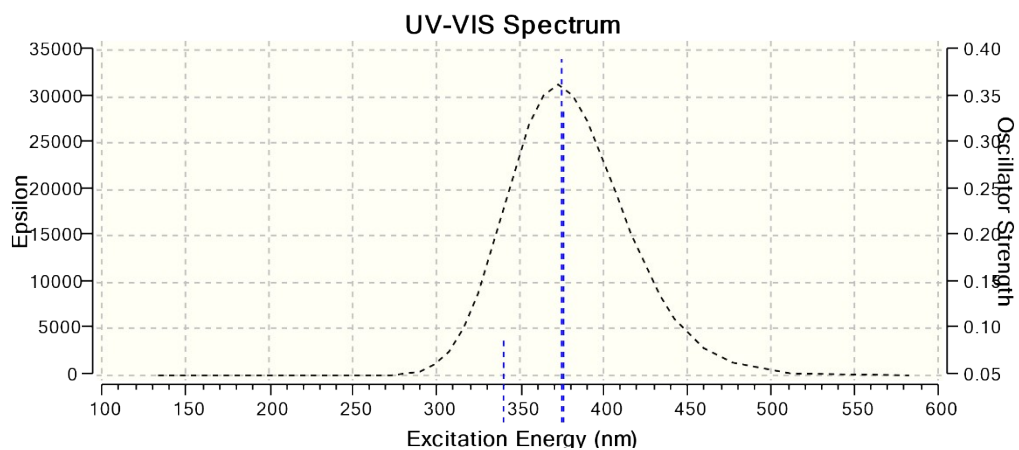
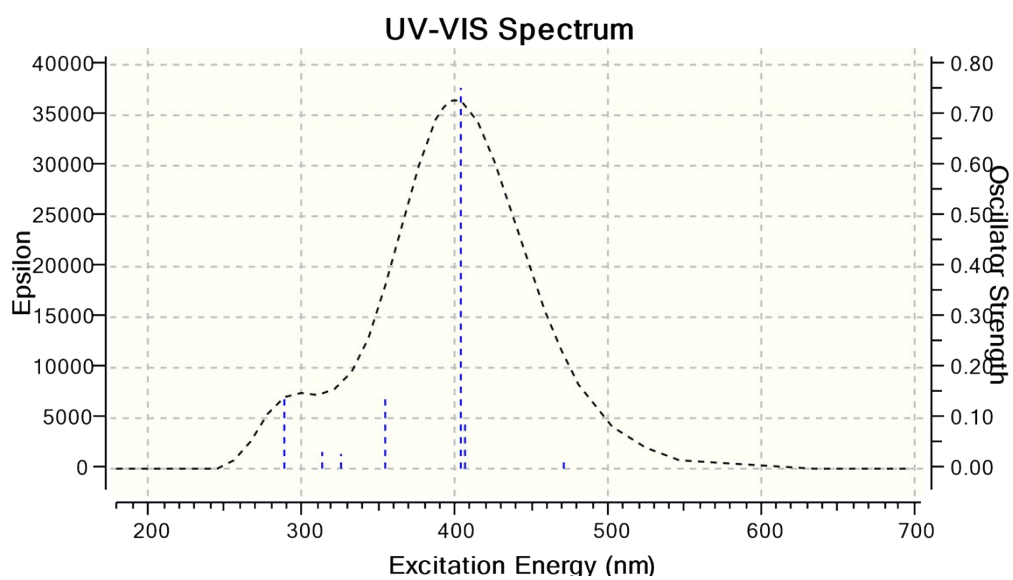


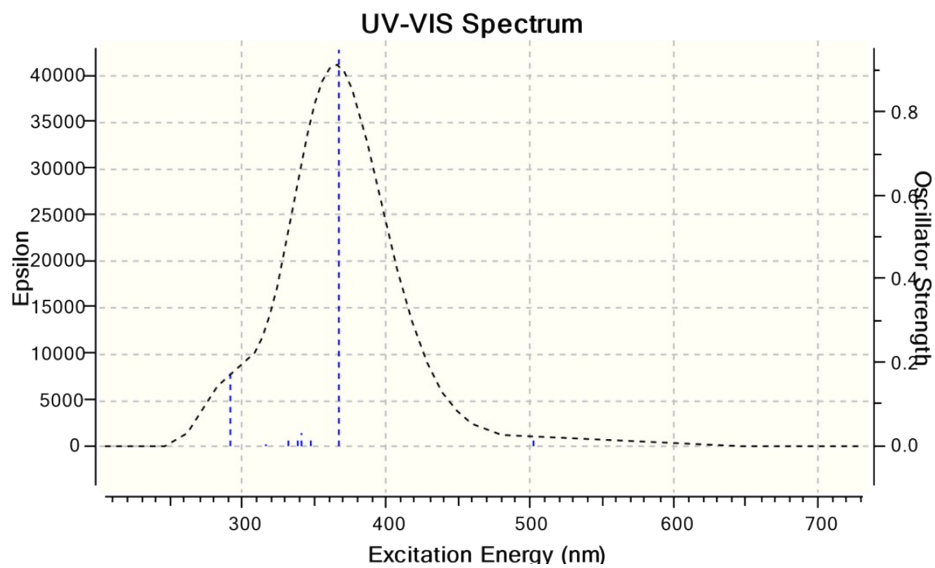
Figure S18. Calculated UV-Vis spectrum of 2a.



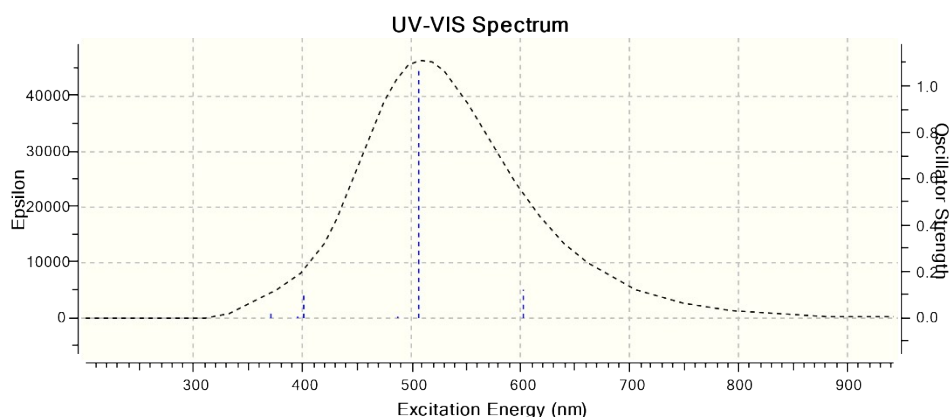
**Figure S19.** Calculated UV-Vis spectrum of **2b**.



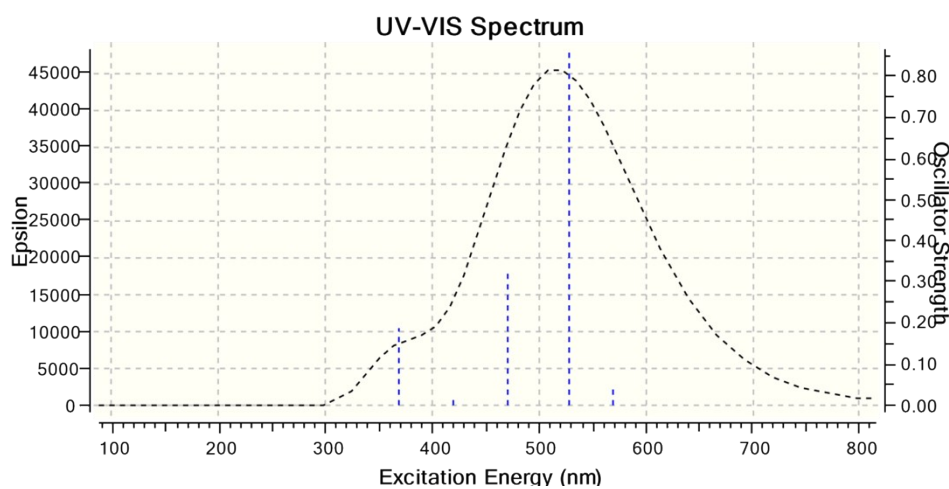
**Figure S20.** Calculated UV-Vis spectrum of complex of **1a** with scandium.



**Figure S21.** Calculated UV-Vis spectrum of complex of **1b** with scandium.



**Figure S22.** Calculated UV-Vis spectrum of complex of **2a** with scandium.



**Figure S23.** Calculated UV-Vis spectrum of complex of **2b** with scandium.

**Table S1.** UV-Vis transitions calculated for the scandium complexes in acetonitrile, considering only the two most intense.

Compound name	Band position (nm)	Oscillator strength (a.u.)	Type of transition
<b>1a</b>	404	0.7546	$\pi(\text{HOMO}) \rightarrow \pi^*$
<b>1a</b>	355	0.1425	$\pi(\text{HOMO}) \rightarrow \text{metal}$
<b>1b</b>	367	0.9514	$\pi(\text{HOMO}) \rightarrow \pi^*$
<b>1b</b>	293	0.1744	$\text{metal} \rightarrow \pi^*$
<b>2a</b>	507	1.0835	$\pi(\text{HOMO}) \rightarrow \text{metal}$
<b>2a</b>	602	0.1249	$\pi(\text{HOMO}) \rightarrow \pi^*$
<b>2b</b>	529	0.86149	$\pi(\text{HOMO}) \rightarrow \pi^*$
<b>2b</b>	471	0.3325	$\pi(\text{HOMO}) \rightarrow \text{metal}$

**Table S2.** Cartesian coordinates for the optimized complexes with Sc (III) (units are in Angstroms)

**1a**

C	-2.17664200	1.40103700	-0.97281900
C	-3.49997200	1.18211700	-0.78164100
C	-3.95889400	0.13021300	0.10748500
C	-2.93792200	-0.67823500	0.76300100
C	-1.61757400	-0.47310100	0.53178000
C	-1.14799100	0.58247900	-0.34681800
H	-1.86564400	2.21586300	-1.62021400
H	-4.21603600	1.83272800	-1.26623900
H	-3.23223300	-1.47683300	1.43101400
H	-0.89958500	-1.09917400	1.04768900
N	-5.25191800	-0.07440800	0.31537800
C	-5.78970400	-1.01206500	1.32243800
H	-6.68351400	-0.55903800	1.75677300
H	-6.07273200	-1.95194400	0.83566400
H	-5.07725400	-1.19744800	2.12238000
C	-6.30277400	0.63859300	-0.44756600
H	-6.50749300	1.60965200	0.01686400
H	-6.00991800	0.76900000	-1.48866800
H	-7.21030900	0.03517100	-0.41595600



C	0.16106500	0.92641400	-0.58873400
H	0.30427800	1.85163100	-1.14216000
C	1.43332500	0.30294100	-0.20370800
C	1.69981700	-1.08597100	-0.29832500
O	2.91962700	-1.58763300	-0.05343500
C	2.51301200	1.19227200	0.08747900
O	0.77268300	-1.90571100	-0.65655200
O	2.28529800	2.45507000	0.11675500
C	1.02134500	-3.34377600	-0.88333700
H	0.05478400	-3.72999300	-1.19748600
H	1.76132100	-3.45662600	-1.67641500
H	1.34676800	-3.80428900	0.05010700
C	3.33182300	3.46963700	0.37767700
H	3.74992900	3.29652700	1.36962300
H	4.08649600	3.40893300	-0.40707900
H	2.79380000	4.41358400	0.33585100
O	3.75531400	0.76444000	0.33511400
Sc	4.58113900	-0.89721600	0.38590800

### 1b

C	-2.02899700	1.40496000	0.97710400
C	-3.33393900	1.08443500	0.74244400
C	-3.69011700	-0.04969600	-0.11282300
C	-2.58452400	-0.82548100	-0.69315600
C	-1.28159200	-0.51051600	-0.43225900
C	-0.91630000	0.62610400	0.41766600
H	-1.79863800	2.26472400	1.60188600
H	-4.11316900	1.70061300	1.17404800
H	-2.80141800	-1.67534300	-1.32863300
H	-0.49981500	-1.10689100	-0.89549200
N	-4.96995600	-0.35383400	-0.35411700
C	-5.41899000	-1.41117600	-1.30837100
H	-6.30468800	-1.04185900	-1.83280900
H	-4.65834200	-1.64611100	-2.05083100
H	-5.69573900	-2.31470900	-0.75116800
C	-6.10269300	0.35783700	0.32159400
H	-5.89361800	0.51287000	1.38197500
H	-6.29186000	1.31887000	-0.17226200
H	-6.99785600	-0.25980600	0.23581000
C	0.37220500	1.03672600	0.69256800
H	0.48010700	1.95878900	1.26506300
C	1.67327800	0.42111900	0.30223100
C	2.04833200	-0.89340900	0.71449900
O	3.29794200	-1.35296200	0.37840900
C	2.62018200	1.27687000	-0.36437600
O	3.87020800	0.80802800	-0.63188000
C	1.25680900	-1.84480300	1.53600500
H	0.31677800	-1.42228100	1.88709500
H	1.05675100	-2.76679700	0.96666100
H	1.85701700	-2.16652200	2.40123100
C	2.36235900	2.67692000	-0.78407400
H	1.31786800	2.83282700	-1.07180000
H	2.56816800	3.36346900	0.05944200

H	3.03322300	2.97434600	-1.59606000
Sc	4.85779300	-0.75186800	-0.42009000

**2a**

C	1.44307700	-2.03006700	0.47280900
C	2.65103700	-2.69016700	0.40788600
C	3.80684200	-2.07716600	-0.21373300
C	3.64793100	-0.72275800	-0.70719000
C	2.43711600	-0.07019400	-0.61232200
C	1.26289100	-0.69764800	-0.05756700
H	0.62484300	-2.50162500	1.00719700
H	2.74123300	-3.66453100	0.87319800
H	4.47784800	-0.22584300	-1.19546400
H	2.35719300	0.92740900	-1.03643200
N	4.98790800	-2.73499900	-0.31641900
C	6.21818700	-2.07060400	-0.82189200
H	7.08689900	-2.65585400	-0.51682200
H	6.20667300	-2.01337500	-1.91825100
H	6.32441900	-1.06683400	-0.40180300
C	5.12325400	-4.16718300	0.06252000
H	5.23865000	-4.27343700	1.14921800
H	4.25883000	-4.74527800	-0.27378200
H	6.01134500	-4.57793700	-0.42036000
C	0.00001100	-0.02143300	0.00008300
C	0.00001000	1.48595400	0.00003000
C	0.57465100	2.20651100	1.08460100
O	0.61419500	3.56206900	1.11078800
C	-0.57464100	2.20642700	-1.08459400
O	-0.61422500	3.56198200	-1.11087800
C	-1.26286700	-0.69764900	0.05770200
C	-2.43712600	-0.07018000	0.61237200
C	-1.44302600	-2.03008000	-0.47265600
C	-3.64794600	-0.72273900	0.70718800
H	-2.35722900	0.92743700	1.03645400
C	-2.65098900	-2.69017800	-0.40778400
H	-0.62476500	-2.50164500	-1.00699700
C	-3.80683000	-2.07716000	0.21375400
H	-4.47789100	-0.22581100	1.19540000
H	-2.74116500	-3.66454900	-0.87308700
N	-4.98790400	-2.73498700	0.31638100
C	-5.12323600	-4.16718800	-0.06250100
H	-4.25879600	-4.74525600	0.27380100
H	-6.01130900	-4.57793600	0.42042000
H	-5.23866100	-4.27348400	-1.14919200
C	-6.21822900	-2.07057800	0.82172300
H	-6.20685900	-2.01340800	1.91808700
H	-6.32437300	-1.06678300	0.40167300
H	-7.08691700	-2.65578500	0.51650400
O	-1.07095500	1.54631400	-2.11275800
O	1.07097200	1.54648600	2.11281700
C	1.67650700	2.22319400	3.31365800
H	1.98098800	1.39307700	3.94819300
H	2.53365200	2.82032900	2.99456200

H	0.91374700	2.83606800	3.79945500
C	-1.67654500	2.22291900	-3.31362600
H	-1.98111500	1.39274700	-3.94804800
H	-2.53363400	2.82014000	-2.99454100
H	-0.91378500	2.83569500	-3.79954700
Sc	-0.00001000	4.97235100	-0.00010000

**2b**

C	1.44156600	-1.87024500	0.50924300
C	2.66038600	-2.51010900	0.50203700
C	3.84358500	-1.87019900	-0.04411700
C	3.68984200	-0.51066100	-0.52775800
C	2.46666800	0.12206800	-0.49356200
C	1.26949100	-0.52819500	-0.00807000
H	0.60382800	-2.36551000	0.98938800
H	2.73940600	-3.48970100	0.95856300
H	4.53708700	0.00585000	-0.96282900
H	2.39708200	1.12340100	-0.90900800
N	5.03570800	-2.50784800	-0.08639600
C	6.28912500	-1.81844500	-0.49676900
H	7.14139700	-2.37966300	-0.10996600
H	6.36772000	-1.77839400	-1.59104100
H	6.33647400	-0.80760000	-0.08471000
C	5.18006800	-3.94697000	0.26739500
H	5.30135600	-4.06831200	1.35175300
H	4.32076600	-4.52645000	-0.07674500
H	6.07054100	-4.34108400	-0.22593400
C	-0.00001900	0.13745700	0.00001000
C	0.00008600	1.64746100	0.00002500
C	0.47369900	2.33752600	1.15494900
O	0.45435300	3.70718300	1.15867200
C	-0.47343600	2.33762700	-1.15491800
O	-0.45364900	3.70719700	-1.15872600
C	0.96969200	1.73977600	2.43227900
H	0.49982600	2.24729900	3.28454800
H	0.78453300	0.66710000	2.49285900
H	2.05243600	1.90837800	2.53439800
C	-0.96992000	1.73985900	-2.43205700
H	-0.50093300	2.24781200	-3.28453200
H	-0.78421400	0.66728500	-2.49293400
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C	-1.26960700	-0.52804900	0.00806300
C	-2.46669300	0.12233900	0.49359900
C	-1.44184800	-1.87005400	-0.50930600
C	-3.68994600	-0.51024200	0.52778500
H	-2.39697200	1.12364200	0.90909700
C	-2.66074500	-2.50977300	-0.50210900
H	-0.60417100	-2.36540400	-0.98947000
C	-3.84385800	-1.86974400	0.04408600
H	-4.53711500	0.00634900	0.96290400
H	-2.73988900	-3.48934500	-0.95865900
N	-5.03603800	-2.50728900	0.08638300
C	-5.18051100	-3.94638600	-0.26745400

H	-4.32124200	-4.52593700	0.07665300
H	-6.07100500	-4.34045400	0.22587400
H	-5.30182100	-4.06768200	-1.35181400
C	-6.28939600	-1.81781700	0.49682500
H	-6.36795800	-1.77781900	1.59110200
H	-6.33669100	-0.80694900	0.08482000
H	-7.14171700	-2.37895500	0.11001600
Sc	0.00054400	5.09199700	-0.00007100