Supporting Information for:

From Red to Blue Shift: Switching the Binding Affinity from Acceptor to the Donor End by Increasing the π-Bridge in Push-Pull Chromophores with Coordinative Ends

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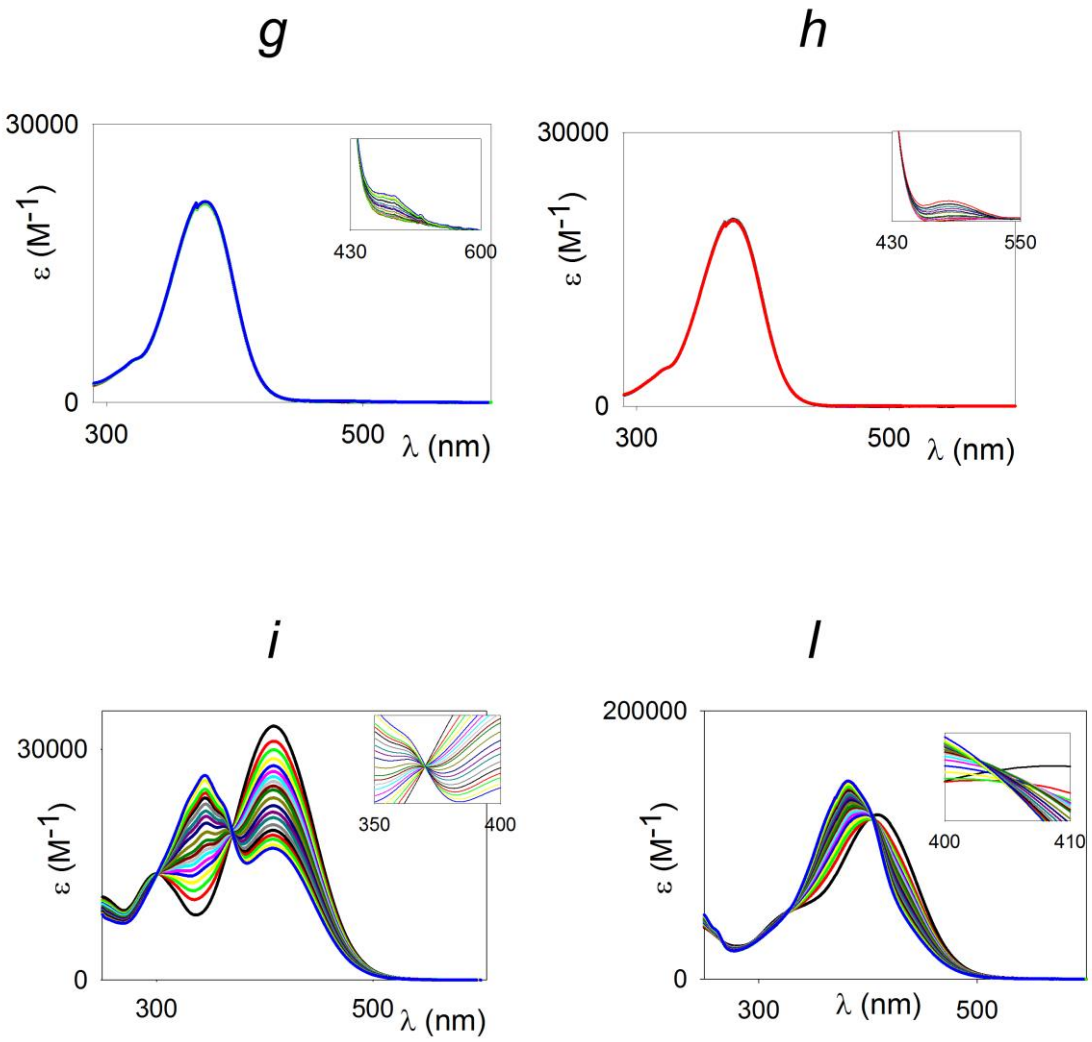


Figure S1. UV/Vis titration experiments with $Er(OTf)_3$ in MeCN for ligands **1** (left, ***g*** and (***h***, with Yb^{3+}), **2** (titration ***i***), and **3** (titration ***l***).

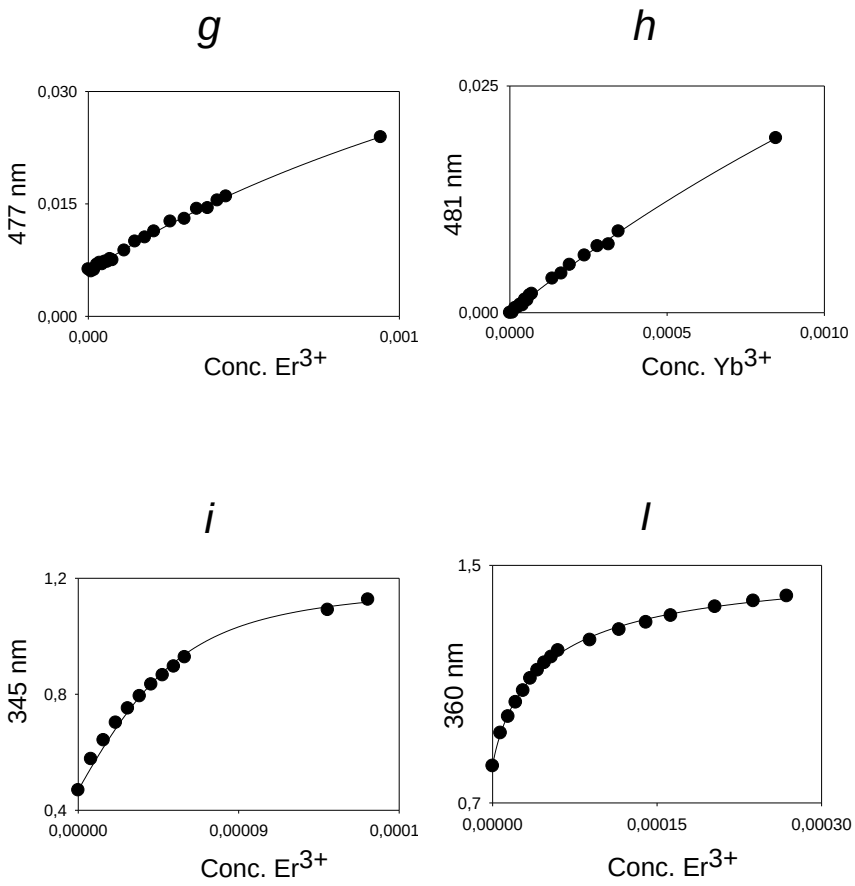


Figure S2. Titration profiles (ascending, wavelenghts indicated on the y axes) and best fit curves corresponding to the titrations shown in Figure S4.

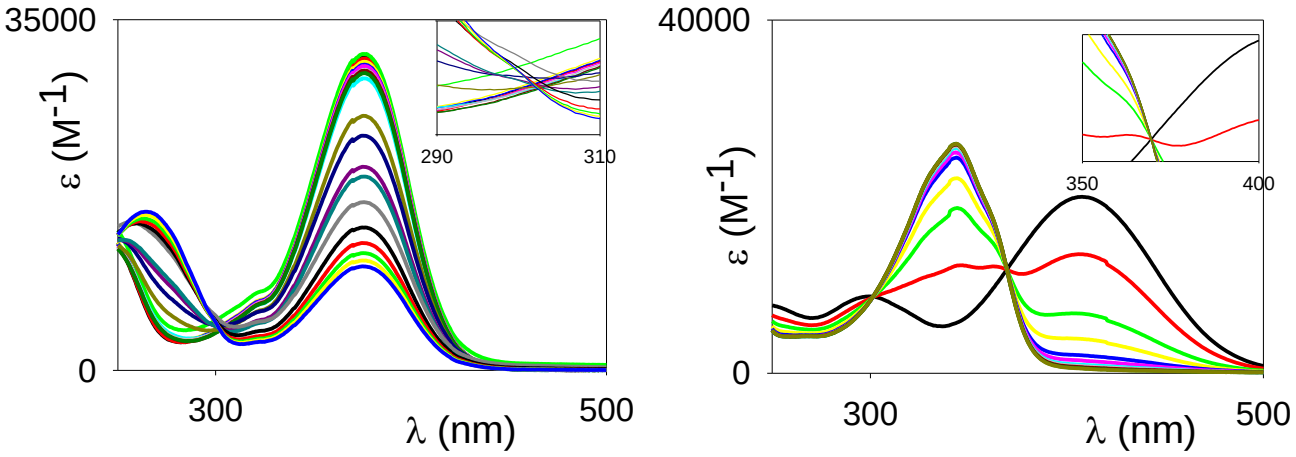


Figure S3. Left: Duplicate titration of **1** with $Sc(OTf)_3$ The isosbestic point is missing. Right: Duplicate titration of **2** with $Sc(OTf)_3$. The isosbestic point is holding.

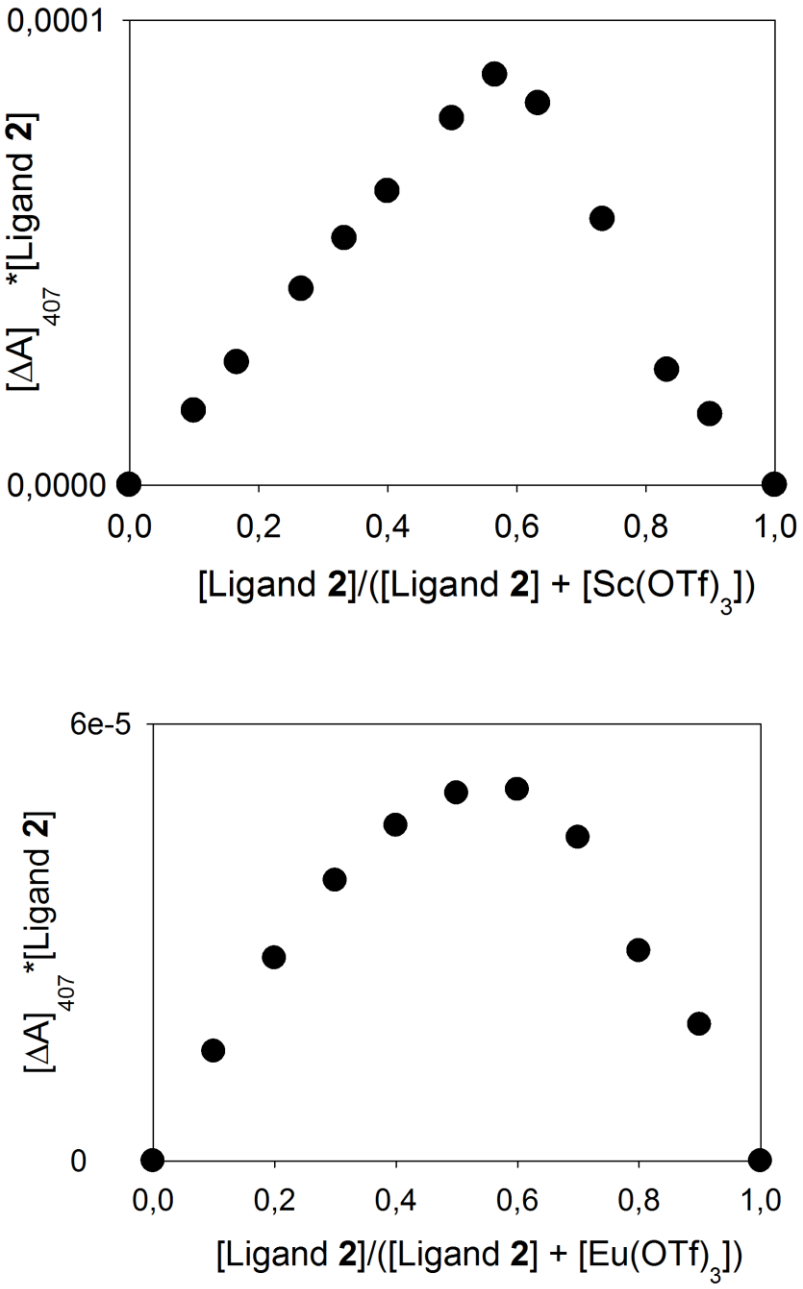


Figure S4. Job plot experiments of **2** with: a) top, $Sc(OTf)_3$ b) bottom, $Eu(OTf)_3$. Total concentration of species in each case: 76 μM in MeCN.

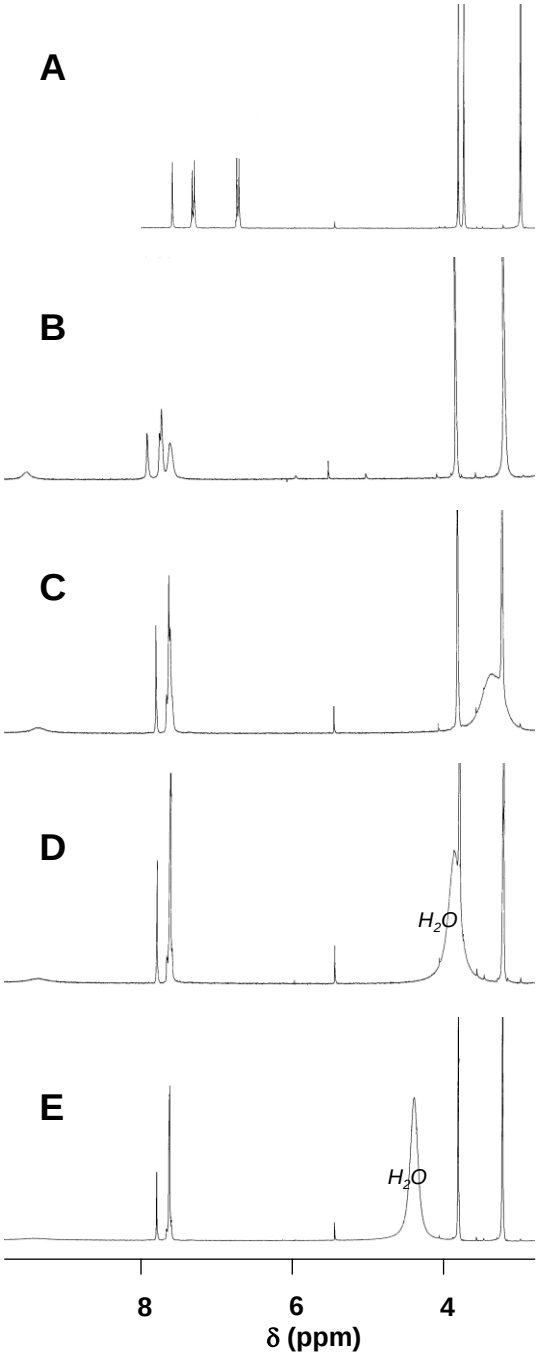


Figure S5. Titration of ligand **1** (0.0126 M in CD_3CN, 300 MHz) with $Sc(OTf)_3$: A) 0 equivalents; B) 0.3 equivalents; C) 0.6 equivalents; D) 0.8 equivalents; E) 1.3 equivalents. This titration has been reduced for the making of Figure 5 in the main text

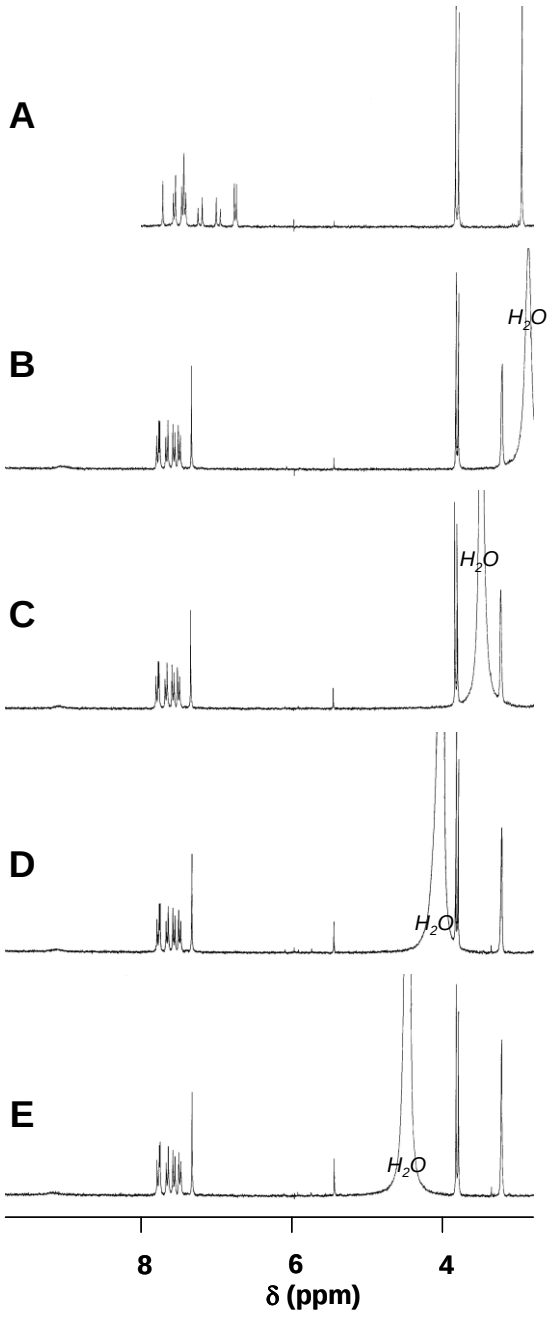
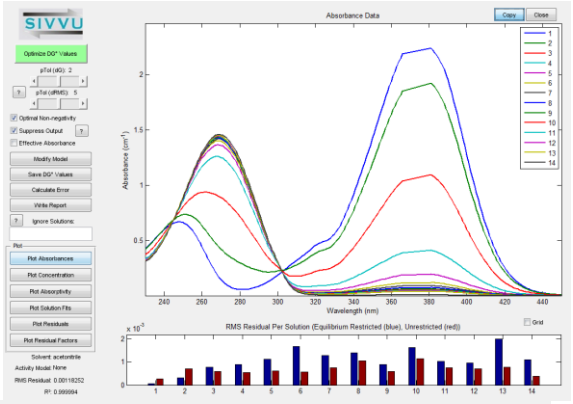
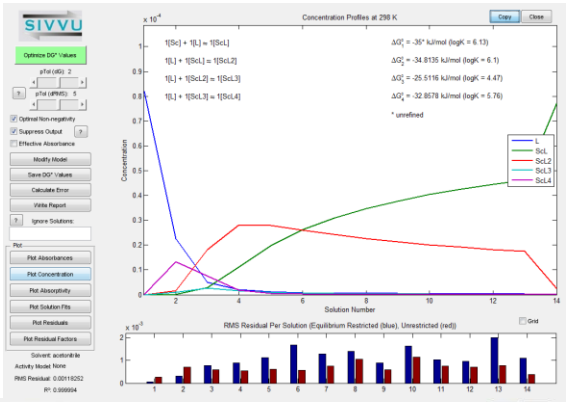
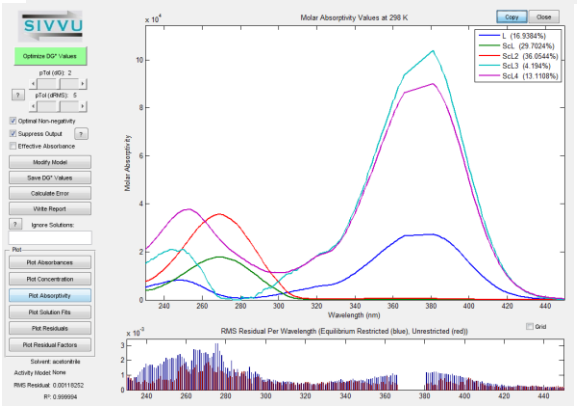


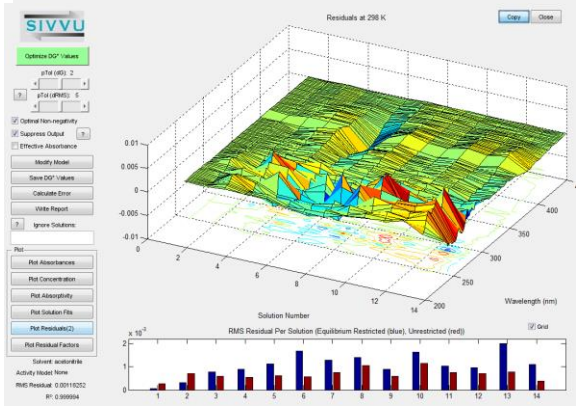
Figure S6. Titration of ligand **2** (0.007 M in CD_3CN) with $Sc(OTf)_3$: A) 0 equivalents; B) 0.3 equivalents; C) 0.6 equivalents; D) 1.1 equivalents; E) 1.9 equivalents. This titration has been reduced for the making of Figure 6 in the main text

Table S1. Titration of Ligand **1** with $Sc(OTf)_3$ (titration ***a*** in Figure 3)



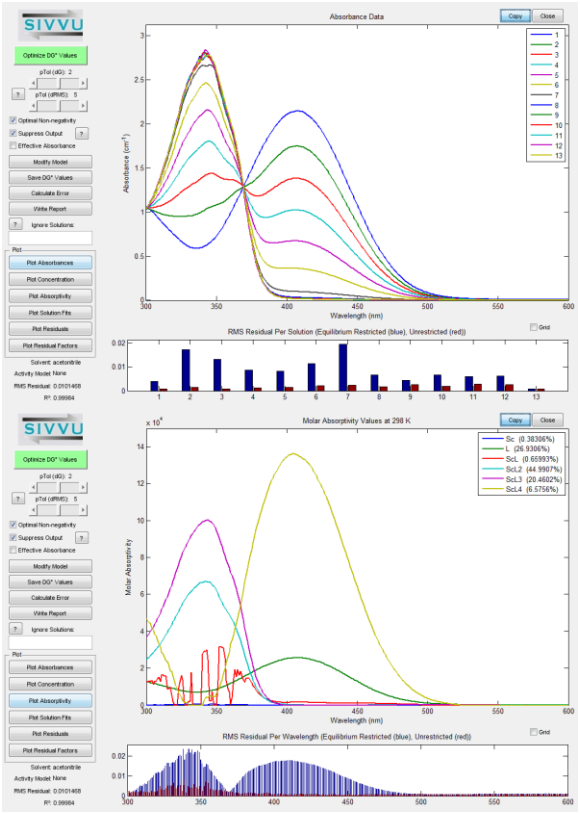


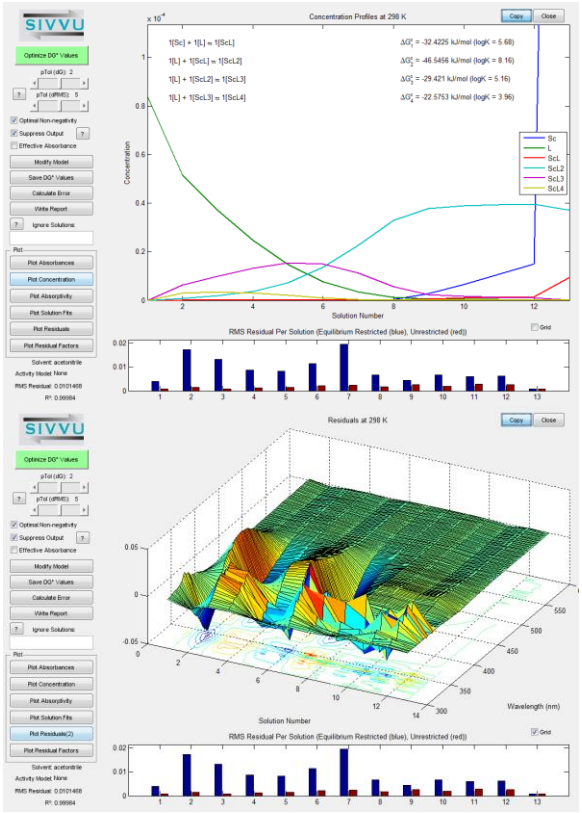




Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -35(unrefined); $\Delta G°_2$ =-34.8(1); $\Delta G°_3$ = -25.5(1); $\Delta G°_4$ = -32.9(1);
Equilibrium Restricted RMS Residual (6 chemical factors): 0.0011557
Unrestricted RMS Residual (6 mathematical factors): 0.0005969
Restricted Data Reconstruction (6 chemical factors): 99.752%
Unrestricted Data Reconstruction (6 mathematical factors): 99.8181%
Remaining Error Imbedded in Absorbance Values: 0.0010009
R^2: 99.9994%

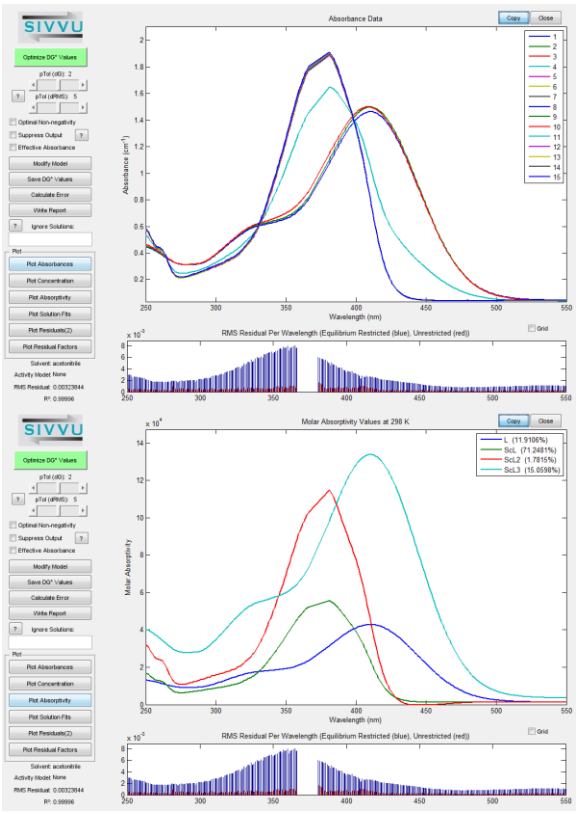
Table S2. Titration of Ligand **2** with $Sc(OTf)_3$ (titration ***c*** in Figure 3)

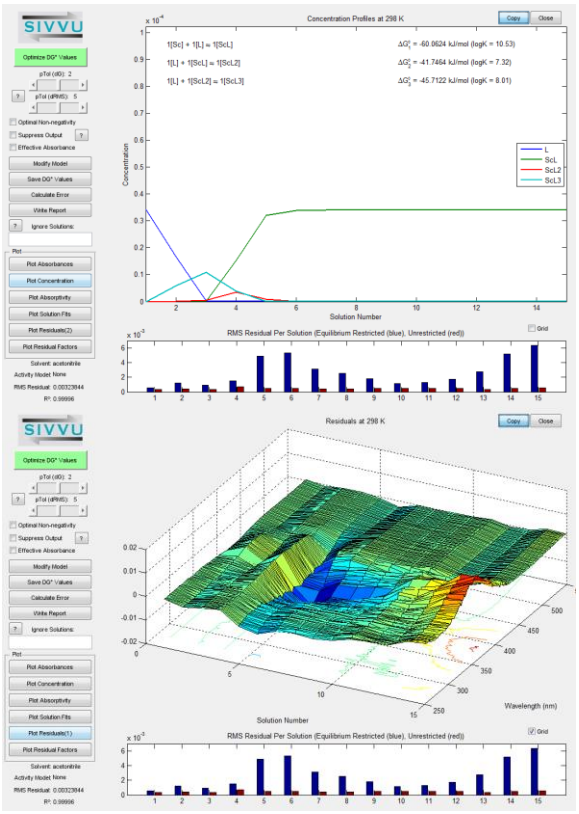




Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -32.4(2); $\Delta G°_2$ = -46.5(1); $\Delta G°_3$ = -29.4(1); $\Delta G°_4$ = -22.6(1);
Equilibrium Restricted RMS Residual (6 chemical factors): 0.010147
Unrestricted RMS Residual (6 mathematical factors): 0.0019111
Restricted Data Reconstruction (6 chemical factors): 99.3834%
Unrestricted Data Reconstruction (6 mathematical factors): 99.6497%
Remaining Error Imbedded in Absorbance Values: 0.0093941
R^2: 99.984%

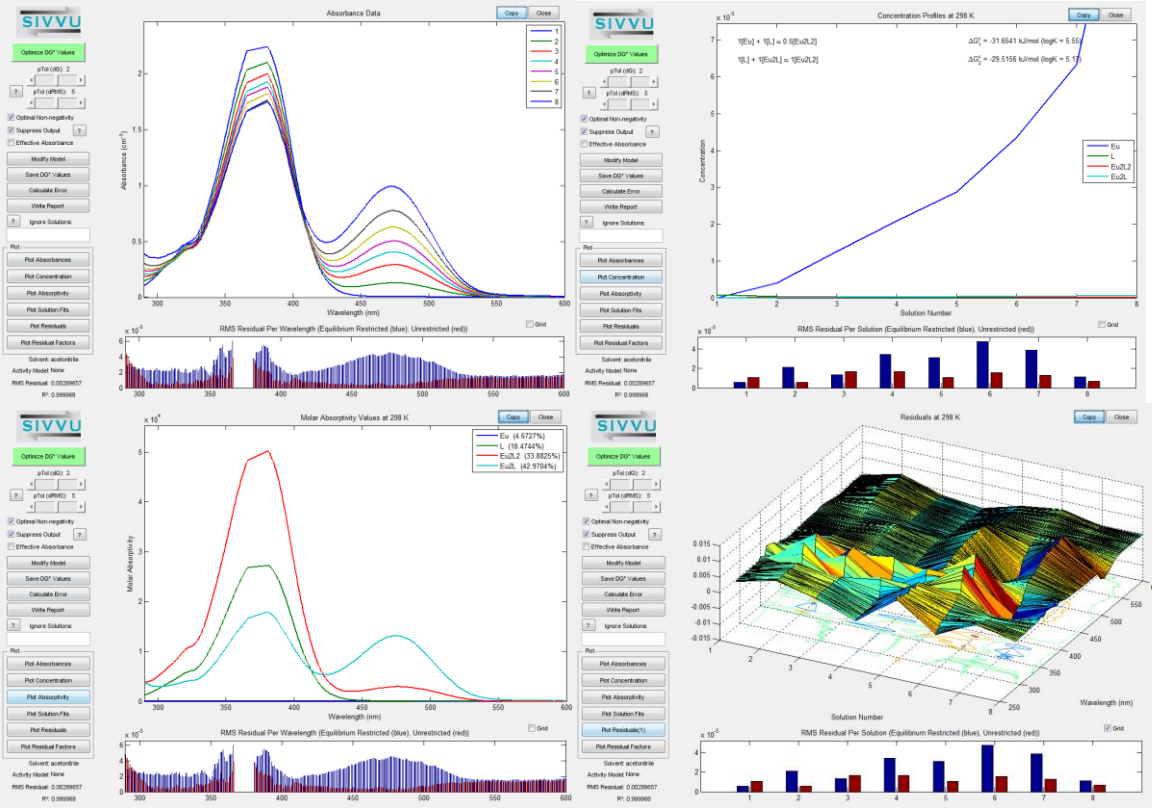
Table S3. Titration of Ligand **3** with $Sc(OTf)_3$ (titration ***e*** in Figure 3)





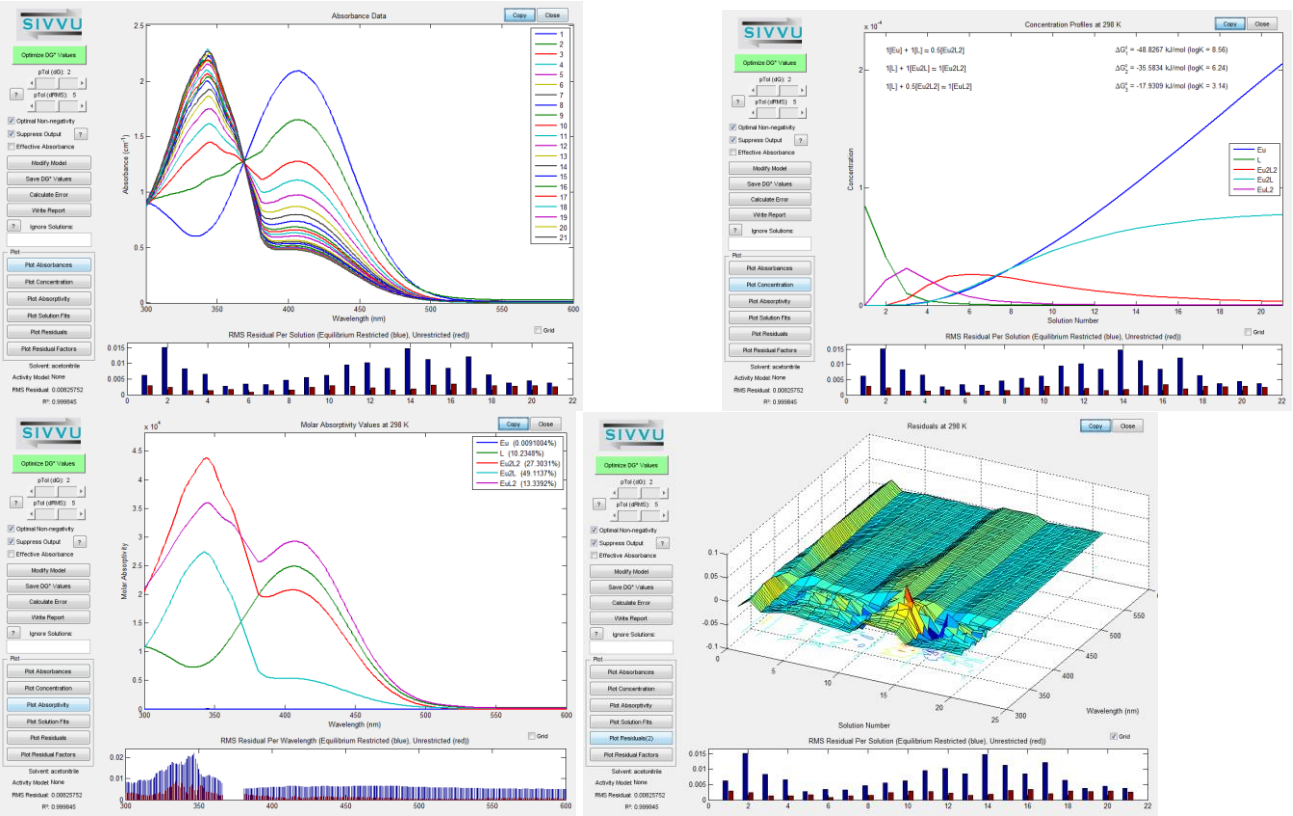
Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -60.1(3); $\Delta G°_2$ = -41.7(2); $\Delta G°_3$ = -45.7(1);
Equilibrium Restricted RMS Residual (4 chemical factors): 0.0032382
Unrestricted RMS Residual (4 mathematical factors): 0.00045912
Restricted Data Reconstruction (4 chemical factors): 99.7735%
Unrestricted Data Reconstruction (4 mathematical factors): 99.8377%
Remaining Error Imbedded in Absorbance Values: 0.0019527
R^2: 99.996%

Table S4. Titration of Ligand **1** with $Eu(OTf)_3$ (titration ***b*** in Figure 3)



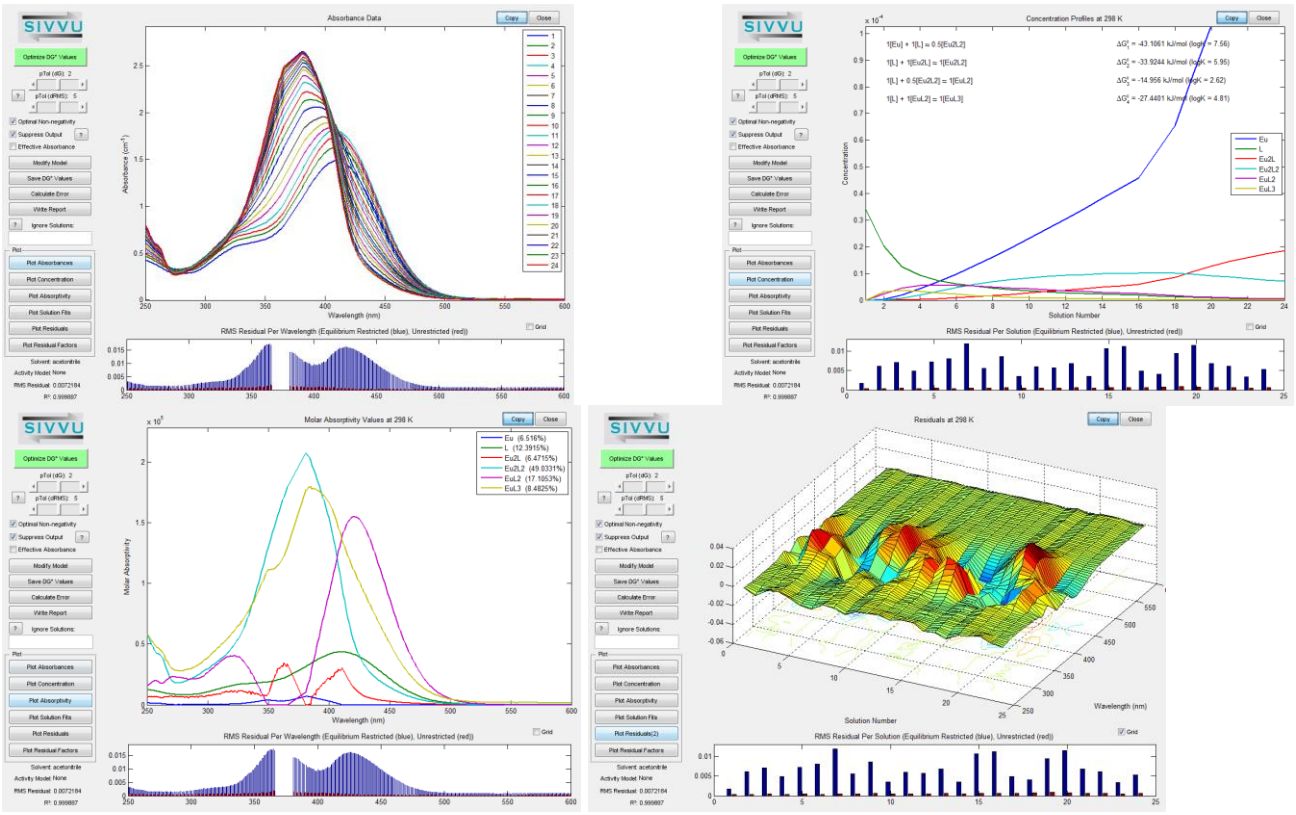
Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -31.65(6); $\Delta G°_2$ = -29.52(5);
Equilibrium Restricted RMS Residual (4 chemical factors): 0.0028966
Unrestricted RMS Residual (4 mathematical factors): 0.0012714
Restricted Data Reconstruction (4 chemical factors): 99.701%
Unrestricted Data Reconstruction (4 mathematical factors): 99.7264%
Remaining Error Imbedded in Absorbance Values: 0.0028966
R^2: 99.9968%

Table S5. Titration of Ligand **2** with $Eu(OTf)_3$ (titration ***d*** in Figure 3)



Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -48.8(1); $\Delta G°_2$ = -35.6(1); $\Delta G°_3$ = -17.9(2);
Equilibrium Restricted RMS Residual (5 chemical factors): 0.0082575
Unrestricted RMS Residual (5 mathematical factors): 0.0022966
Restricted Data Reconstruction (5 chemical factors): 98.8921%
Unrestricted Data Reconstruction (5 mathematical factors): 99.3284%
Remaining Error Imbedded in Absorbance Values: 0.0046161
R^2: 99.9845%

Table S6. Titration of Ligand **3** with $Eu(OTf)_3$ (titration ***f*** in Figure 3)



Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -43.1(1); $\Delta G°_2$ = -33.9(1); $\Delta G°_3$ = -15.0(2); $\Delta G°_4$ = -27.4(2).9;
Equilibrium Restricted RMS Residual (6 chemical factors): 0.0072184
Unrestricted RMS Residual (6 mathematical factors): 0.00055748
Restricted Data Reconstruction (6 chemical factors): 99.847%
Unrestricted Data Reconstruction (6 mathematical factors): 99.7912%
Remaining Error Imbedded in Absorbance Values: 0.0041675
R^2: 99.9887%