Supporting Information for:

From Red to Blue Shift: Switching the Binding Affinity from Acceptor to the Donor End by Increasing the \( \pi \)-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 Yb³⁺), 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$_3$CN, 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$_3$CN) 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 SI. 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): \(\Delta G^\circ_1 = \text{-}35\) (unrefined); \(\Delta G^\circ_2 = \text{-}34.8(1); \Delta G^\circ_3 = \text{-}25.5(1); \Delta G^\circ_4 = \text{-}32.9(1); \)
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 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): \( \Delta G°₁ = -32.4(2) \); \( \Delta G°₂ = -46.5(1) \); \( \Delta G°₃ = -29.4(1) \); \( \Delta G°₄ = -22.6(1) \);
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): $\Delta G^\circ_1 = -60.1(3)$; $\Delta G^\circ_2 = -41.7(2)$; $\Delta G^\circ_3 = -45.7(1)$;
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): ΔG°₁ = -31.65(6); ΔG°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
R²: 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): Δ\(G°\)_1 = -48.8(1); Δ\(G°\)_2 = -35.6(1); Δ\(G°\)_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): ΔG°₁ = -43.1(1); ΔG°₂ = -33.9(1); ΔG°₃ = -15.0(2); ΔG°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
R²: 99.9887%