Electronic Supplementary Material (ESI) for Dalton Transactions.

Thermodynamic Study of the Complexation between Nd^{3+} and Functionalized Diacetamide Ligands in Solution

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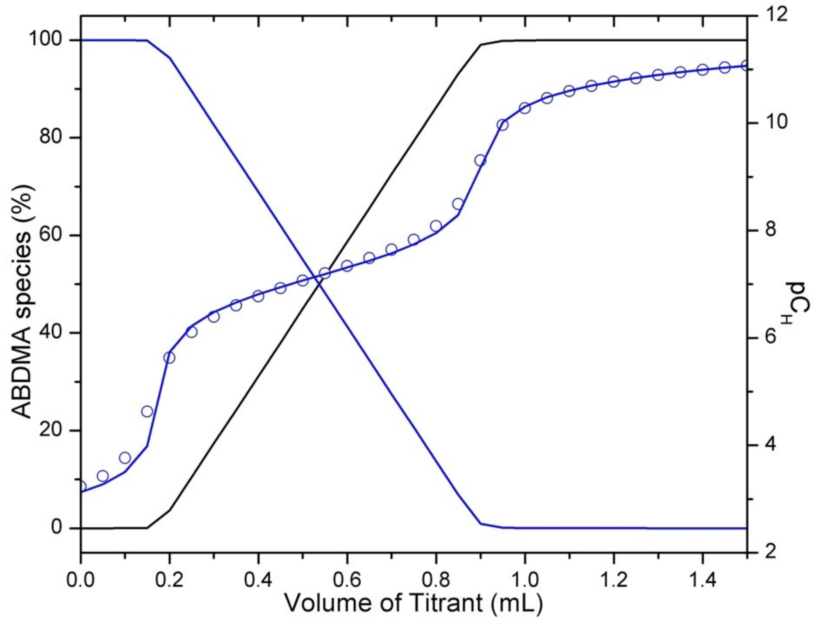

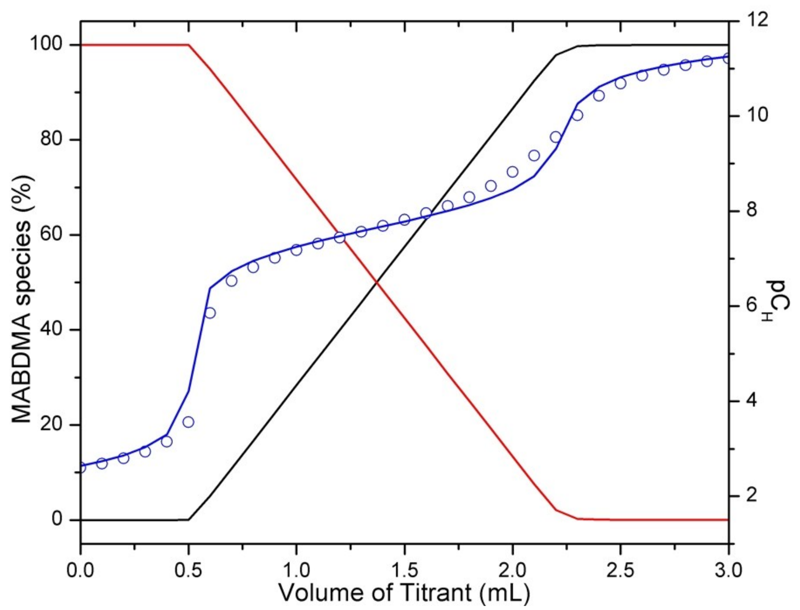

Figure S1. Potentiometric titrations to determine the protonation stability constant of ABDMA (top) and MABDMA (bottom). Black line represents L, red line represents HL^+, emptied blue circles represent observed pC_H, and blue line represents calculated pC_H. Detailed titration conditions are in Table S1.

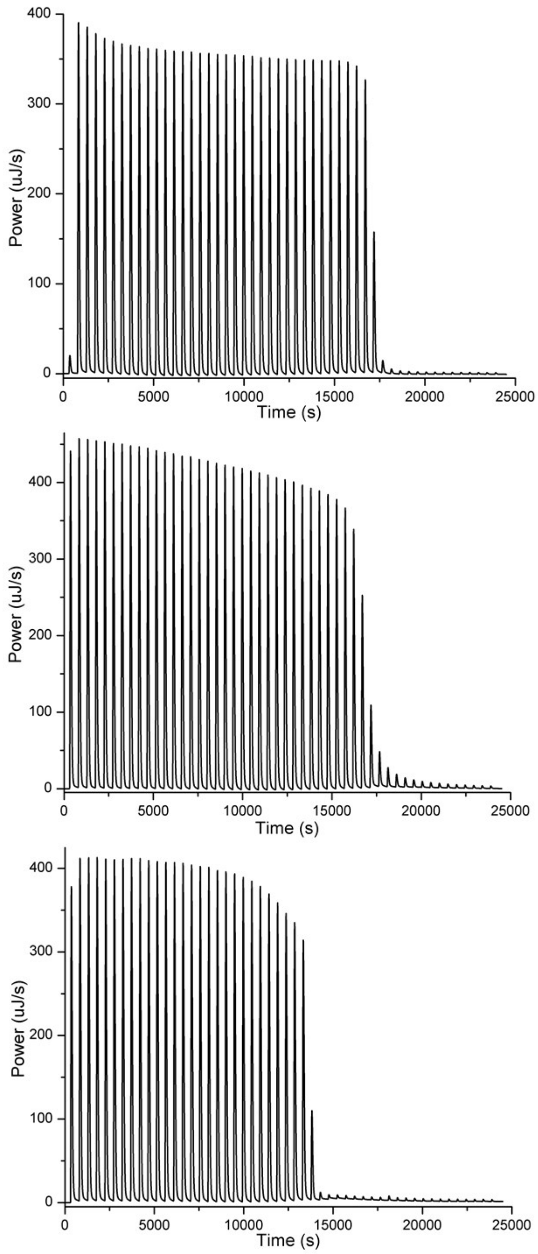

Figure S2. Thermograms of calorimetric titrations to determine the enthalpy for the protonation of BnABDMA (top), ABDMA (middle), and MABDMA (bottom).

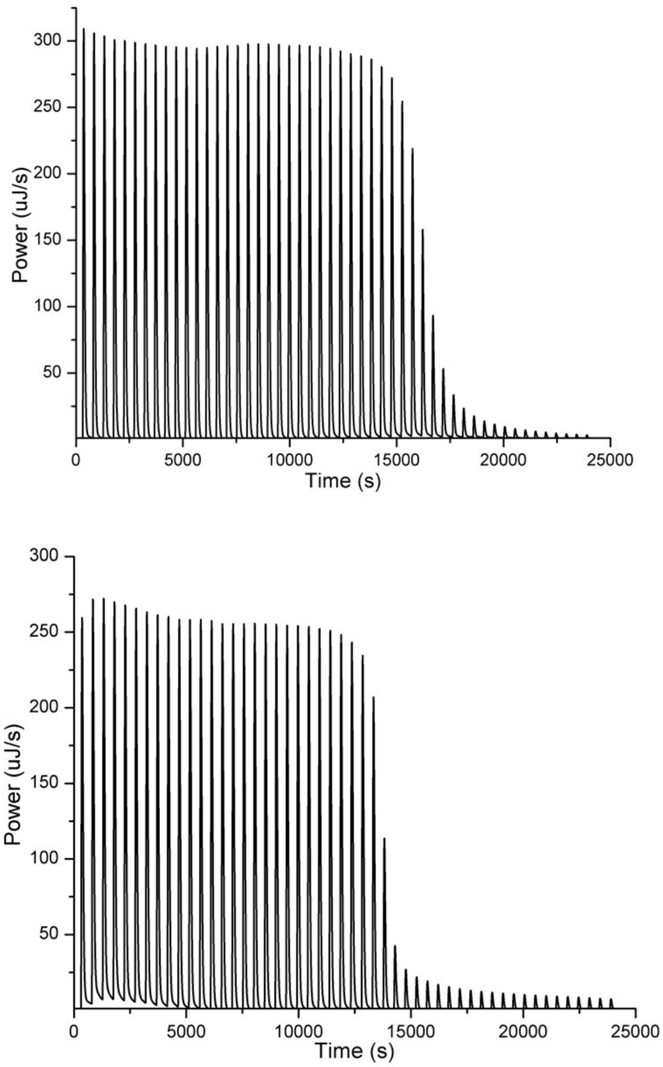

Figure S3. Thermograms of calorimetric titrations to determine the enthalpy for the formation of Nd^{3+} complexes with ABDMA (top) and MABDMA (bottom).

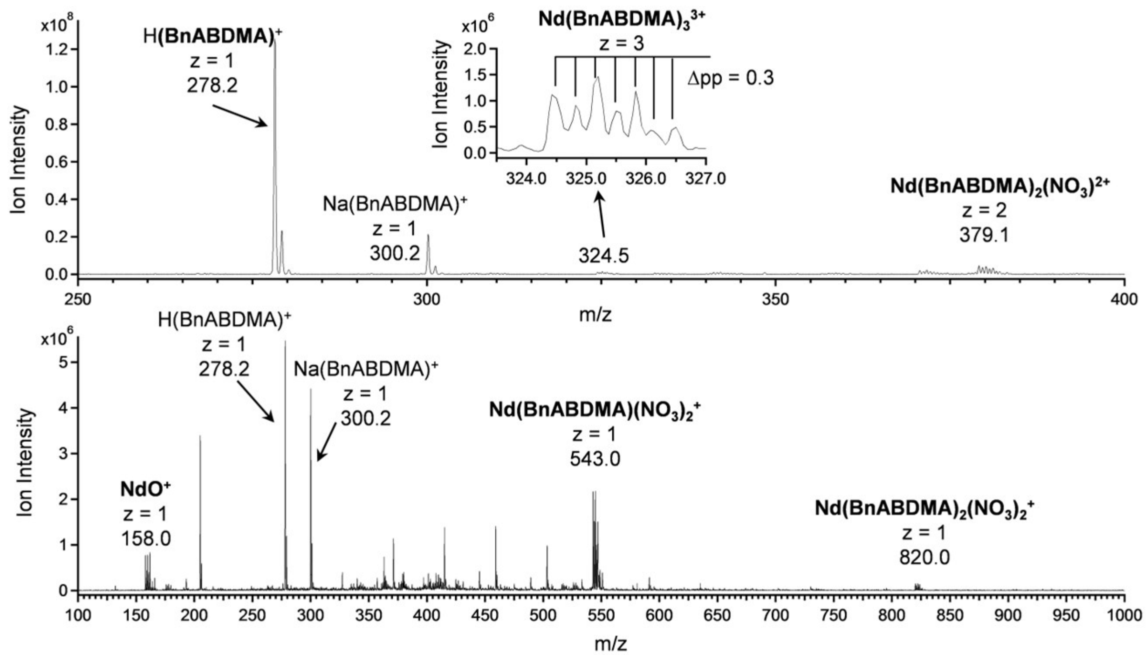

Figure S4. ESI-MS characterization of Nd^{3+} complexes with BnABDMA. In the top spectrum, triply and doubly charged Nd^{3+} complexes were observed, including $Nd(ABDMA)_3^{3+}$ and $Nd(BnABDMA)_2(NO_3)^{2+}$. An inset figure shows a peak to peak separation of Δpp = 0.3 m/z for $Nd(ABDMA)_3^{3+}$. The bottom spectrum shows singly charged complexes of $Nd(BnABDMA)(NO_3)_2^+$ and $Nd(BnABDMA)_2(NO_3)_2^+$. NdO^+ is suggested to produce by reaction of Nd^{3+} with the anodic oxidation products of water.

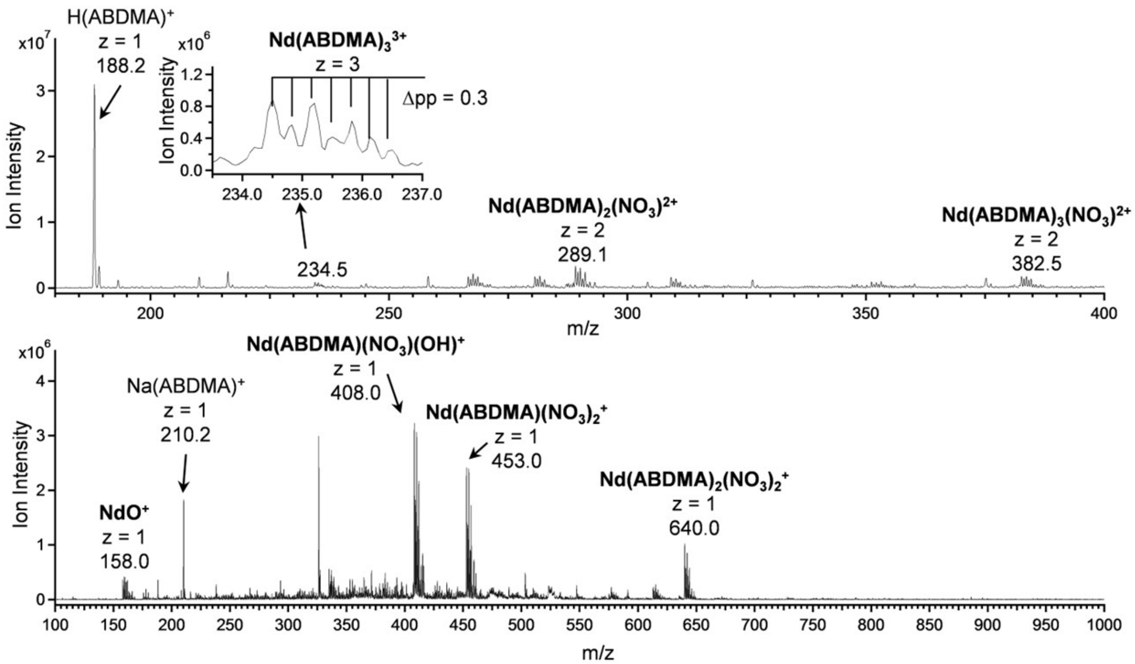

Figure S5. ESI-MS characterization of Nd^{3+} complexes with ABDMA. In the top spectrum, triply and doubly charged Nd^{3+} complexes were observed, including $Nd(ABDMA)_3^{3+}$, $Nd(ABDMA)_2(NO_3)^{2+}$, and $Nd(ABDMA)_3(NO_3)^{2+}$. An inset figure shows a peak to peak separation of Δpp = 0.3 m/z for $Nd(ABDMA)_3^{3+}$. The bottom spectrum shows singly charged complexes of $Nd(ABDMA)(NO_3)_2^+$, $Nd(ABDMA)_2(NO_3)_2^+$, and $Nd(ABDMA)(NO_3)(OH)^+$. NdO^+ is suggested to produce by reaction of Nd^{3+} with the anodic oxidation products of water.

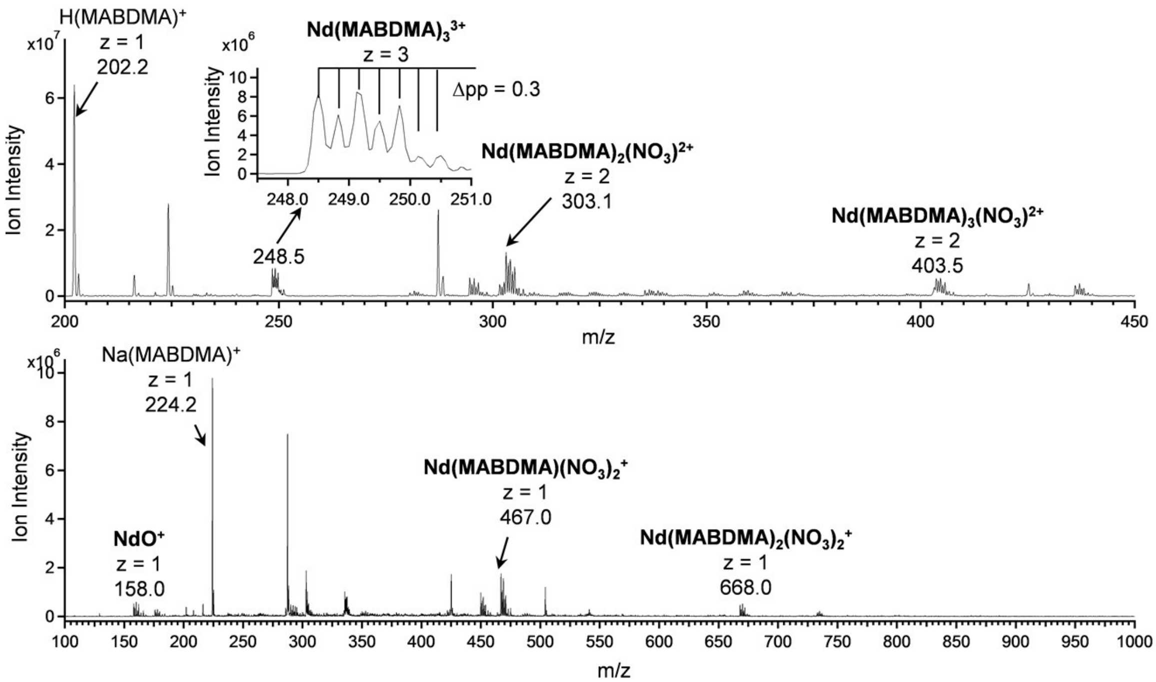

Figure S6. ESI-MS characterization of Nd^{3+} complexes with MABDMA. In the top spectrum, triply and doubly charged Nd^{3+} complexes were observed, including $Nd(MABDMA)_3^{3+}$, $Nd(MABDMA)_2(NO_3)^{2+}$, and $Nd(MABDMA)_3(NO_3)^{2+}$. An inset figure shows a peak to peak separation of $\Delta pp = 0.3$ m/z for $Nd(MABDMA)_3^{3+}$. The bottom spectrum shows singly charged complexes of $Nd(MABDMA)(NO_3)_2^{+}$, $Nd(MABDMA)_2(NO_3)_2^{+}$. NdO^{+} is suggested to produce by reaction of Nd^{3+} with the anodic oxidation products of water.

Ligand	Titration 1[a]		Titration 2[a]		Titration 3[a]	
	Initial Conditions	Final Conditions	Starting Conditions	Final Conditions	Starting Conditions	Final Conditions
BnABDMA	n_L = 0.12 mmol pH = 10.68	n_L = 0.12 mmol pH = 2.64	n_L = 0.13 mmol pH = 8.93	n_L = 0.13 mmol pH = 2.66	n_L = 0.13 mmol pH = 3.04	n_L = 0.13 mmol pH = 10.40
ABDMA	n_L = 0.067 mmol pH = 3.13	n_L = 0.067 mmol pH = 11.07	n_L = 0.066 mmol pH = 2.61	n_L = 0.066 mmol pH = 10.74	n_L = 0.070 mmol pH = 10.58	n_L = 0.070 mmol pH = 3.05
MABDMA	n_L = 0.17 mmol pH = 11.24	n_L = 0.17 mmol pH = 2.48	n_L = 0.17 mmol pH = 2.64	n_L = 0.17 mmol pH = 11.26	n_L = 0.33 mmol pH = 3.13	n_L = 0.33 mmol pH = 11.86

Table S1. Experimental conditions for potentiometric titrations to determine protonation stability constant of BnABDMA, ABDMA, and MABDMA in 1M $NaNO_3$ solution. [a] Initial volume for each titration is at least 22.0 mL, and the final volume for each titration is ~30.0-35.0 mL; the titrant is a 0.1 M HNO_3 in 0.9 M $NaNO_3$ solution, or a 0.10M NaOH in 0.90M $NaNO_3$ solution.

Ligand	Titration 1[a]		Titration 2[a]		Titration 3[a]	
	Initial Conditions	Final Conditions	Starting Conditions	Final Conditions	Starting Conditions	Final Conditions
BnABDMA	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.34 mmol $n_{nitrate}$ = 21.81 mmol pH = 2.15	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.34 mmol $n_{nitrate}$ = 21.81 mmol pH = 7.17	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.30 mmol $n_{nitrate}$ = 19.20 mmol pH = 3.21	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.30 mmol $n_{nitrate}$ = 19.20 mmol pH = 7.39	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.33 mmol $n_{nitrate}$ = 20.51 mmol pH = 2.90	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.33 mmol $n_{nitrate}$ = 20.51 mmol pH = 6.87
ABDMA	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.31 mmol $n_{nitrate}$ = 21.88 mmol pH = 3.12	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.31 mmol $n_{nitrate}$ = 21.88 mmol pH = 6.63	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.51 mmol $n_{nitrate}$ = 26.18 mmol pH = 3.20	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.51 mmol $n_{nitrate}$ = 26.18 mmol pH = 7.09	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.25 mmol $n_{nitrate}$ = 20.85 mmol pH = 2.99	$n_{Nd(III)}$ = 0.10 mmol n_{ligand} = 0.25 mmol $n_{nitrate}$ = 20.85 mmol pH = 6.80
MABDMA	$n_{Nd(III)}$ = 0.16 mmol n_{ligand} = 0.37 mmol $n_{nitrate}$ = 18.79 mmol pH = 3.04	$n_{Nd(III)}$ = 0.16 mmol n_{ligand} = 0.37 mmol $n_{nitrate}$ = 18.79 mmol pH = 6.18	$n_{Nd(III)}$ = 0.14 mmol n_{ligand} = 0.38 mmol $n_{nitrate}$ = 18.56 mmol pH = 3.08	$n_{Nd(III)}$ = 0.14 mmol n_{ligand} = 0.38 mmol $n_{nitrate}$ = 18.56 mmol pH = 6.44	$n_{Nd(III)}$ = 0.36 mmol n_{ligand} = 2.48 mmol $n_{nitrate}$ = 28.01 mmol pH = 3.75	$n_{Nd(III)}$ = 0.36 mmol n_{ligand} = 2.48 mmol $n_{nitrate}$ = 28.01 mmol pH = 6.02

Table S2. Experimental conditions for potentiometric titrations to determine the stability constant for the formations of Nd^{3+} complexes with BnABDMA, ABDMA, and MABDMA. [a] Initial volume for each titration is at least 22.0 mL, and the final volume for each titration is ~30.0-35.0 mL; The ionic strength of solutions was adjusted to be ~1.0 using 1.0 M $NaNO_3$, the titrant is a 0.10M NaOH in 0.90M $NaNO_3$ solution.

Conditions/Ligands	***BnABDMA***[a]	***ABDMA***[b]	***MABDMA***[c]
$n_{Nd(III)}$ *(mmol)*	0.20	0.20	0.20
n_{H+} *(mmol)*	0.01	0.01	0.01
$n_{nitrate}$ *(mmol)*	2.45	1.66	2.46
n_{ligand} *(mmol)*	0	0	0

Table S3. Experimental conditions for spectrophotometric titrations to verify the stability constant for the formation of Nd^{3+} complexes with BnABDMA, ABDMA, and MABDMA. The initial total volume in cuvette was 2.20 ml, and ~1.50-1.80 mL of titrant was added with a volume of 0.1 ml for each addition. [a] The titrant contained BnABDMA (0.613 M), H^+ (0.20 M), and $NaNO_3$ (0.80 M). [b] The titrant contained ABDMA (0.880 M), H^+ (0.10 M), and $NaNO_3$ (0.90 M). [c] The titrant contained MABDMA (0.480 M), H^+ (0.20 M), and $NaNO_3$ (0.80 M)

Ligand	**Titration 1[a]**	**Titration 2[a]**	**Titration 3[a]**
	Initial conditions	Initial conditions	Initial conditions
BnABDMA	n_L = 34.1 µmol n_{H+} = 0 µmol	n_L = 33.9 µmol n_{H+} = 0 µmol	n_L = 34.9 µmol n_{H+} = 0 µmol
ABDMA	n_L = 50.0 µmol n_{H+} = 25.7 µmol	n_L = 50.0 µmol n_{H+} = 16.8 µmol	n_L = 50.0 µmol n_{H+} = 12.4 µmol
MABDMA	n_L = 31.5 µmol n_{H+} = 5.0 µmol	n_L = 31.5 µmol n_{H+} = 4.8 µmol	n_L = 33.0 µmol n_{H+} = 23.2 µmol

Table S4. Experimental conditions for calorimetric titrations to determine the enthalpy of the protonation of BnABDMA, ABDMA, and MABDMA in 1M $NaNO_3$ solution. [a] Initial volume is 750 µL, and the final volume is 1.0 mL; the titrant is a 0.20 M HNO_3 in 0.80M $NaNO_3$ solution.

Ligand	**Titration 1[a]**	**Titration 2[a]**	**Titration 3[a]**
	Initial conditions	Initial conditions	Initial conditions
BnABDMA	$n_{Nd(III)}$ = 9.0 μmol n_{ligand} = 60.0 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 14.0 μmol	$n_{Nd(III)}$ = 15. 0 μmol n_{ligand} = 59.0 μmol $n_{nitrate}$ = 740.0 μmol n_{H+} = 14.0 μmol	$n_{Nd(III)}$ = 14.8 μmol n_{ligand} = 41.5 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 0 μmol
ABDMA	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 57.7 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 3.62 μmol	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 56.8 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 25.0 μmol	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 56.0 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 23.5 μmol
MABDMA	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 38.04 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 11.0 μmol	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 45.0 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 4.1 μmol	$n_{Nd(III)}$ = 14.78 μmol n_{ligand} = 35.0 μmol $n_{nitrate}$ = 750.0 μmol n_{H+} = 8.5 μmol

Table S5. Experimental conditions for calorimetric titrations to determine the enthalpy for the formations of Nd^{3+} complexes with BnABDMA, ABDMA, and MABDMA. [a] Initial volume is 750 μL, and the final volume is 1.0 mL; the titrant is a 0.20 M HNO_3 in 0.80 M $NaNO_3$ solution.

Ligand	Method[a]	Log*β*	Δ*H* (kJ mol⁻¹)	Δ*S* (J K⁻¹ mol⁻¹)	Ref
TMDGA					8
Nd^{3+} + L = NdL^{3+}	sp, cal	(3.53 ± 0.10)	-(10.9 ± 0.9)	(26 ± 1)	
NdL^{3+} + L = NdL_2^{3+}	sp, cal	(2.31 ± 0.19)	-(4.7 ± 1.5)	(13 ± 2)	
NdL_2^{3+} + L = NdL_3^{3+}	sp, cal	(0.96 ± 0.19)	-(3.7 ± 2.2)	(20 ± 7)	
BnABDMA					*this work*
H + L = HL^+	pot,cal	(6.36 ± 0.09)	-(31.2 ± 0.3)	(17+1)	
Nd^{3+} + L = NdL^{3+}	pot, sp, cal	(2.92 ± 0.09)	-(13.3 ± 0.6)	(11 ± 1)	
NdL^{3+} + L = NdL_2^{3+}	pot, sp, cal	(2.16 ± 0.09)	-(9.3 ± 1.2)	(10 ± 3)	
NdL_2^{3+} + L = NdL_3^{3+}	pot, sp, cal	(2.05 ± 0.09)	-(8.3 ± 0.9)	(12 ± 2)	
ABDMA					*this work*
H + L = HL^+	pot, cal	(7.12 ± 0.09)	-(37.2 ± 2.1)	(11+6)	
Nd^{3+} + L = NdL^{3+}	pot, sp, cal	(4.08 ± 0.09)	-(13.5 ± 0.6)	(32± 2)	
NdL^{3+} + L = NdL_2^{3+}	pot, sp, cal	(2.85 ± 0.09)	-(7.0 ± 2.1)	(32 ± 6)	
NdL_2^{3+} + L = NdL_3^{3+}	pot, sp, cal	(3.99 ± 0.9)	-(18.9 ± 1.5)	-(4 ± 4)	
MABDMA					*this work*
H + L = HL^+	pot, cal	(7.64 ± 0.09)	-(33.5 ± 0.6)	(34+2)	
Nd^{3+} + L = NdL^{3+}	pot, sp, cal	(4.40 ± 0.09)	-(11.4 ± 0.3)	(46 ± 1)	
NdL^{3+} + L = NdL_2^{3+}	pot, sp, cal	(3.12 ± 0.36)	-(12.0 ± 1.2)	(19 ± 3)	
NdL_2^{3+} + L = NdL_3^{3+}	sp, cal	(2.98 ± 0.50)	-(10.9 ± 1.5)	(21 ± 4)	

Table S6: Stepwise equilibrium constants, ΔH, and Δ*S* for the protonation and complexation of BnABDMA, ABDMA, and MABDMA, with Nd^{3+} at 25 °C and *I* = 1.0 $NaNO_3$. [a] Pot: potentiometry, sp: spectrophotometry, cal: calorimetry.