Supplementary Information for:

Predicting Stability Constants for Terbium(III) Complexes with Dipicolinic Acid and 4-Substituted Dipicolinic Acid Analogues Using Density Functional Theory

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Table S1. Energy terms from DFT calculations used to construct Table S3.

Complex	Functional/ Basis Sets[a]	Total DFT Energy (a.u.)	Thermal Correction to Enthalpy (kcal/mol)	Total Entropy (cal/mol/K)	$G°_g$ (kcal/mol)	ΔG^*_{solv} (COSMO) (kcal/mol)	ΔG^*_{solv} (SMD) (kcal/mol)
$[Tb(H_2O)_8]^{3+}$	B3LYP/ 6-31+G*	-1433.814	143.692	140.019	-899616.4	-386.19	-394.55
	B3LYP/ 6-311++G**	-1434.096	144.854	140.16	-899792.3	-386.2	-394
	M06/ 6-31+G*	-1433.478	140.988	144.628	-899409.6	-386.75	-395.12
	M06/ 6-311++G**	-1433.722	142.177	144.005	-899561.5	-387.02	-394.76
DPA^{2-}	B3LYP/ 6-31+G*	-624.2566	63.799	101.979	-391687.6	-196.41	-202.28
	B3LYP/ 6-311++G**	-624.4209	63.494	101.988	-391791	-196.15	-201.95
	M06/ 6-31+G*	-623.9022	64.187	100.635	-391464.5	-197.64	-203.92
	M06/ 6-311++G**	-624.051	63.881	100.742	-391558.2	-196.85	-202.93
$[Tb(DPA)(H_2O)_8]^{+}$	B3LYP/ 6-31+G*	-2059.083	210.833	179.39	-1291917	-71.05	-75
	B3LYP/ 6-311++G**	-2059.527	210.877	181.394	-1292196	-69.72	-72.56
	M06/ 6-31+G*	-2058.326	209.078	186.961	-1291446	-72.99	-76.98
	M06/ 6-311++G**	-2058.718	209.296	187.509	-1291692	-71.16	-74.05

[a]Non Tb basis sets.

Table S2. Energy terms from DFT calculations used to construct Table S3.

Complex	Functional/ Basis Sets[a]	Total DFT Energy (a.u.)	Thermal Correction to Enthalpy (kcal/mol)	Total Entropy (cal/mol/K)	$G°_g$ (kcal/mol)	ΔG^*_{solv} (COSMO) (kcal/mol)	ΔG^*_{solv} (SMD) (kcal/mol)
$XDPA^{2-}$ (-X = -F)	B3LYP	-723.7013	58.87	106.74	-454095.5	-189.23	-193.64
	M06	-723.3042	59.387	105.328	-453845.4	-190.18	-194.9
$XDPA^{2-}$ (-X = -Cl)	B3LYP	-1084.058	58.224	109.728	-680221	-186.79	-190.58
	M06	-1083.659	58.642	106.923	-679969.5	-187.8	-191.95
$XDPA^{2-}$ (-X = -Br)	B3LYP	-3197.979	57.991	112.767	-2006707	-186.06	-189.2
	M06	-3197.485	58.445	111.242	-2006396	-187.6	-191.17
$XDPA^{2-}$ (-X = -I)	B3LYP	-7543.361	57.825	115.062	-4733435	-184.79	-192.19
	M06	-7542.736	58.29	113.32	-4733043	-186.76	-194.68
$XDPA^{2-}$ (-X = -OH)	B3LYP	-699.6742	66.888	108.177	-439010.9	-197.64	-204.48
	M06	-699.2754	67.502	106.464	-438759.6	-198.76	-205.76
$XDPA^{2-}$ (-X = $-NH_2$)	B3LYP	-679.7979	74.938	108.642	-426530.6	-202.36	-207.8
	M06	-679.3957	75.375	107.255	-426277.4	-203.13	-208.89
$XDPA^{2-}$ (-X = $-CH_2OH$)	B3LYP	-738.9945	85.646	119.982	-463669.2	-193.4	-200.09
	M06	-738.5613	86.133	116.699	-463395.9	-193.61	-200.81
$XDPA^{2-}$ (-X = -imidazole)	B3LYP	-849.5184	97.994	123.054	-533011.5	-188.01	-193.17
	M06	-848.9985	98.306	121.518	-532684.5	-188.22	-193.65
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -F)	B3LYP	-2158.791	205.947	185.669	-1354491	-71.38	-73.77
	M06	-2157.956	204.762	191.881	-1353970	-72.64	-75.06
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -Cl)	B3LYP	-2519.145	205.416	191.154	-1580615	-70.54	-73.59
	M06	-2518.309	203.992	194.684	-1580093	-71.77	-74.79
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -Br)	B3LYP	-4633.065	205.237	191.447	-2907100	-70.34	-73.99
	M06	-4632.135	203.767	197.522	-2906520	-71.63	-75.19
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -I)	B3LYP	-8978.445	205.111	193.427	-5633827	-70.21	-73.74
	M06	-8977.385	203.617	199.623	-5633165	-71.48	-75.21
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -OH)	B3LYP	-2134.779	214.293	186.28	-1339415	-73.31	-76.68
	M06	-2133.944	212.936	192.551	-1338895	-74.71	-78.17
$[Tb(XDPA)(H_2O)_8]^+$ (-X = $-NH_2$)	B3LYP	-2114.917	222.181	188.401	-1326945	-71.16	-74.2
	M06	-2114.078	220.716	194.361	-1326421	-72.46	-75.61
$[Tb(XDPA)(H_2O)_8]^+$ (-X = $-CH_2OH$)	B3LYP	-2174.094	232.921	195.688	-1364070	-72.48	-76.06
	M06	-2173.223	231.383	201.986	-1363526	-73.83	-77.49
$[Tb(XDPA)(H_2O)_8]^+$ (-X = -imidazole)	B3LYP	-2284.598	245.103	202.514	-1433401	-76.63	-80.3
	M06	-2283.64	243.513	208.401	-1432803	-77.62	-81.2

[a]6-311++G** basis set was used for all atoms except Tb.

Table S3. Compiled $\Delta G°_g$, ΔG_{aq}, and log K_1 calculated in this work.

Equilibrium	Functional/ Basis Sets[a]	$\Delta G°_g$ (kcal/mol)	ΔG_{aq} (COSMO) (kcal/mol)	ΔG_{aq} (SMD) (kcal/mol)	log K_1 (COSMO)	log K_1 (SMD)
$Tb^{3+} + DPA^{2-} \rightleftharpoons [Tb(DPA)]^{+}$	B3LYP/ 6-31+G*	-613.2968	-103.6368	-93.35681	75.886653	68.359262
	B3LYP/ 6-311++G**	-612.9136	-102.1736	-91.41359	74.815229	66.936364
	M06/ 6-31+G*	-572.0165	-62.50649	-51.84649	45.769532	37.963891
	M06/ 6-311++G**	-572.7467	-61.92669	-50.99669	45.344979	37.341634
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -F)	B3LYP/ 6-311++G**	-602.7796	-100.6196	-90.79962	73.677354	66.486792
	M06/ 6-311++G**	-563.3082	-60.63821	-50.59821	44.401513	37.049859
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -Cl)	B3LYP/ 6-311++G**	-601.8254	-101.2654	-92.72542	74.150239	67.896939
	M06/ 6-311++G**	-561.9203	-60.76032	-51.89032	44.490922	37.995984
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -Br)	B3LYP/ 6-311++G**	-600.3686	-100.3386	-93.04863	73.471603	68.133599
	M06/ 6-311++G**	-562.0628	-60.96276	-53.21276	44.639156	38.964323
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -I)	B3LYP/ 6-311++G**	-598.9842	-100.0942	-88.4242	73.292627	64.747427
	M06/ 6-311++G**	-561.1077	-60.69772	-48.76772	44.445085	35.709504
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -OH)	B3LYP/ 6-311++G**	-611.9632	-103.3232	-92.05324	75.657048	67.404742
	M06/ 6-311++G**	-573.4662	-64.28616	-53.00616	47.072669	38.813042
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -NH_2)	B3LYP/ 6-311++G**	-621.6244	-106.1144	-95.91439	77.700827	70.232015
	M06/ 6-311++G**	-582.5997	-66.79972	-56.44972	48.913195	41.334548
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -CH_2OH)	B3LYP/ 6-311++G**	-608.1989	-102.9689	-92.05892	75.397604	67.408904
	M06/ 6-311++G**	-568.7147	-63.80466	-52.52466	46.720099	38.460472
$Tb^{3+} + XDPA^{2-} \rightleftharpoons [Tb(XDPA)]^{+}$ (-X = -imidazole)	B3LYP/ 6-311++G**	-596.7788	-101.0888	-91.79885	74.020943	67.218466
	M06/ 6-311++G**	-556.9563	-61.22629	-51.63629	44.832125	37.809977

[a]Non Tb basis sets.

Table S4. Natural electron configurations of Tb in different complexes from Mulliken analysis.

Complex	Functional/ Basis Sets[a]	6s			4f			5d		
		gas	solution COSMO	solution SMD	gas	solution COSMO	solution SMD	gas	solution COSMO	solution SMD
$[Tb(H_2O)_8]^{3+}$	B3LYP	0.47	0.49	0.49	8.15	8.14	8.14	0.38	0.37	0.37
$[Tb(DPA)(H_2O)_8]^{+}$		0.42	0.46	0.48	8.17	8.16	8.15	0.45	0.44	0.44
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -F)		0.43	0.47	0.49	8.17	8.15	8.15	0.45	0.44	0.43
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -Cl)		0.43	0.47	0.50	8.17	8.16	8.15	0.44	0.44	0.43
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -Br)		0.42	0.47	0.49	8.17	8.16	8.15	0.44	0.44	0.43
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -I)		0.42	0.47	0.49	8.17	8.16	8.15	0.45	0.44	0.43
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -OH)		0.42	0.46	0.48	8.17	8.16	8.15	0.45	0.44	0.44
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -NH_2)		0.42	0.46	0.48	8.17	8.16	8.16	0.45	0.44	0.44
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -CH_2OH)		0.43	0.47	0.49	8.17	8.16	8.15	0.45	0.44	0.44
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -imidazole)		0.44	0.48	0.50	8.17	8.16	8.16	0.44	0.44	0.43
$[Tb(H_2O)_8]^{3+}$	M06	0.47	0.49	0.49	8.14	8.14	8.13	0.37	0.36	0.36
$[Tb(DPA)(H_2O)_8]^{+}$		0.41	0.46	0.47	8.18	8.17	8.17	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -F)		0.41	0.46	0.48	8.18	8.17	8.17	0.42	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -Cl)		0.42	0.46	0.48	8.18	8.17	8.17	0.42	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -Br)		0.41	0.46	0.48	8.18	8.17	8.16	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -I)		0.41	0.46	0.48	8.18	8.17	8.17	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -OH)		0.41	0.46	0.48	8.18	8.17	8.17	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -NH_2)		0.42	0.46	0.48	8.18	8.17	8.17	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -CH_2OH)		0.42	0.46	0.48	8.18	8.17	8.16	0.43	0.42	0.42
$[Tb(XDPA)(H_2O)_8]^{+}$ (-X = -imidazole)		0.42	0.47	0.49	8.18	8.17	8.17	0.42	0.42	0.42

[a]6-311++G** basis set was used for all atoms except Tb.

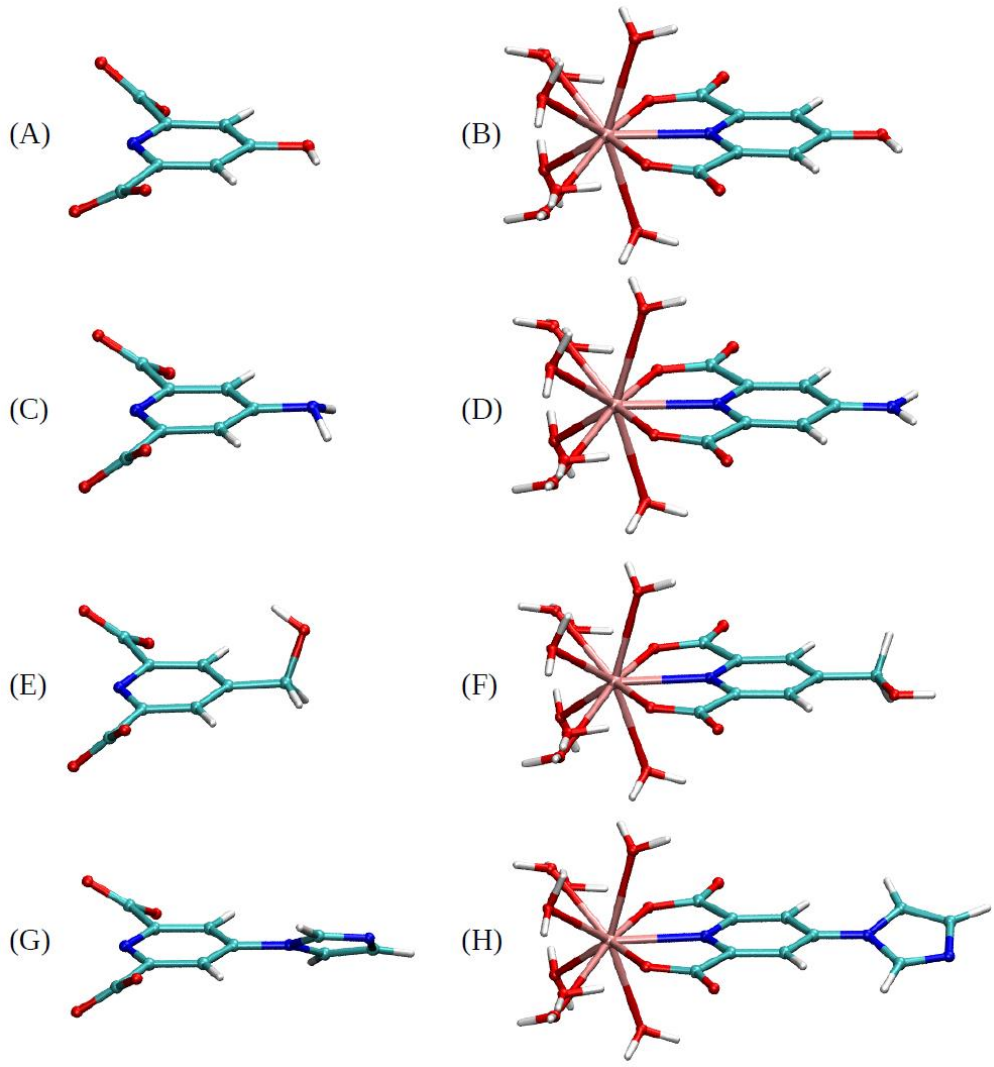

Figure S1. Equilibrium geometries of the $XDPA^{2-}$ (A, C, E, and G) and $[Tb(XDPA)(H_2O)_8]^+$ (B, D, F, and H) complexes with X = -OH (A and B), $-NH_2$ (C and D), $-CH_2OH$ (E and F), and -imidazole (G and H). (Note the geometries for the X = halide substitutes were similar to Figure 1 and were not duplicated here.)

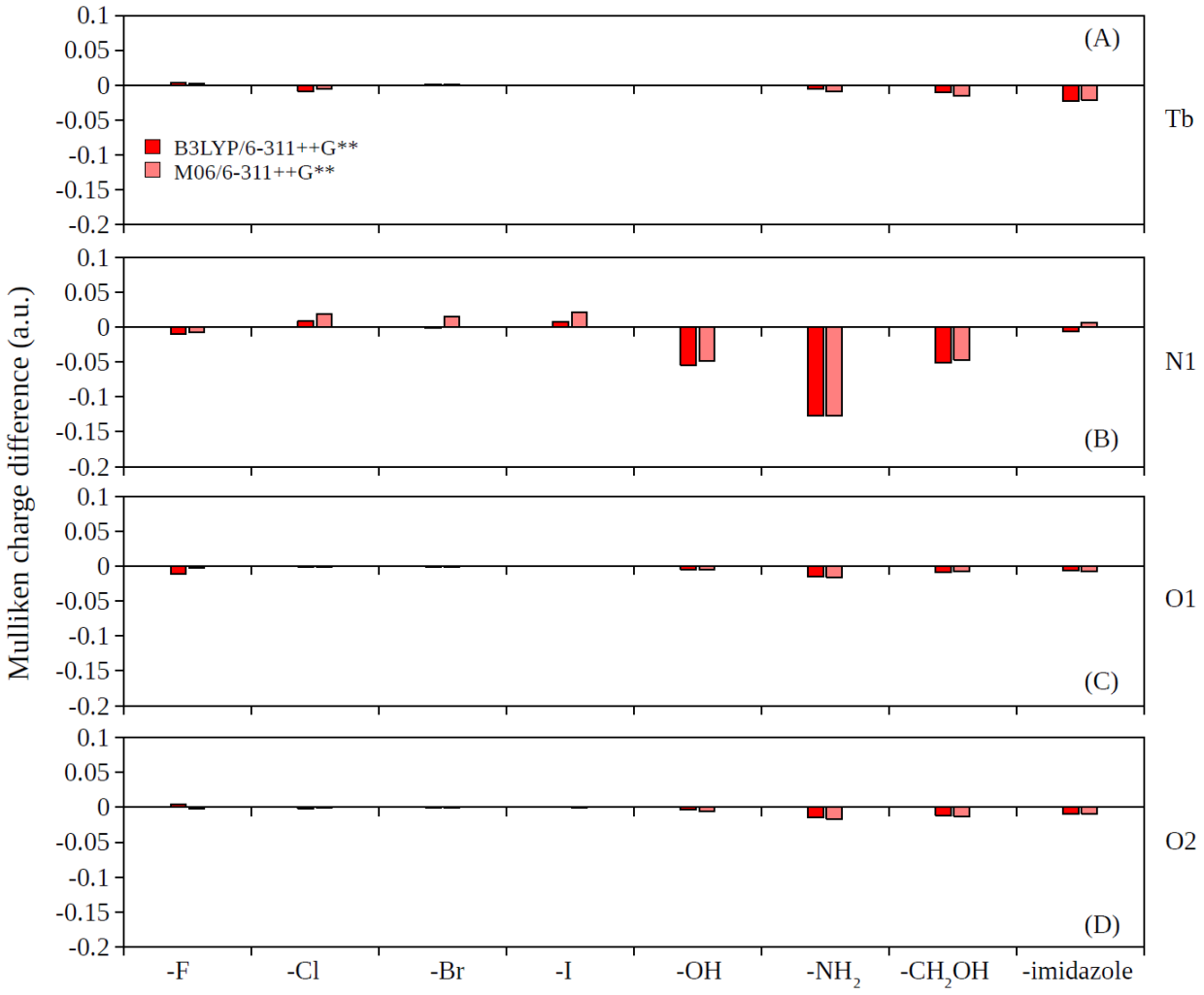

Figure S2. Partial charge differences predicted by Mulliken population analysis in gas phase for (A) Tb, (B) N1, (C) O1, and (D) O2 atoms in $[Tb(XDPA)(H_2O)_8]^+$ complexes compared to in $[Tb(DPA)(H_2O)_8]^+$ complex.

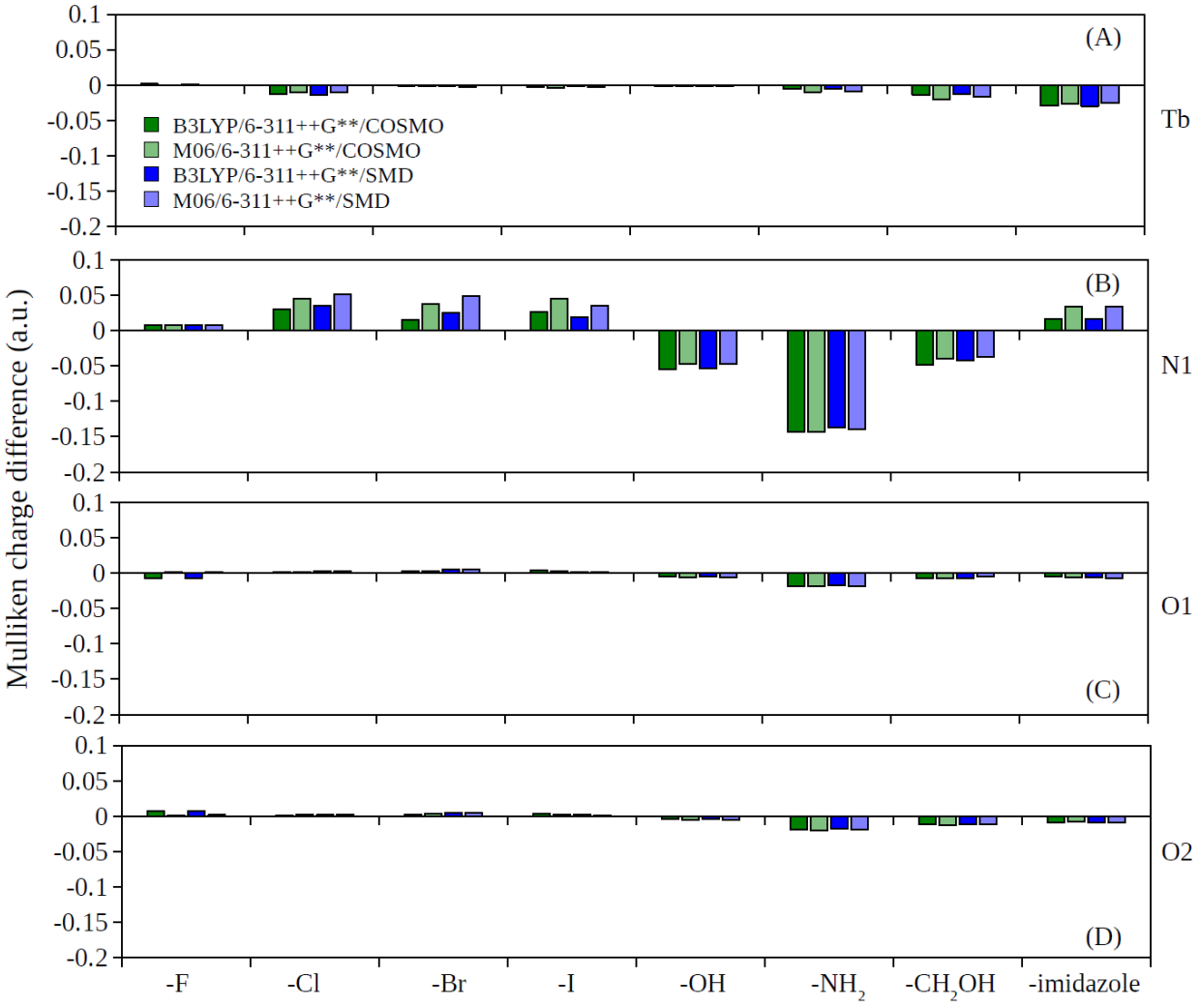

Figure S3. Partial charge differences predicted by Mulliken population analysis in solution phase for (A) Tb, (B) N1, (C) O1, and (D) O2 atoms in $[Tb(XDPA)(H_2O)_8]^+$ complexes compared to in $[Tb(DPA)(H_2O)_8]^+$ complex.

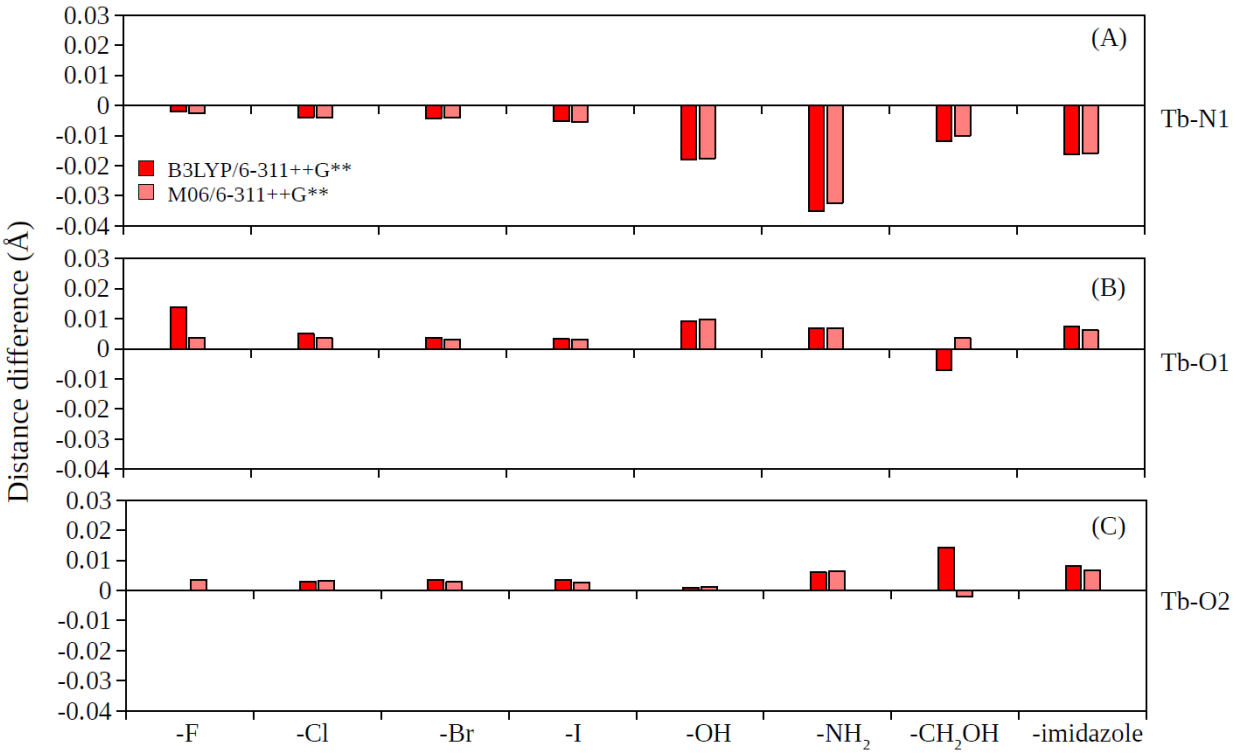

Figure S4. Interatomic distance differences in $[Tb(XDPA)(H_2O)_8]^+$ complexes compared to in $[Tb(DPA)(H_2O)_8]^+$ complex for (A) Tb-N1, (B) Tb-O1, and (C) Tb-O2 pairs.