On the Consequences of the Stereochemical Activity of the Bi(III) 6s2 Lone Pair in Cyclen-based Complexes. The [Bi(DO3A)] Case

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Electronic Supplementary Information (ESI)

Index

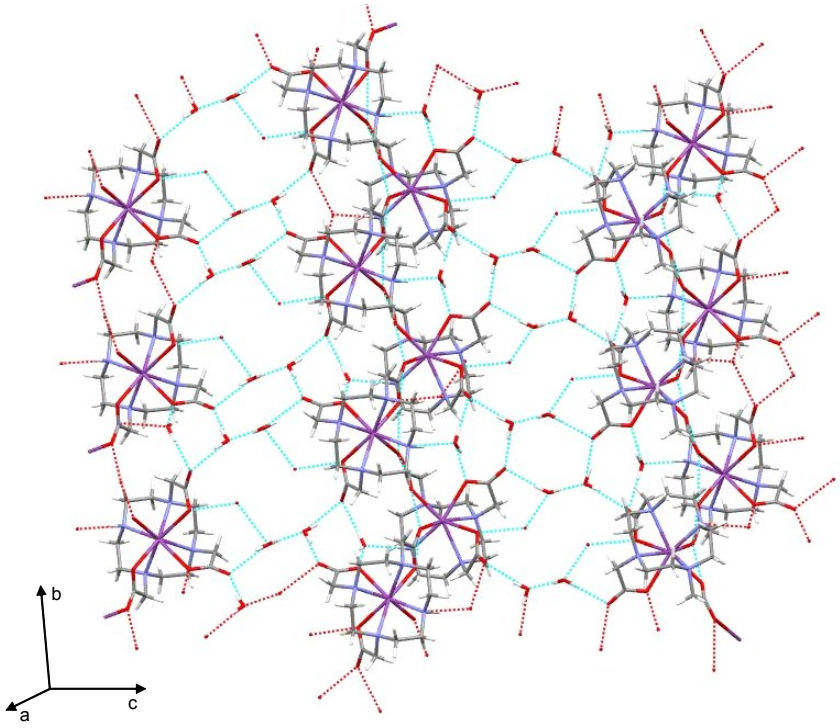

Figure S1. 2D sheets obtained through hydrogen bond interactions between the 1D zig-zag chains in [Bi(DO3A)]·2.5H_2O.

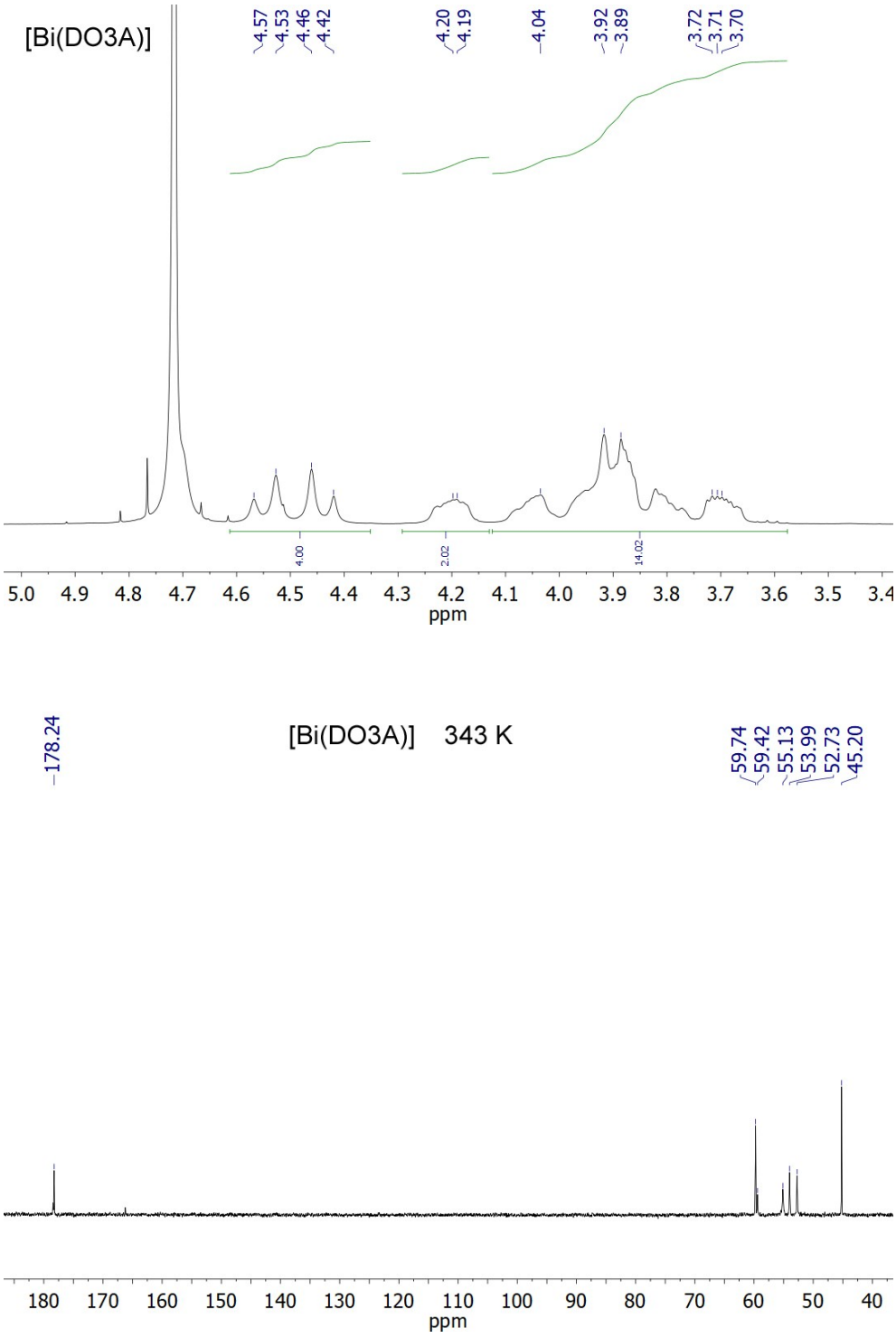

Figure S2. ^{1}H (top, 400 MHz) and ^{13}C NMR spectra (bottom) of [Bi(DO3A)]·recorded in D_2O solution at 343 K.

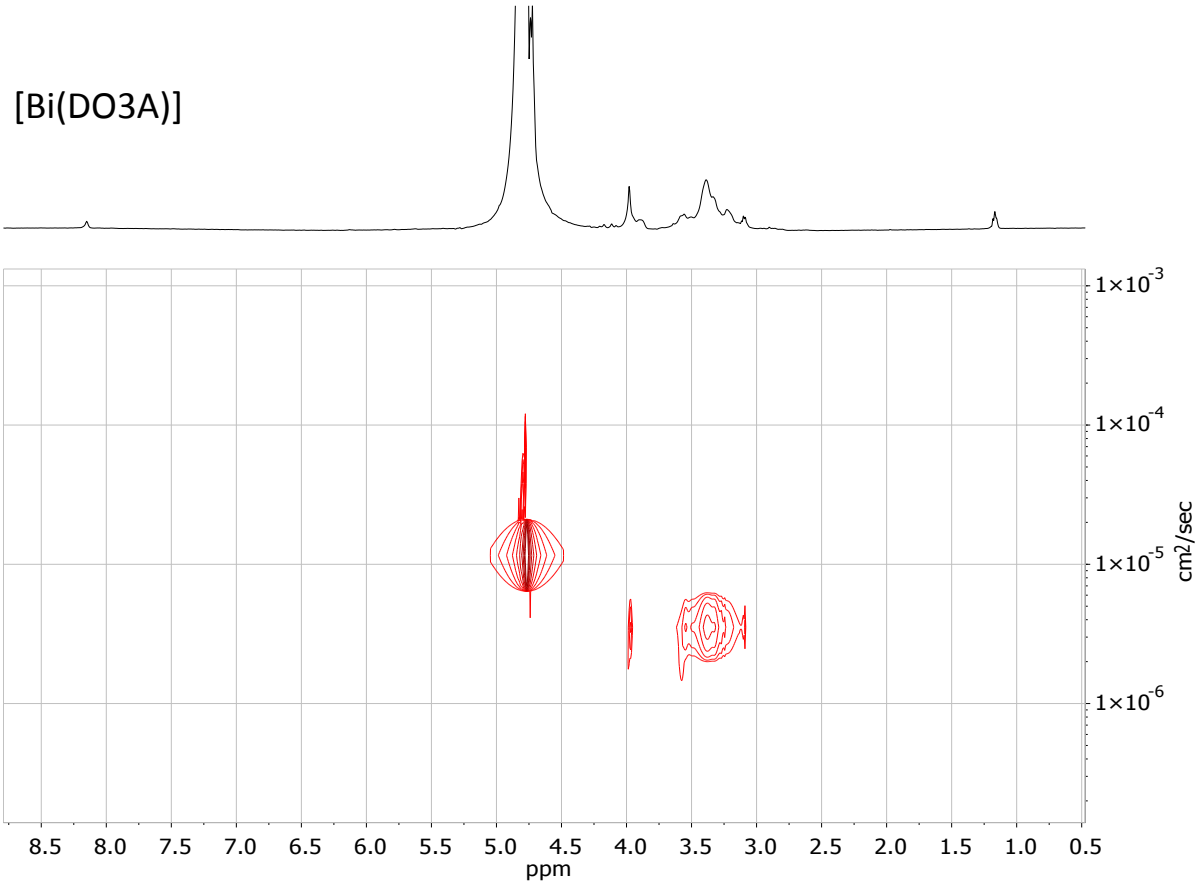

Figure S3. ^{1}H DOSY NMR spectrum (500 MHz) of [Bi(DO3A)] in D_2O solution at 298 K.

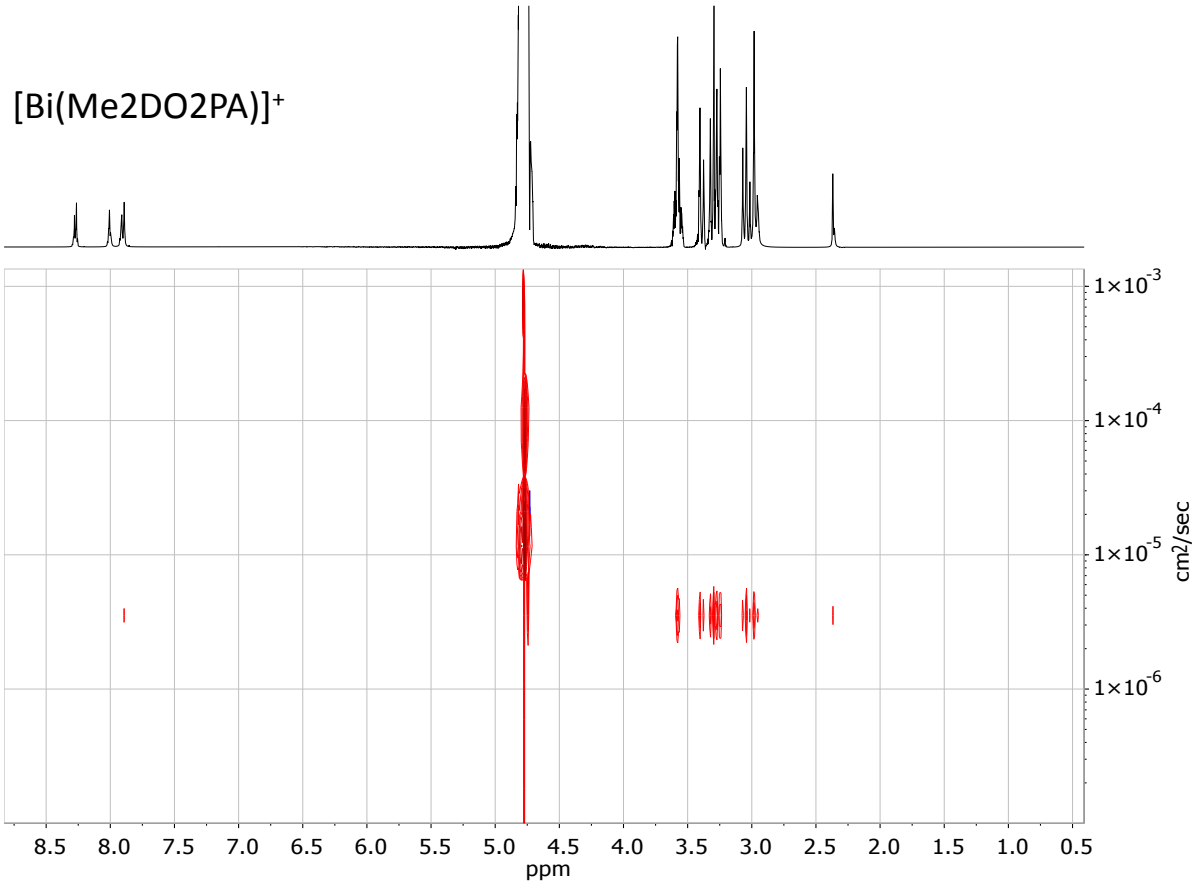

Figure S4. ^{1}H DOSY NMR spectrum (500 MHz) of [Bi(MeDO2PA)]$^{+}$ in D_2O solution at 298 K.

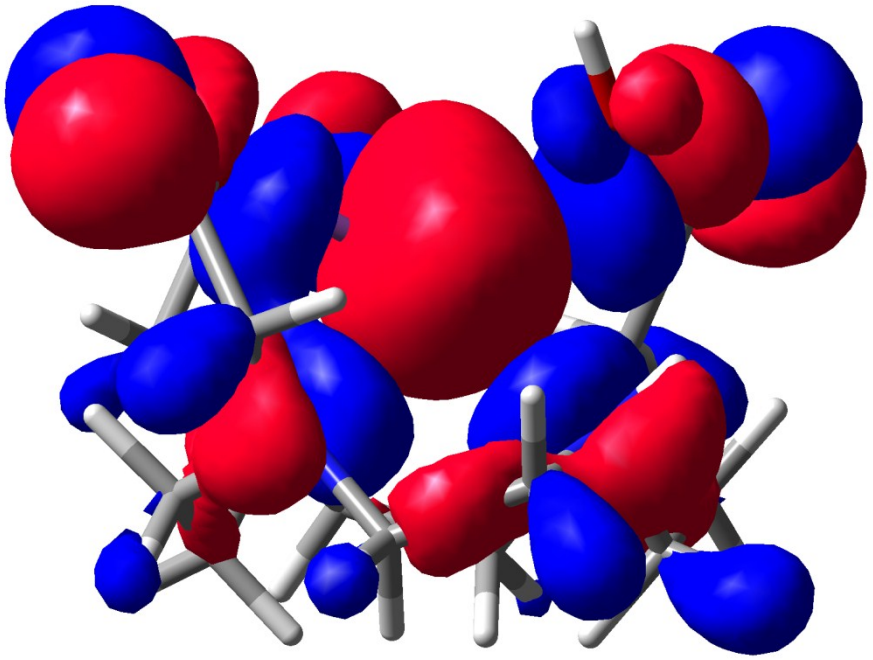

Figure S5. Views of the isodensity surface (0.02 a. u.) of the HOMO of [Bi(DO3A)(H_2O)]·obtained with DFT calculations (TPSSh functional).

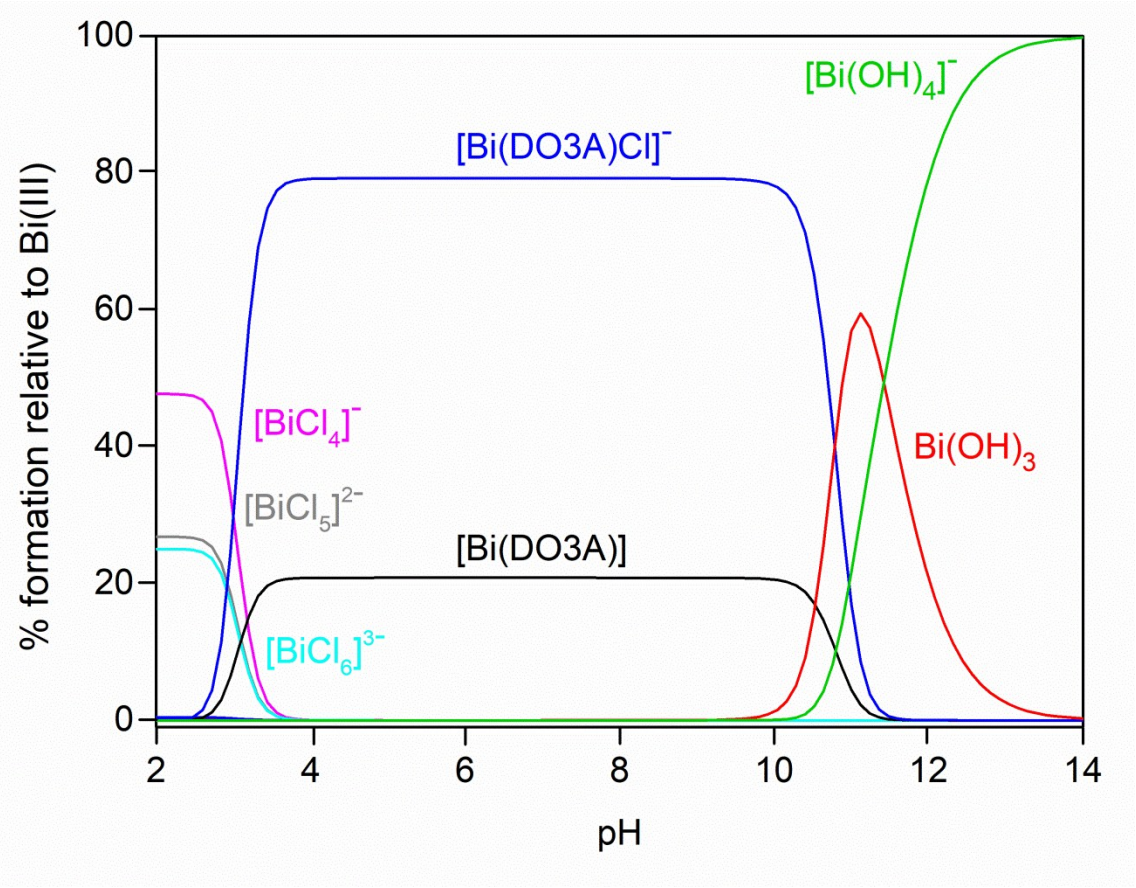

Figure S6. Species distribution diagram of an aqueous solution of [Bi(DO3A)] (5×10^{-5} M) in the presence of 1 M NaCl.

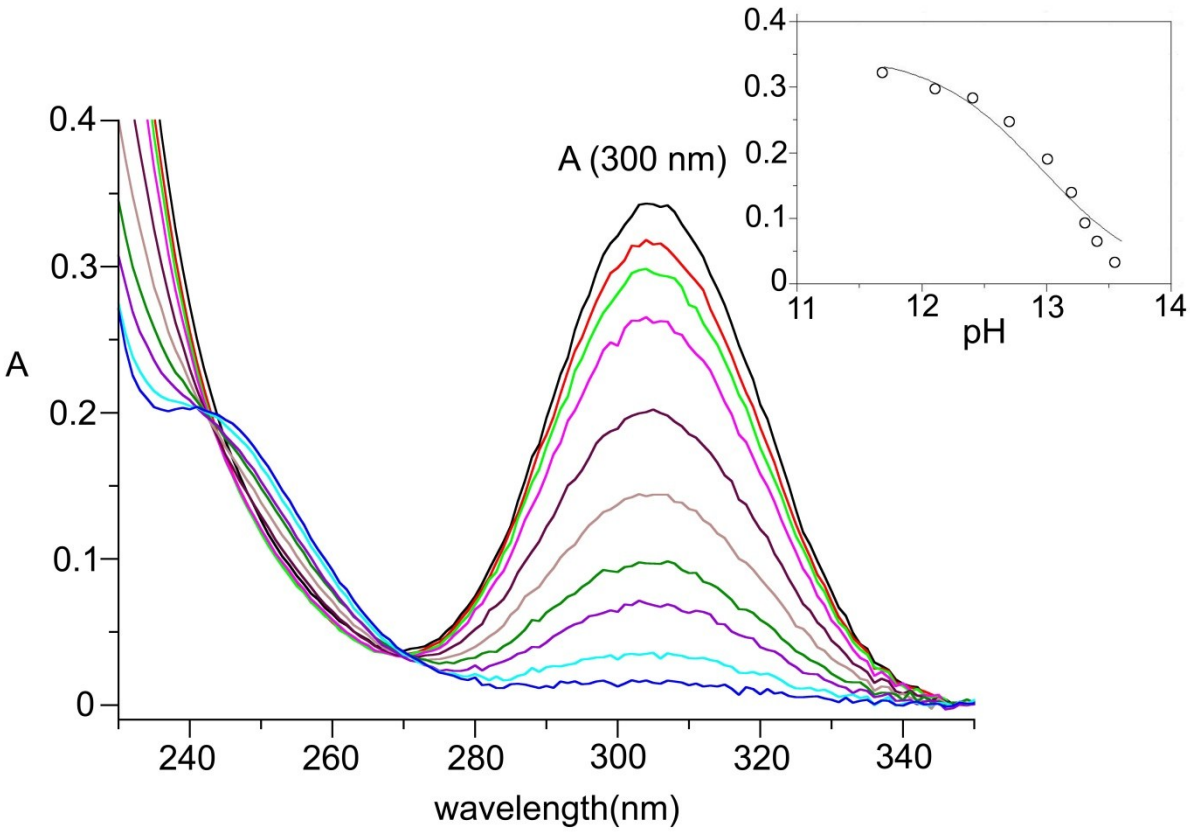

Figure S7. Spectra of the [Bi(DO3A)] complex (5 10^{-5} M) recorded using different hydroxyl ion concentrations. The upper curve corresponds to the complex in [OH^-] = 0.01 M (black line) and last curve with [OH^-] = 1 M corresponds to the blue line**.** The inset shows the absorption data used to calculate the hydrolysis constant log$K_{BiDO3AOH}$ = -13.0. This constant must be regarded as a pseudo-equilibrium constant that can be determined because of the slow dissociation of the complex.

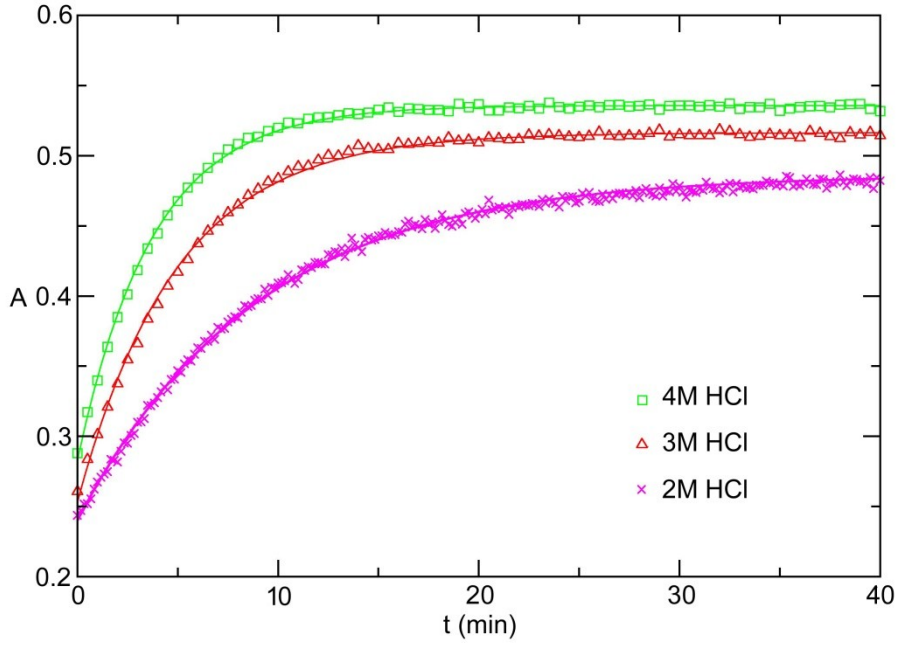

Figure S8. Kinetic traces (37 ºC) obtained for the dissociation of the [Bi(DO3A)] complex (5 10^{-5} M) by recording the absorption at 308 nm at different proton concentrations.

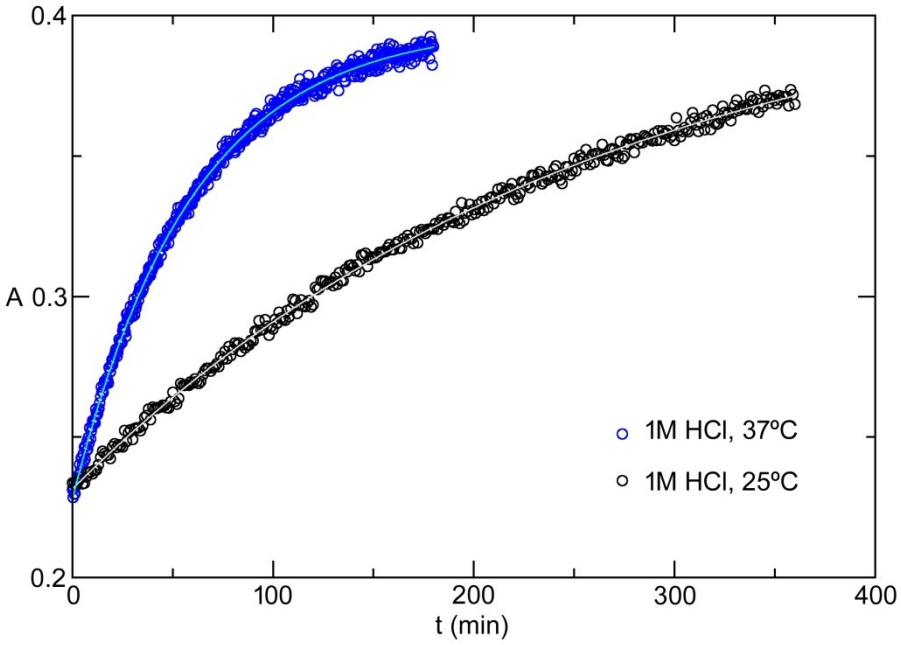

Figure S9. Kinetic traces obtained for the dissociation of the [Bi(DO3A)] complex (5 10^{-5} M) in 1 M HCl by recording the absorption at 308 nm at different temperatures.

Table S1. Hydrogen bond interactions present in the crystal structure of [Bi(DO3A)]·2.5H_2O.

D-H···A	d(H···A) (Å)	D-H···A (º)
O1W-H1WB...O3	1.98(1)	156.6(1)
O1W-H1WB...O4	2.83(1)	140.8(1)
O2W-H2WA...O4	1.86(1)	166.3(1)
O3W-H3WA...O2W	1.87(1)	171.4(1)
N1-H1...O1W_$1	1.88(1)	157.2(1)
O3W-H3WB...O4_$2	2.02(1)	151.1(1)
O2W-H2WB...O2_$3	1.98(1)	168.3(1)
O1W-H1WA...O2_$3	1.95(1)	173.3(1)

$1 -x+1,+y-1/2,-z+1/2; $2 -x,-y+1,-z+1; $3 x,+y+1,+z

Table S2. Optimized Cartesian coordinates obtained for [Bi(DO3A)(H_2O)] with DFT calculations.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-0.213163	-2.534373	0.283275
2	6	-1.184971	-2.708656	1.377312
3	6	-2.393630	-1.815649	1.148003
4	7	-2.047688	-0.367662	1.056972
5	6	-1.757568	0.198423	2.396969
6	6	-0.959630	1.489269	2.310197
7	7	0.340919	1.326095	1.599281
8	6	1.368235	0.727776	2.493413
9	6	2.558137	0.175953	1.722977
10	7	2.171696	-0.863151	0.737274
11	6	1.979340	-2.183715	1.384336
12	6	1.118636	-3.118769	0.542183
13	8	-0.188661	-1.828411	-2.714838
14	6	-3.161809	0.349456	0.390428
15	6	-3.258341	0.032463	-1.112764
16	8	-2.169421	-0.368341	-1.675395
17	6	0.771326	2.649115	1.084327
18	6	-0.086240	3.115104	-0.101204
19	8	-0.729858	2.193196	-0.742407
20	6	3.190735	-0.927859	-0.332093
21	6	3.154224	0.288621	-1.275933
22	8	2.052265	0.953343	-1.326691
23	1	-0.690339	-2.471969	2.320427
24	1	-1.524758	-3.747945	1.448007
25	1	-2.865631	-2.092865	0.204207
26	1	-3.128147	-1.969707	1.946517
27	1	-1.210655	-0.550244	2.970181
28	1	-2.690299	0.395706	2.937427
29	1	-1.531061	2.245425	1.772261
30	1	-0.780902	1.872313	3.320364
31	1	0.889337	-0.061331	3.073558
32	1	1.721227	1.481010	3.206446
33	1	3.053084	0.979363	1.176899
34	1	3.288396	-0.223676	2.436650
35	1	1.504373	-2.017466	2.352421
36	1	2.948197	-2.658613	1.580539
37	1	1.585963	-3.306826	-0.425310
38	1	1.037041	-4.083092	1.056004
39	1	-4.114857	0.112212	0.873484
40	1	-2.992134	1.424065	0.478435
41	1	0.736726	3.400492	1.878642
42	1	1.798114	2.573047	0.724662
43	1	4.196877	-1.023403	0.090333
44	1	3.006851	-1.814507	-0.943314
45	8	4.169219	0.529599	-1.939932
46	8	-0.099478	4.314389	-0.381891
47	8	-4.341324	0.205118	-1.678211
48	83	-0.026305	-0.035662	-0.503327

49	1	-1.081348	-1.444382	-2.820134
50	1	0.279322	-1.659925	-3.543598
51	1	-0.586984	-2.944452	-0.570562

E(RTPSSh) = -1509.33504396 Hartree
Zero-point correction = 0.416381
Thermal correction to Energy = 0.443432
Thermal correction to Enthalpy = 0.444377
Thermal correction to Gibbs Free Energy = 0.360489
Sum of electronic and zero-point Energies = -1508.918663
Sum of electronic and thermal Energies = -1508.891611
Sum of electronic and thermal Enthalpies = -1508.890667
Sum of electronic and thermal Free Energies = -1508.974555

Table S3. Optimized Cartesian coordinates obtained for $[Bi(DO3A)(H_2O)]\cdot 2H_2O$ with DFT calculations.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.359975	0.551488	2.480761
2	6	1.573774	-0.132177	2.969928
3	6	2.705072	0.017214	1.966206
4	7	2.377139	-0.551395	0.628751
5	6	2.453490	-2.032268	0.647140
6	6	1.691023	-2.656110	-0.510134
7	7	0.247514	-2.289772	-0.520853
8	6	-0.512220	-3.095317	0.469989
9	6	-1.875381	-2.499058	0.783846
10	7	-1.792982	-1.122069	1.332126
11	6	-1.449318	-1.122626	2.774572
12	6	-0.870624	0.213406	3.228184
13	8	-1.249181	2.539600	0.335949
14	6	3.299314	0.023878	-0.377609
15	6	3.007709	1.502125	-0.671830
16	8	1.801226	1.899658	-0.425743
17	6	-0.277511	-2.469038	-1.894870
18	6	0.231997	-1.385301	-2.858003
19	8	0.650557	-0.283926	-2.322119
20	6	-3.068358	-0.420860	1.085125
21	6	-3.227947	0.040670	-0.368548
22	8	-2.213312	-0.048322	-1.139252
23	1	1.332269	-1.182109	3.139789
24	1	1.898850	0.279060	3.931869
25	1	2.918245	1.078080	1.824709
26	1	3.613611	-0.455245	2.357432
27	1	2.050750	-2.379792	1.598537
28	1	3.498014	-2.361724	0.602963
29	1	2.116233	-2.327756	-1.458572
30	1	1.796109	-3.745864	-0.466989
31	1	0.090348	-3.163270	1.376551
32	1	-0.646241	-4.117022	0.096730
33	1	-2.478860	-2.452777	-0.122552

34	1	-2.398094	-3.158790	1.486858
35	1	-0.723177	-1.918480	2.947093
36	1	-2.332187	-1.359412	3.380306
37	1	-1.584214	1.020421	3.057426
38	1	-0.679727	0.167801	4.306172
39	1	4.340171	-0.080142	-0.054115
40	1	3.180109	-0.517123	-1.318163
41	1	-0.011333	-3.456181	-2.285156
42	1	-1.364827	-2.388779	-1.872734
43	1	-3.926017	-1.043855	1.364394
44	1	-3.107741	0.478435	1.702734
45	8	-4.331444	0.527405	-0.690203
46	8	0.196620	-1.614176	-4.068549
47	8	3.909284	2.202854	-1.135256
48	83	0.006224	0.224845	-0.111850
49	1	-0.608110	3.289350	0.244042
50	1	-1.994233	2.745589	-0.282828
51	1	0.506551	1.556812	2.542768
52	8	0.789301	4.332066	0.016711
53	8	-3.383274	3.011386	-1.369174
54	1	-3.856836	2.149380	-1.279387
55	1	-4.004819	3.677290	-1.047417
56	1	0.741269	4.900034	-0.762987
57	1	1.331393	3.546579	-0.254297

E(RTPSSh) = -1662.28701442 Hartree
Zero-point correction = 0.466448
Thermal correction to Energy = 0.498179
Thermal correction to Enthalpy = 0.499123
Thermal correction to Gibbs Free Energy = 0.404900
Sum of electronic and zero-point Energies = -1661.820566
Sum of electronic and thermal Energies = -1661.788836
Sum of electronic and thermal Enthalpies = -1661.787892
Sum of electronic and thermal Free Energies = -1661.882114

Table S4. Optimized Cartesian coordinates obtained for $[Bi(DO3A)N_3]^-$ with DFT calculations.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-0.051941	-1.807988	1.769698
2	6	-1.233474	-1.629145	2.629637
3	6	-2.466087	-1.352694	1.781948
4	7	-2.317315	-0.153584	0.918988
5	6	-2.446019	1.095399	1.703225
6	6	-1.853663	2.295296	0.978466
7	7	-0.411295	2.139280	0.661099
8	6	0.434067	2.396218	1.850221
9	6	1.846808	1.853678	1.688668
10	7	1.885762	0.388724	1.459113
11	6	1.718070	-0.362319	2.725062
12	6	1.241885	-1.789322	2.482152
13	6	-3.306094	-0.216711	-0.176781

14	6	-2.959833	-1.274941	-1.240040
15	8	-1.733578	-1.649543	-1.311719
16	6	-0.065714	3.037838	-0.461173
17	6	-0.632639	2.555972	-1.808310
18	8	-0.936905	1.309798	-1.900205
19	6	3.148270	0.032767	0.779563
20	6	3.194406	0.504607	-0.685497
21	8	2.069073	0.735871	-1.260039
22	1	-1.036220	-0.806747	3.318820
23	1	-1.417401	-2.519691	3.241474
24	1	-2.640349	-2.204848	1.122364
25	1	-3.345527	-1.247809	2.429574
26	1	-1.946043	0.946922	2.660998
27	1	-3.500531	1.303590	1.925098
28	1	-2.376828	2.451953	0.034835
29	1	-2.010391	3.194013	1.587842
30	1	-0.049479	1.937328	2.713755
31	1	0.490232	3.473542	2.052484
32	1	2.331112	2.329949	0.836153
33	1	2.432302	2.115145	2.579111
34	1	0.991426	0.172151	3.339598
35	1	2.659993	-0.382195	3.287392
36	1	1.952796	-2.329466	1.856792
37	1	1.172495	-2.311773	3.443109
38	1	-4.311213	-0.412613	0.214001
39	1	-3.324858	0.746465	-0.689857
40	1	-0.414857	4.058073	-0.266194
41	1	1.019337	3.064741	-0.571580
42	1	4.012202	0.441055	1.316746
43	1	3.239838	-1.055262	0.762328
44	8	4.309922	0.606831	-1.217203
45	8	-0.737147	3.389382	-2.718577
46	8	-3.879667	-1.674502	-1.968877
47	83	0.020432	-0.265600	-0.313136
48	1	-0.122190	-2.686418	1.259087
49	7	1.355401	-2.414546	-0.694284
50	7	1.825522	-2.702355	-1.754841
51	7	2.291698	-3.000368	-2.778851

E(RTPSSh) = -1597.27605215 Hartree
Zero-point correction = 0.403147
Thermal correction to Energy = 0.431239
Thermal correction to Enthalpy = 0.432183
Thermal correction to Gibbs Free Energy = 0.344392
Sum of electronic and zero-point Energies = -1596.872905
Sum of electronic and thermal Energies = -1596.844813
Sum of electronic and thermal Enthalpies = -1596.843869
Sum of electronic and thermal Free Energies = -1596.931660

Table S5. Optimized Cartesian coordinates obtained for $[Bi(DO3A)I]^-$ with DFT calculations.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	7	0.620884	-0.920431	2.130786
2	6	-0.484742	-1.464631	2.937099
3	6	-1.453025	-2.235624	2.053138
4	7	-2.046914	-1.405194	0.971461
5	6	-3.075268	-0.481378	1.501731
6	6	-3.353414	0.662195	0.539056
7	7	-2.146552	1.479350	0.246571
8	6	-1.872411	2.425126	1.355797
9	6	-0.459905	2.984405	1.309553
10	7	0.579180	1.928707	1.366565
11	6	0.804618	1.472354	2.757301
12	6	1.449364	0.092858	2.814854
13	6	-2.613969	-2.297211	-0.063708
14	6	-1.536604	-2.975226	-0.924626
15	8	-0.387305	-2.405302	-0.963539
16	6	-2.346220	2.187966	-1.036868
17	6	-2.256454	1.247233	-2.247764
18	8	-1.622048	0.135968	-2.075782
19	6	1.820725	2.434069	0.746128
20	6	1.693227	2.598335	-0.778757
21	8	0.772842	1.916196	-1.362488
22	1	-0.985244	-0.636688	3.441271
23	1	-0.113715	-2.135560	3.720337
24	1	-0.918766	-3.056258	1.570620
25	1	-2.248980	-2.672303	2.668705
26	1	-2.726519	-0.095363	2.459979
27	1	-4.011213	-1.019192	1.695451
28	1	-3.719566	0.270250	-0.409995
29	1	-4.143274	1.299945	0.952720
30	1	-2.043348	1.898983	2.295479
31	1	-2.586185	3.257275	1.322868
32	1	-0.312826	3.541959	0.384696
33	1	-0.331513	3.693699	2.136724
34	1	-0.162950	1.451495	3.262124
35	1	1.433046	2.189646	3.300173
36	1	2.417227	0.100539	2.310321
37	1	1.621724	-0.176374	3.863412
38	1	-3.252949	-3.061543	0.392002
39	1	-3.229798	-1.704201	-0.741950
40	1	-3.312078	2.703822	-1.049196
41	1	-1.556361	2.930048	-1.157771
42	1	2.123253	3.390271	1.189064
43	1	2.621122	1.709860	0.918358
44	8	2.493296	3.357349	-1.343741
45	8	-2.773409	1.611857	-3.308406
46	8	-1.854302	-4.003396	-1.539170
47	83	-0.127018	-0.085636	-0.246941
48	1	1.231116	-1.678894	1.827441
49	53	3.108981	-1.084431	-0.564094

E(RTPSSh) = -1728.67724668 Hartree
Zero-point correction = 0.391776 (Hartree/Particle)
Thermal correction to Energy = 0.418248
Thermal correction to Enthalpy = 0.419192

Thermal correction to Gibbs Free Energy = 0.334539
Sum of electronic and zero-point Energies = -1728.285471
Sum of electronic and thermal Energies = -1728.258998
Sum of electronic and thermal Enthalpies = -1728.258054
Sum of electronic and thermal Free Energies = -1728.342707