Electronic Supporting Information

Impacts of Hydrogen Bonding Interactions with $Np(V/VI)O_2Cl_4$ Complexes: Vibrational Spectroscopy, Redox Behavior, and Computational Analysis.

Mikaela M. Pyrch, Jennifer L. Bjorklund, James M. Williams, Daniel L. Parr IV, S. E. Mason, Johna Leddy, and Tori Z. Forbes*

Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States

*corresponding author: tori-forbes@uiowa.edu; 319-384-1320

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1. Crystallographic tables

Table S1. Select bond lengths (Å) and angles (°) for Compound **Np(V)Morph**.

Np(1)-O(1)	1.8304(13)	O(1)-Np(1)-O(2)	178.66(5)
Np(1)-O(2)	1.8356(13)	O(1)-Np(1)-Cl(4)	92.99(4)
Np(1)-Cl(4)	2.7358(7)	O(2)-Np(1)-Cl(4)	88.27(4)
Np(1)-Cl(2)	2.7466(7)	O(1)-Np(1)-Cl(2)	86.29(4)
Np(1)-Cl(3)	2.7497(8)	O(2)-Np(1)-Cl(2)	92.44(4)
Np(1)-Cl(1)	2.7622(8)	Cl(4)-Np(1)-Cl(2)	177.376(12)
O(3)-C(2)	1.424(2)	O(1)-Np(1)-Cl(3)	92.87(4)
O(3)-C(3)	1.425(2)	O(2)-Np(1)-Cl(3)	87.58(4)
O(4)-C(6)	1.422(2)	Cl(4)-Np(1)-Cl(3)	91.396(12)
O(4)-C(7)	1.425(2)	Cl(2)-Np(1)-Cl(3)	91.158(12)
O(5)-C(10)	1.422(2)	O(1)-Np(1)-Cl(1)	88.72(4)
O(5)-C(11)	1.422(2)	O(2)-Np(1)-Cl(1)	90.84(4)
N(1)-C(4)	1.487(2)	Cl(4)-Np(1)-Cl(1)	88.076(12)
N(1)-C(1)	1.492(2)	Cl(2)-Np(1)-Cl(1)	89.388(12)
N(2)-C(8)	1.492(2)	Cl(3)-Np(1)-Cl(1)	178.357(13)
N(2)-C(5)	1.494(2)	C(2)-O(3)-C(3)	110.12(13)
		C(6)-O(4)-C(7)	109.81(14)
		C(10)-O(5)-C(11)	110.05(14)
		C(4)-N(1)-C(1)	110.60(14)
		C(10)-O(5)-C(11)	110.05(14)
		C(8)-N(2)-C(5)	112.13(13)
		C(12)-N(3)-C(9)	110.75(14)

Table S2. Select bond lengths (Å) and angles (°) for Compound **Np(VI)Morph**

Np(1)-O(1)[a]	1.7526(18)	O(1)[a]-Np(1)-O(1)	180.0
Np(1)-O(1)	1.7526(18)	O(1)[a]-Np(1)-Cl(2)[a]	90.65(7)
Np(1)-Cl(2)[a]	2.6558(8)	O(1)-Np(1)-Cl(2)[a]	89.35(7)
Np(1)-Cl(2)	2.6558(8)	O(1)[a]-Np(1)-Cl(2)	89.35(7)
Np(1)-Cl(1)[a]	2.6884(8)	O(1)-Np(1)-Cl(2)	90.65(7)
Np(1)-Cl(1)	2.6884(8)	Cl(2)[a]-Np(1)-Cl(2)	180.00(3)
O(2)-C(3)	1.417(4)	O(1)[a]-Np(1)-Cl(1)[a]	91.05(7)
O(2)-C(2)	1.423(4)	O(1)-Np(1)-Cl(1)[a]	88.95(7)
O(3)-C(8)	1.398(4)	Cl(2)[a]-Np(1)-Cl(1)[a]	91.14(3)
O(3)-C(5)	1.412(4)	Cl(2)-Np(1)-Cl(1)[a]	88.86(3)
N(1)-C(1)	1.474(4)	O(1)[a]-Np(1)-Cl(1)	88.95(7)
N(1)-C(4)	1.489(4)	O(1)-Np(1)-Cl(1)	91.05(7)
N(2)-C(6)	1.469(4)	Cl(2)[a]-Np(1)-Cl(1)	88.86(3)
N(2)-C(7)	1.485(4)	Cl(2)-Np(1)-Cl(1)	91.14(3)
C(1)-C(2)	1.498(5)	Cl(1)[a]-Np(1)-Cl(1)	180.00(3)
C(3)-C(4)	1.508(5)	C(3)-O(2)-C(2)	110.7(2)
C(5)-C(6)	1.475(5)	C(8)-O(3)-C(5)	110.3(3)
C(7)-C(8)	1.475(5)	C(1)-N(1)-C(4)	110.5(2)
		C(6)-N(2)-C(7)	110.9(2)

Symmetry transformations used to generate equivalent atoms: a: -x,-y+1,-z+1

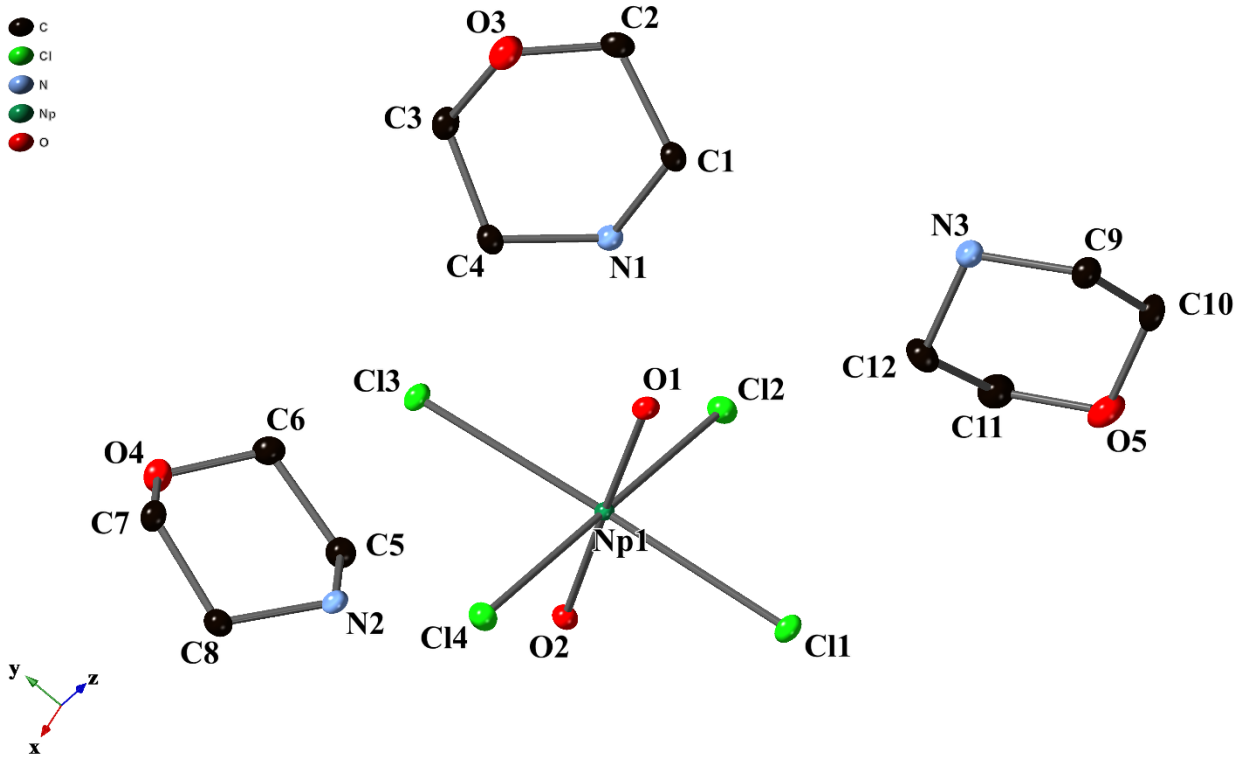

Figure S1. Thermal ellipsoid plots of **Np(V)morph** drawn at 50% probability.

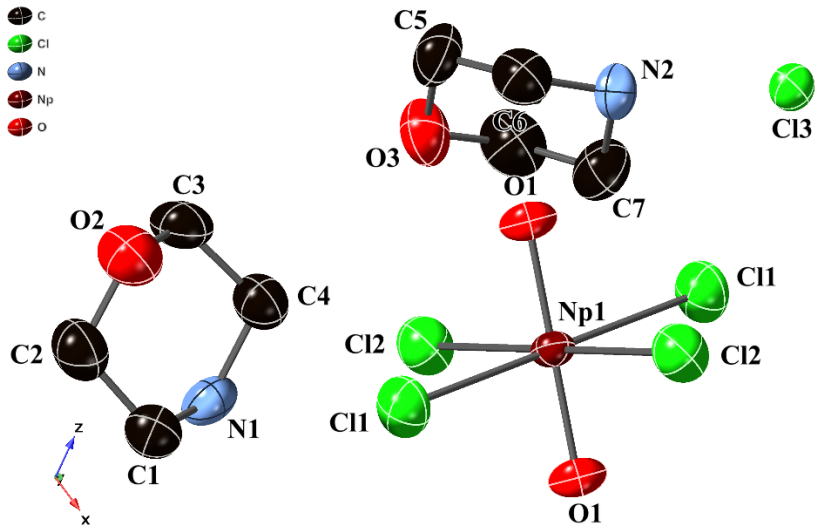

Figure S2. Thermal ellipsoid plots of **Np(VI)morph** drawn at 50% probability.

I. Vibrational Spectra of Stocks

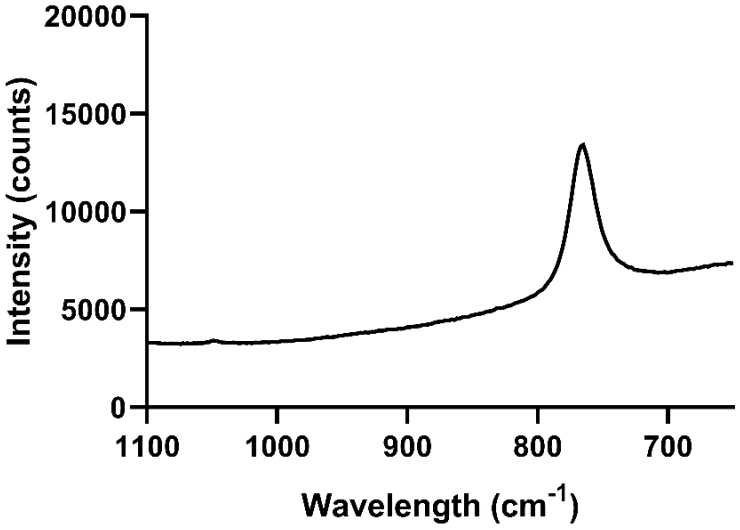

Figure S3. Solution state Raman spectra for Np(V) in 1M HCl stock.

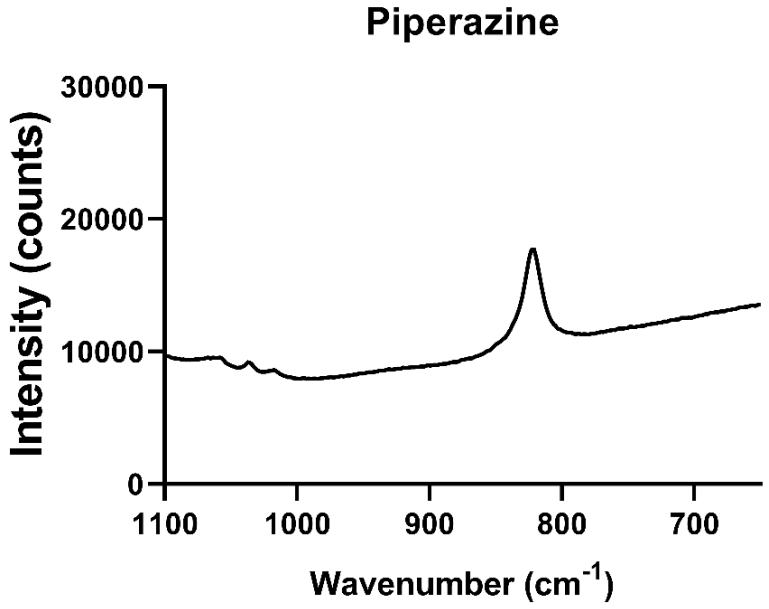

Figure S4. Solution state Raman spectra for piperazine.

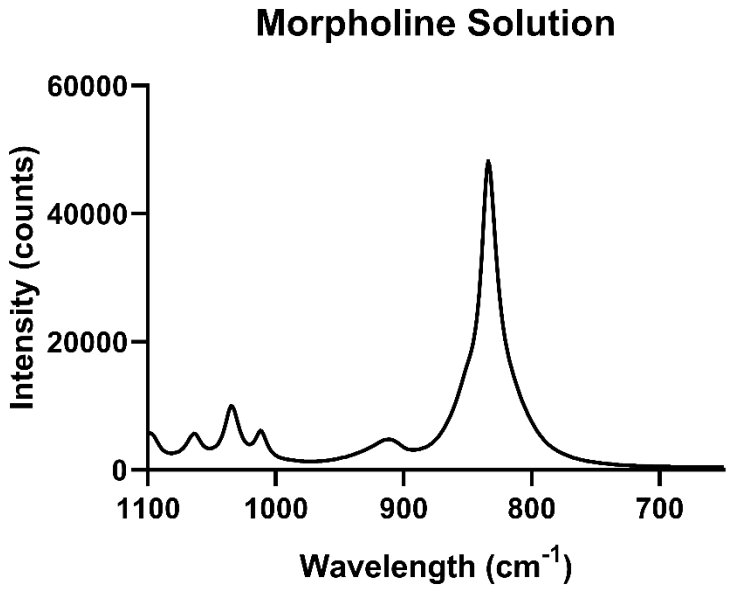

Figure S5. Solution state Raman spectra for morpholine.

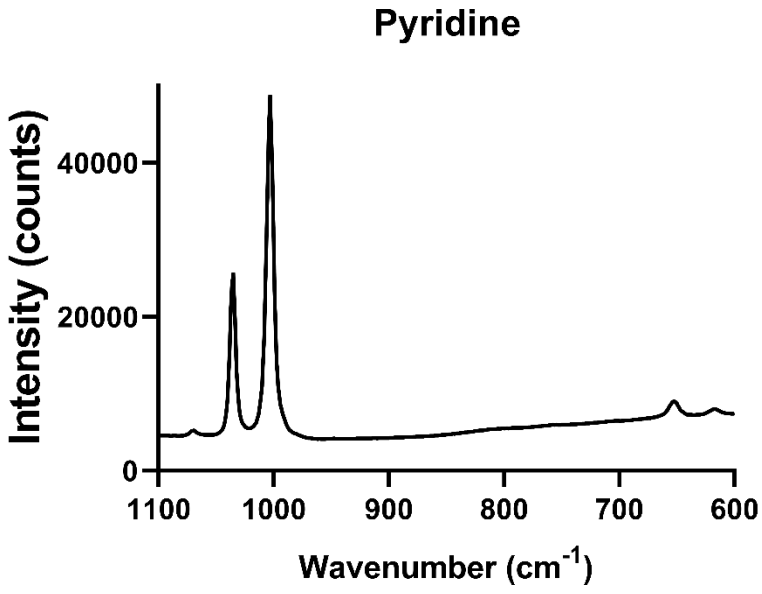

Figure S6. Solution state Raman spectra for pyridine.

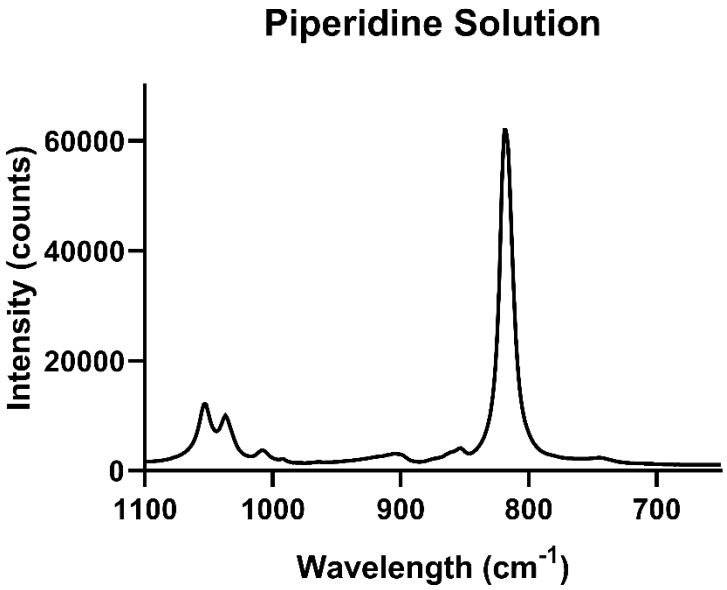

Figure S7. Solution state Raman spectra for piperidine.

II. Solid-state Raman Spectroscopy of Np Compounds

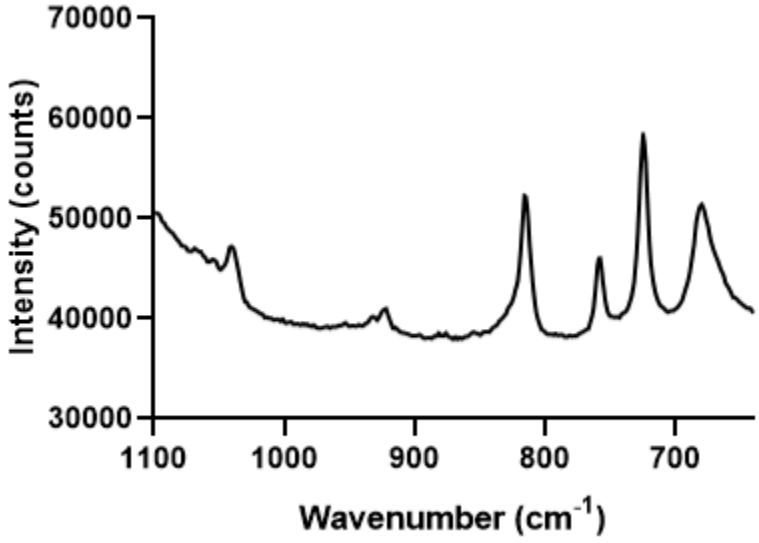

Figure S8. Solid state Raman spectra for compound **Np(V)pipz** containing Piperazine.

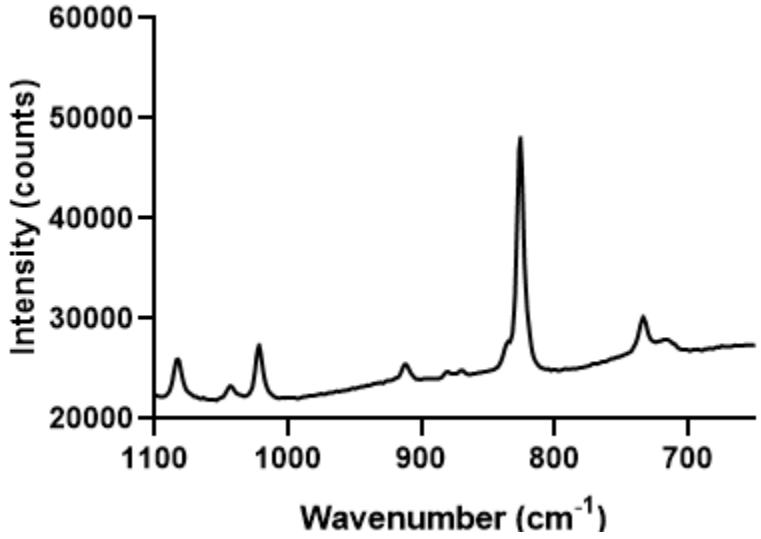

Figure S9. Solid state Raman spectra for **Np(V)morph** containing Morpholine.

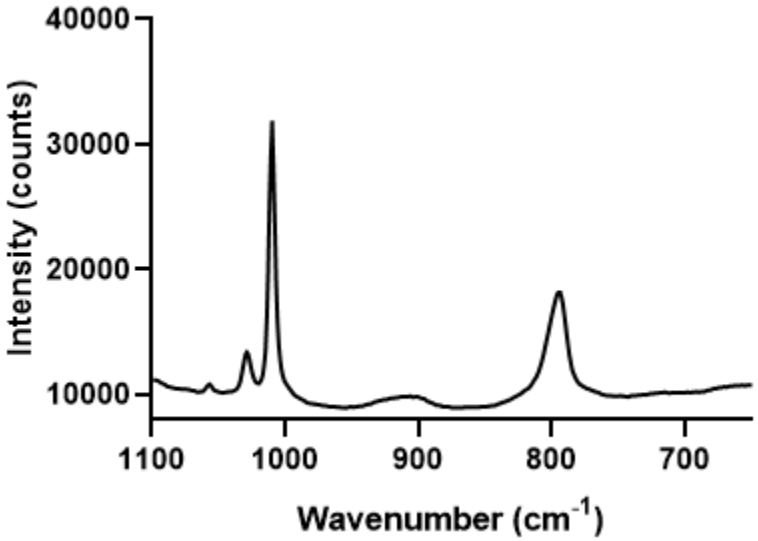

Figure S10. Solid state Raman spectra for compound **Np(VI)pyr** containing Pyridine.

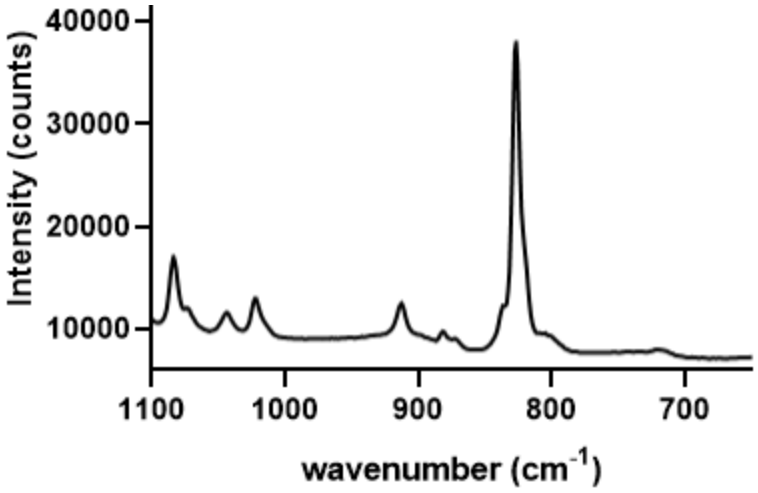

Figure S11. Solid state Raman spectra for **Np(VI)morph** containing morpholine.

Table S3: Spectral results from figure S8-S10, including the peaks and their associated peak centers, full width half maxes.

		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
Np 1	Peak Centroid	670 ± 2	680 ± 2	724 ± 2	758 ± 2	815 ± 2	823 ± 2
	FWHM	20 ± 0.6	12 ± 0.6	8 ± 0.6	6 ± 0.6	7 ± 0.6	18 ± 0.6
Np2	Peak Centroid	717 ± 2	734 ± 2	826 ± 2	836 ± 2	-	-
	FWHM	12 ± 0.6	9 ± 0.6	6 ± 0.6	4 ± 0.6	-	-
Np3	Peak Centroid	609 ± 2	636 ± 2	795 ± 2	-	-	-
	FWHM	6 ± 0.6	7 ± 0.6	17 ± 0.6	-	-	-
Np4	Peak Centroid	760 ± 2	770 ± 2	837 ± 2	-	-	-
	FWHM	5 ± 0.6	6 ± 0.6	5 ± 0.6	-	-	-

III. Solution Raman Spectroscopy of Np Heterocycles

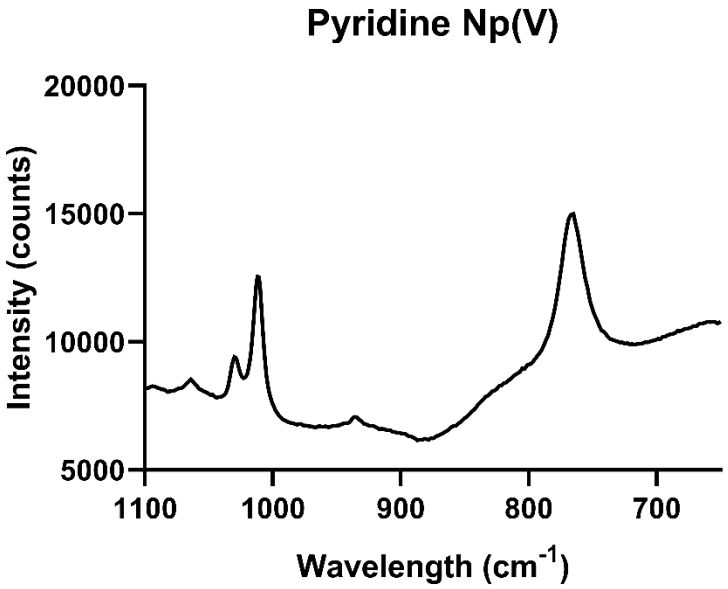

Figure S12. Solution state Raman spectra for Np(V) stock containing Pyridine.

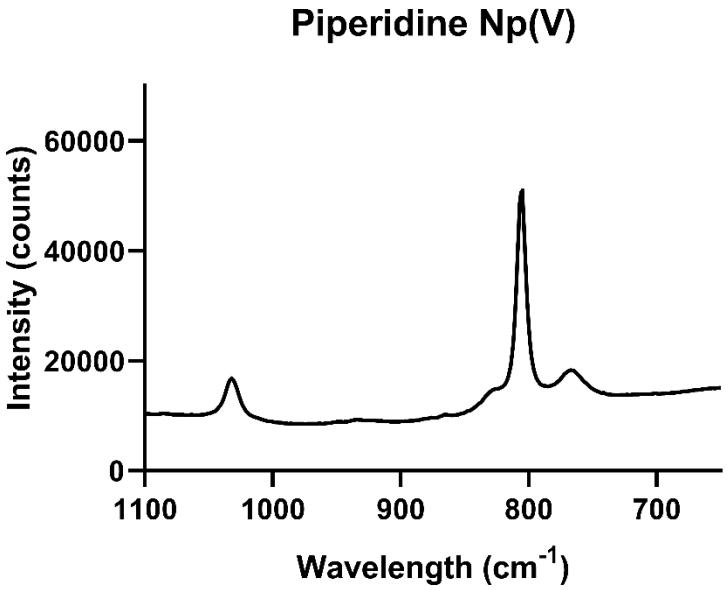

Figure S13. Solution state Raman spectra for Np(V) stock containing Piperidine.

Table S4. Raman band positions associated with the fitting of the Raman spectra from the Np-heterocycle solutions.

Raman Mode (cm^{-1})	Np(V)Piperazine	Np(V) Morpholine	Np(V) Pyridine	Np(V) Piperidine
	765	765	767	766
	815	823	805	805
	-	839	-	827
	-	875	-	-
	1044	1022	1011	1032
	1064	1046	1031	
		1077		

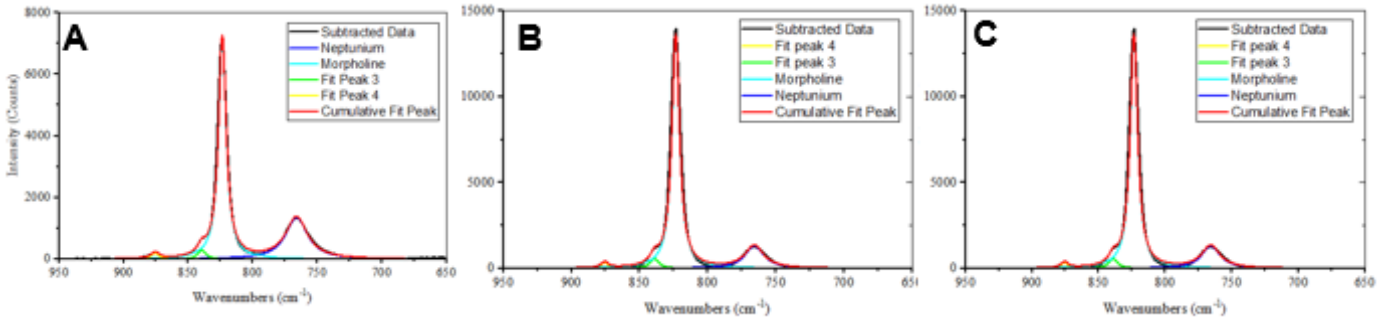

Figure S14. Peak fitting for morpholine titration experiments A (Np to morph 1:2), B (Np to morph 1:6) and C (Np to morph 1:8)

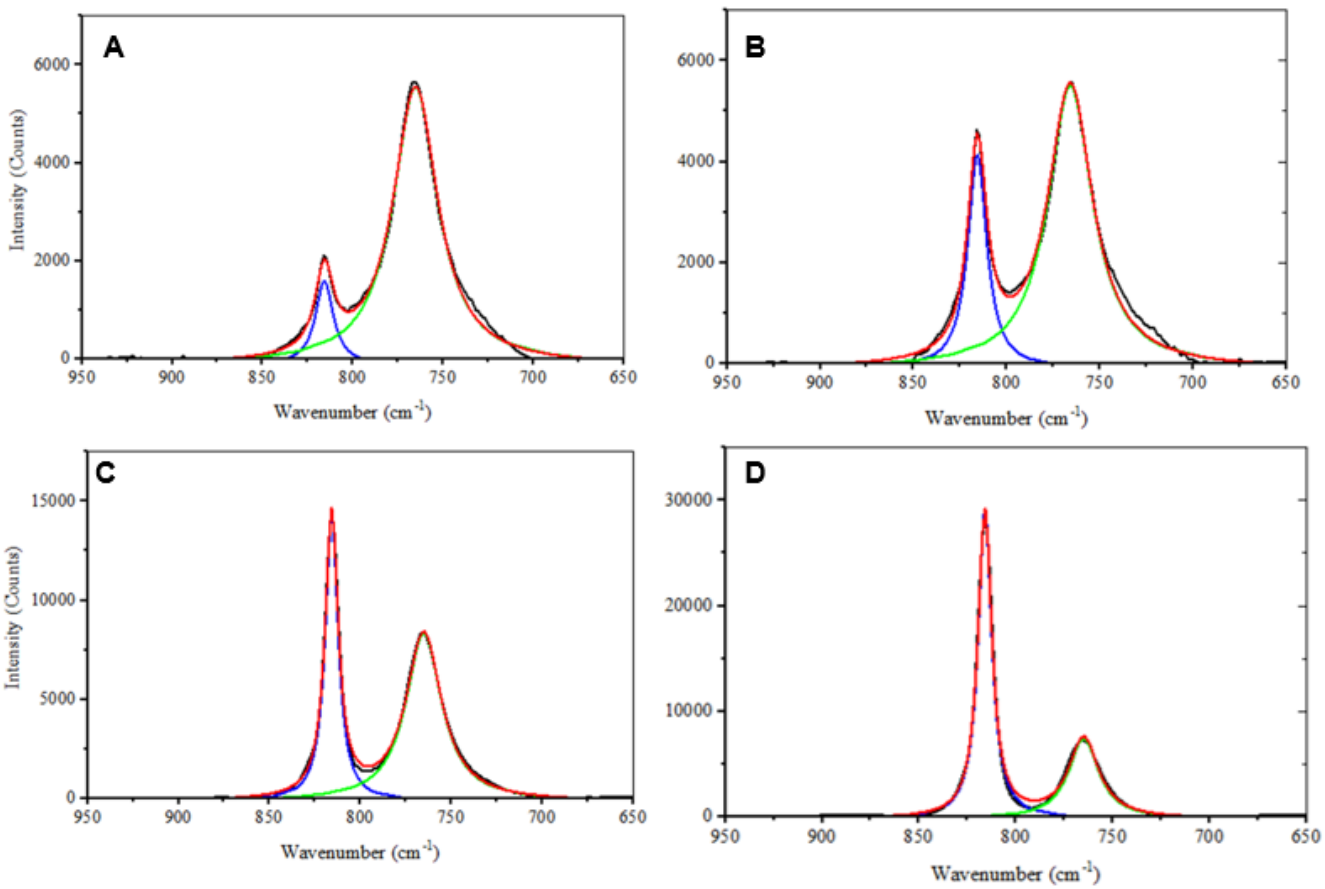

Figure S15. Peak fitting for piperazine titration experiments A (Np to Pipz 1:2), B (Np to Pipz 1:4), C (Np to Pipz 1:6), and D (Np to Pipz 1:9)

Table S5: The peak center, full width half max, and total area underneath the titration experiments for Np(V) piperazine, and Np(V) Morpholine.

Piperazine	**Center**	**FWHM**	**Area**
Np:Pipz 1:2	815 765	12. 30.	31787 249642
Np:Pipz 1:4	815 765	12.5 29.3	80775. 241147.
Np:Pipz 1:6	815. 765	8. 23	193276. 300480.
Np:Pipz 1:9	815 764	8. 18.	389697. 215567
Morpholine	**Peak center**	**FWHM**	**Area**
Np:Morph 1:2	875 839 823	7.5 7.5 7.3	2299 3440 81682

	766	20.4	41518
Np:Morph 1:6	875 839 823 765	6.5 8 7 17	3435 7068 147716 33669
Np:Morph 1:8	875 839 823 765	7.5 7.5 7.3 14	7829 10320 280538 24219

IV. Details on Computational Analysis

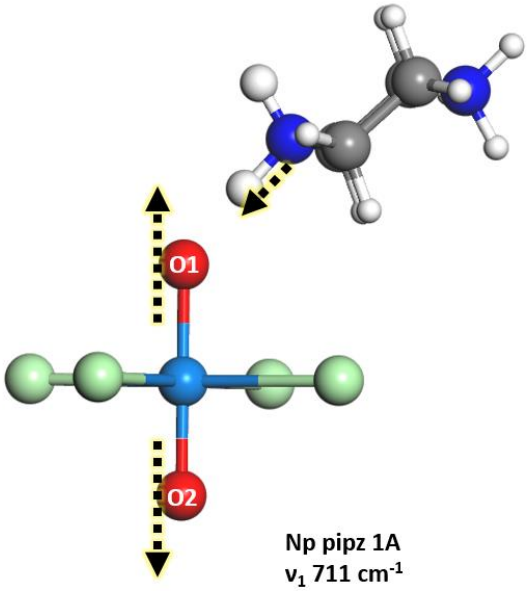

Figure S16. Example of the **NP pipz 1A** computational model which shows the concerted motions of Np=O stretch and NH_2 motions.

a. XYZ Coordinates of DFT-Optimized Structures

$[NpO_2Cl_4]^{3-}$

Np	-0.0000318	-0.0002877	-0.0000670	Cl	-0.0296995	-2.7957120	-0.4139549
Cl	-0.5015225	0.4209561	-2.7483018	O	-1.7865627	-0.0265642	0.3141238
O	1.7865493	0.0259561	-0.3136038	Cl	0.0299151	2.7964836	0.4133047
Cl	0.5013522	-0.4208319	2.7484991				

$[NpO_2Cl_4]$-1APipz (Long Pip)

N	2.2217106	-1.1223717	-1.4598314	H	1.8121168	0.8502382	1.3026734
H	2.5114927	-0.4215675	-2.1462156	H	1.8800283	1.4152620	-0.3716958
H	2.7868979	-1.9494427	-1.6595999	C	2.5232980	-0.6330288	-0.0700152
N	0.2119316	0.2277783	0.0791736	H	3.5750074	-0.3623616	-0.0297132
H	-0.4189265	1.0436615	0.3198584	H	2.3440520	-1.4679958	0.6046710
H	-0.1070492	-0.4792286	0.7730667	Np	-3.1473369	1.1702687	1.7834446
C	0.7655941	-1.4510606	-1.6474980	Cl	-4.6153819	3.4780259	1.2781240
H	0.5482350	-2.3016071	-1.0035146	Cl	-3.9530373	0.0755799	-0.6640060
H	0.6174595	-1.7428241	-2.6837406	Cl	-2.2297610	2.1598566	4.2150128
C	-0.0883461	-0.2479621	-1.3042673	Cl	-1.5928250	-1.2035397	2.2104922
H	0.0965527	0.5815464	-1.9858805	O	-4.5627479	0.4167332	2.6128425
H	-1.1447918	-0.5082903	-1.3516709	O	-1.6867773	1.9105770	0.9323349
C	1.6526046	0.5617530	0.2659548				

$[NpO_2Cl_4]$-1BPipz (Short Pip)

N	-1.8014701	1.2144320	1.6768841	Cl	4.2096425	-3.0502267	-0.9830966
H	-1.0584588	1.9079669	1.7931177	O	1.4462333	-1.2913953	-1.6156703
H	-2.5746804	1.5444381	2.2571584	O	4.8217008	-0.0717247	-2.3315593
C	-0.2164056	-0.6499254	1.2944602	N	-0.6342150	-0.6925759	-0.1408709
H	0.6801618	-0.0302951	1.3467452	H	-1.3607735	-1.3974122	-0.2753638
H	0.0468243	-1.6585478	1.6037786	H	0.2089336	-0.9896786	-0.7434595
C	-1.3348310	-0.1264023	2.1729185	C	-2.2362912	1.1653657	0.2383765
H	-2.2025286	-0.7837923	2.1643120	H	-3.1166284	0.5265794	0.1965769
H	-0.9894636	-0.0050471	3.1962064	H	-2.5109593	2.1719069	-0.0656561
Np	3.1531803	-0.6705959	-1.9756154	C	-1.1121514	0.6365993	-0.6292587
Cl	2.0694381	1.7167543	-2.9384930	H	-0.2510458	1.3051519	-0.6363183
Cl	2.9728776	-1.7859615	-4.5318953	H	-1.4632777	0.5205196	-1.6515086
Cl	3.2541881	0.4938666	0.5782312				

NpO_2Cl_4-2Pipz

N	5.5107435	-2.1692555	-2.7883066	H	3.8721919	-3.3760152	-2.2820564
H	5.8197189	-1.5621412	-3.5514304	H	4.0518712	-3.0712957	-4.0182567
H	6.1351225	-2.9773987	-2.8134436	C	3.1503034	-1.4379638	-2.9477458
N	3.3014130	-0.7304490	-1.6381633	H	3.3476235	-0.7117476	-3.7344641
H	2.6309090	0.0899438	-1.6025554	H	2.1186850	-1.7722768	-3.0363721
H	2.9516283	-1.3327929	-0.8780407	C	4.7054637	-0.2863996	-1.3929705
C	4.0961426	-2.6185715	-3.0312644	H	4.7591806	0.1631236	-0.4041250

H	4.9402059	0.4741412	-2.1360138
C	5.6638154	-1.4580213	-1.4721828
H	6.6913443	-1.1129716	-1.3935884
H	5.4725969	-2.1922850	-0.6920252
N	-4.7320813	2.0347765	3.6650496
H	-4.0258324	2.7738046	3.7044132
H	-5.3955951	2.2523864	4.4105381
C	-3.1380259	0.3406313	2.8130148
H	-2.2905284	1.0248699	2.7554880
H	-2.7581442	-0.6662496	2.9680800
C	-4.0946369	0.6992194	3.9320876
H	-4.9036853	-0.0228405	4.0271596
H	-3.5618533	0.7637753	4.8772042
Np	-0.3291664	0.6353648	-0.9300323
Cl	-1.3130395	3.0122252	-1.9151109
Cl	-0.6167000	-0.5676757	-3.4057382
Cl	-0.0223081	1.7986703	1.5639473
Cl	0.7608065	-1.7674779	0.0297866
O	-2.0333666	0.1133244	-0.4690300
O	1.3829305	1.1322018	-1.3878471
N	-3.8245887	0.3830064	1.4824928
H	-4.5148024	-0.3673485	1.4185993
H	-3.1102249	0.2120909	0.7105455
C	-5.4371498	2.0681433	2.3381736
H	-6.2664325	1.3659379	2.4028501
H	-5.8296288	3.0704473	2.1885883
C	-4.4752950	1.7060378	1.2250195
H	-3.6765638	2.4408821	1.1255224
H	-5.0130471	1.6461734	0.2822032

NpO_2Cl_2-3Pipz

N	2.5285188	-5.4664634	-2.0627774
H	3.1979888	-4.9826577	-2.6664435
H	2.7584922	-6.4587367	-2.1437275
N	0.9192306	-3.3547691	-0.9699857
H	0.6200092	-2.3595495	-0.8573161
H	0.2220423	-3.8464433	-0.3706857
C	1.1285507	-5.2369980	-2.5594407
H	0.4762408	-5.8953185	-1.9882917
H	1.0907117	-5.5218563	-3.6073455
C	0.7449109	-3.7802971	-2.3936423
H	1.3632798	-3.1320164	-3.0138776
H	-0.2983855	-3.6408286	-2.6688361
C	2.3138175	-3.5719688	-0.4792295
H	2.3590722	-3.2918687	0.5707689
H	2.9707093	-2.9124659	-1.0450887
C	2.7101772	-5.0263736	-0.6368373
H	3.7551995	-5.1636669	-0.3727435
H	2.0984769	-5.6831442	-0.0212063
Np	-2.0909990	-1.1483472	0.3884726
Cl	-2.3673012	1.6586190	0.2373180
Cl	-3.3080869	-1.4830641	-2.0387854
Cl	-0.7844392	-0.8010736	2.8720488
Cl	-1.6694348	-3.9077255	0.6597406
O	-3.6513954	-1.2940923	1.2598257
O	-0.4683776	-0.9868652	-0.5341283
N	-0.1591873	3.4903995	-3.7016106
H	0.1128401	4.1601341	-4.4237123
H	-0.7924876	4.0016234	-3.0819316
N	-0.4313189	3.0596143	5.8041652
H	-0.6186005	4.0645142	5.8451744
H	-0.0543556	2.8162104	6.7220972
C	-0.8818005	2.3343879	-4.3364549
H	-0.2202469	1.9270741	-5.0990005
H	-1.7796050	2.7191746	-4.8126573
C	0.0409337	3.0608956	3.3711777
H	-0.1941138	4.1164566	3.2432148
H	0.7650417	2.7689318	2.6141279
C	1.0607988	3.0495168	-2.9423401
H	1.4924983	3.9222707	-2.4596980
H	1.7667099	2.6610500	-3.6741221
C	0.6003208	2.7704633	4.7496916
H	0.8839455	1.7251918	4.8611521
H	1.4672635	3.3957661	4.9453176
N	-0.0272552	0.8538091	-2.5397780
H	-0.2857656	0.1559308	-1.7909655
H	0.6044181	0.3688409	-3.1795688
N	-1.2184356	2.2837137	3.1544220
H	-1.0121438	1.2567049	3.1557926

H	-1.6009583	2.4496844	2.2073227	C	-1.2488769	1.3028015	-3.2897835
C	0.6896708	2.0096890	-1.9042717	H	-1.6986588	0.4340066	-3.7626918
H	0.0204214	2.4101110	-1.1435590	H	-1.9455236	1.6957721	-2.5508999
H	1.5907143	1.6340499	-1.4257038	C	-2.2537027	2.5945008	4.1897539
C	-1.7128144	2.3065352	5.5759092	H	-2.5326909	3.6406516	4.0736815
H	-1.4908387	1.2498970	5.7161594	H	-3.1278932	1.9757179	4.0003449
H	-2.4273120	2.6218796	6.3314586				

NpO_2Cl_4-4Pipz

N	4.1928635	-4.4701144	-1.6539485	O	0.6085248	-0.3479499	-0.3414514
H	4.7989783	-3.8746972	-2.2239706	N	-5.1693185	-1.3506574	1.3740671
H	4.6085736	-5.4025744	-1.6996665	H	-5.8851895	-1.8920363	0.8846573
N	2.1539048	-2.6687419	-0.7162650	H	-4.3636604	-1.2492986	0.7045405
H	1.7010802	-1.7273265	-0.6572038	C	-6.8420228	-0.0981205	2.7043322
H	1.5046627	-3.2544031	-0.1610252	H	-7.6926476	-0.6313068	2.2841860
C	2.8096316	-4.5077592	-2.2405880	H	-7.1621006	0.8916795	3.0185591
H	2.2522007	-5.2658392	-1.6936028	C	-5.6985957	0.0078979	1.7161412
H	2.8912637	-4.8086199	-3.2814839	H	-4.8663364	0.5840418	2.1205246
C	2.1601023	-3.1434207	-2.1388240	H	-6.0442217	0.4847820	0.8025880
H	2.6958449	-2.4012941	-2.7294726	N	1.4585411	3.8032710	-4.7513562
H	1.1306482	-3.1903728	-2.4864612	H	1.9798704	4.2990813	-5.4771835
C	3.5276979	-2.6356609	-0.1233821	H	0.8782517	4.5154518	-4.3008219
H	3.4458286	-2.3607756	0.9258245	N	2.6022715	3.2623062	3.5816285
H	4.0935911	-1.8678919	-0.6490710	H	3.4570739	3.5096823	3.0763488
C	4.1933364	-3.9934820	-0.2293776	H	2.6445773	3.7855137	4.4583522
H	5.2245995	-3.9324969	0.1072050	C	0.5899152	2.7553026	-5.3882577
H	3.6704877	-4.7450135	0.3583085	H	1.2411077	2.1235202	-5.9891574
N	-6.4077632	-0.8580231	3.9269899	H	-0.1205100	3.2558555	-6.0406350
H	-5.7170691	-0.3143658	4.4503058	C	2.4602644	0.9809885	2.6044109
H	-7.2028980	-0.9647572	4.5599096	H	3.3532815	1.0628900	1.9867144
C	-4.7170587	-2.0898237	2.5962794	H	2.3020288	-0.0634921	2.8652729
H	-3.8689221	-1.5416576	3.0068867	C	2.4216455	3.2173409	-3.7599136
H	-4.3815906	-3.0793497	2.2966062	H	2.9681674	4.0328359	-3.2941746
C	-5.8517861	-2.2146435	3.5925222	H	3.1182767	2.5959731	-4.3192614
H	-6.6755454	-2.8061501	3.1970359	C	2.5844318	1.7908708	3.8808763
H	-5.4968406	-2.6695646	4.5133548	H	1.7491617	1.6132152	4.5554478
Np	-1.2379535	-0.6827780	-0.2953427	H	3.5106727	1.5388082	4.3903397
Cl	-1.5318252	1.9822083	-0.9169943	N	0.8228144	1.3696342	-3.3476905
Cl	-1.0837800	-1.2403944	-2.9760376	H	0.2980651	0.8456676	-2.6299551
Cl	-1.3501964	-0.0707560	2.4268353	H	1.4079767	0.6796851	-3.8244674
Cl	-0.7191085	-3.3289603	0.3071579	N	1.2915317	1.4367622	1.7839337
O	-3.0323969	-0.9948862	-0.2707791	H	0.3979506	1.1535852	2.2420448

H	1.2496816	0.8968990	0.8952747	C	-0.1490826	1.9653058	-4.3294899
C	1.6765369	2.4228665	-2.7062893	H	-0.7034756	1.1514004	-4.7889040
H	1.0087399	3.0482817	-2.1160022	H	-0.8367139	2.5829422	-3.7540546
H	2.3903750	1.9318860	-2.0491664	C	1.3103017	2.9088816	1.5048603
C	1.3965503	3.6931774	2.7969806	H	2.1652458	3.1116834	0.8607607
H	0.5279179	3.5275734	3.4315081	H	0.3951108	3.1641690	0.9743305
H	1.4864514	4.7555389	2.5878259				

V. Electrochemical analysis

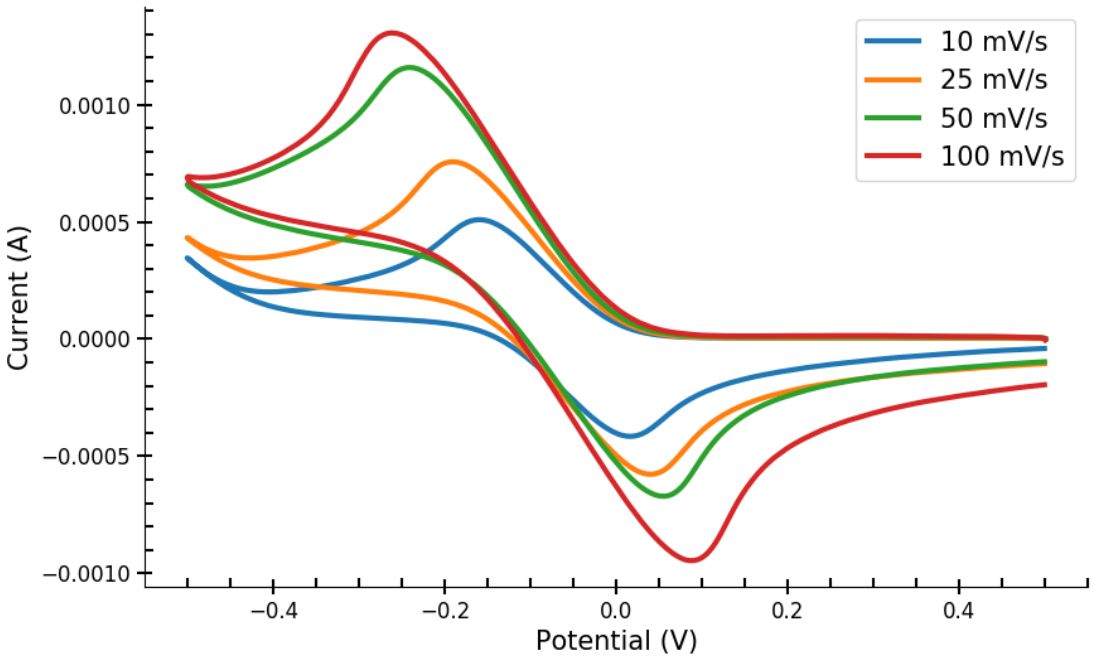

Figure S17. Overlay displaying varying scan rates of a 33.3mM $Np(V)O_2$ solution with added morpholine. The potential was measured against Ag|AgCl.

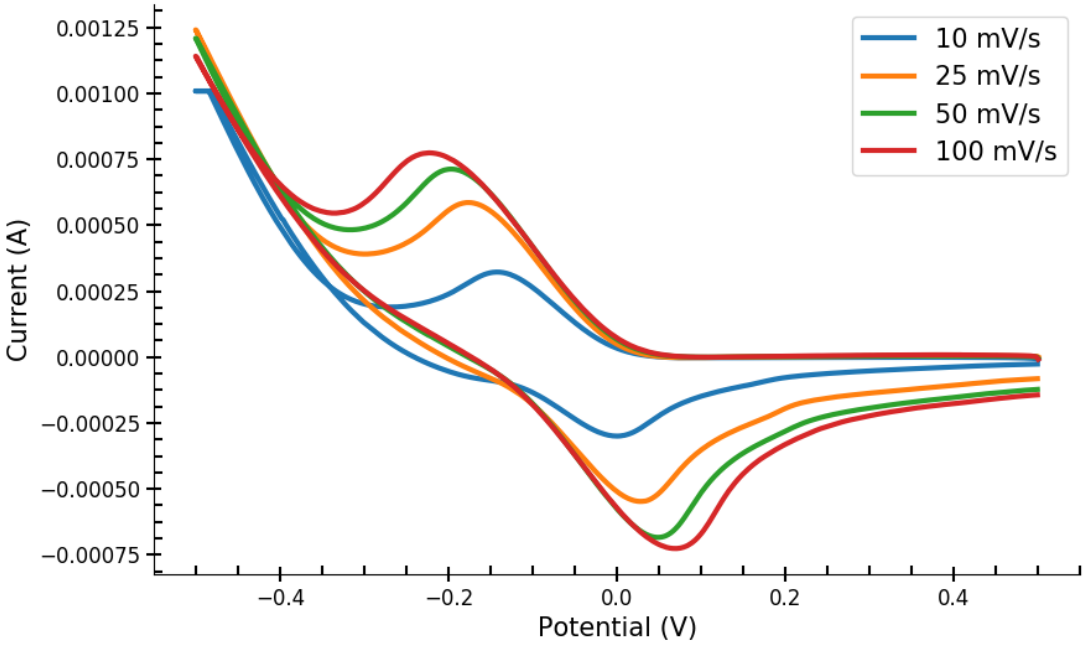

Figure S18. Overlay displaying varying scan rates of a 33.3mM $Np(V)O_2$ solution with added piperidine The potential was measured against Ag|AgCl.

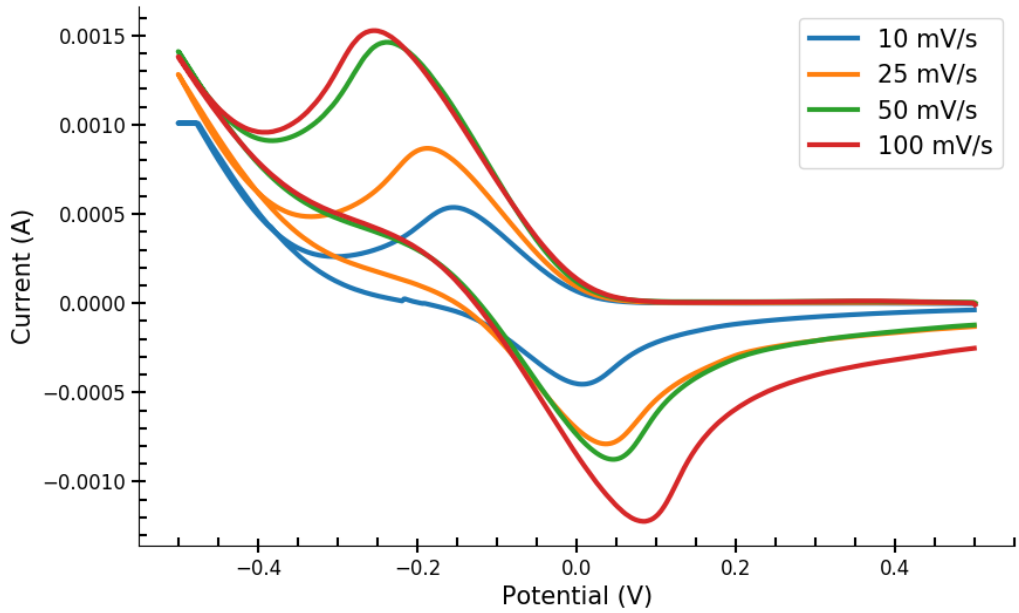

Figure S19. Overlay displaying varying scan rates of a 33.3mM $Np(V)O_2$ solution with added pyridine. The potential was measured against Ag|AgCl.

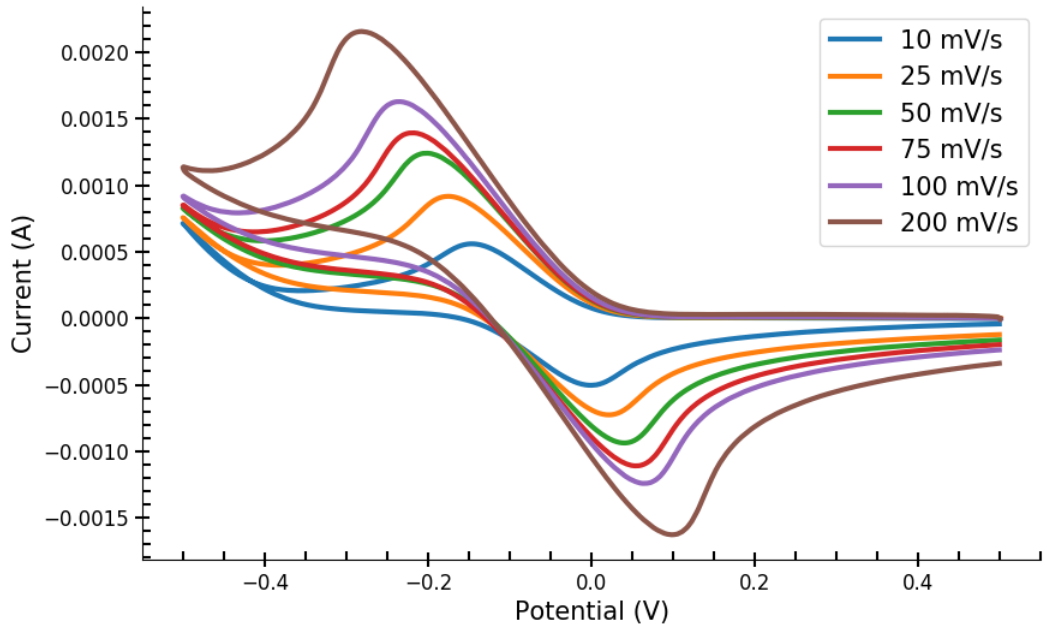

Figure S20. Overlay displaying varying scan rates of the 33.3mM $Np(V)O_2$ stock solution . The potential was measured against Ag|AgCl.