

Cation $\cdots\pi$ interaction and microhydration effects in complexes formed by pyrrolidinium cation and aromatic species in amino acid side chains

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Table S1. M062X/6-31+G* optimized geometries for the minima of non-hydrated complexes shown in Figure 1.

0H₂O

27
PB-1.xyz

C	1.691718	-1.147751	-0.674400
N	0.936821	0.139367	-0.911899
C	1.781737	1.284544	-0.364851
C	2.963540	0.599190	0.335553
C	2.477546	-0.832715	0.589571
H	0.972509	-1.964447	-0.597408
H	2.349806	-1.308592	-1.532060
H	1.144405	1.846933	0.319449
H	3.839953	0.590677	-0.318925
H	3.235805	1.123211	1.253145
H	1.818431	-0.876384	1.464553
H	3.294602	-1.539812	0.743570
H	2.072373	1.929718	-1.193876
H	0.043533	0.099901	-0.398988
H	0.692076	0.269603	-1.896840
H	-1.054228	0.846012	2.395135
C	-1.406586	0.471427	1.437957
C	-1.874644	1.362756	0.466649
C	-1.423087	-0.905009	1.189468
C	-2.354525	0.878190	-0.753311
H	-1.886180	2.429975	0.669440
C	-1.908158	-1.389185	-0.029831
H	-1.083498	-1.599109	1.953504
C	-2.371575	-0.497745	-1.001401
H	-2.738037	1.569555	-1.497987
H	-1.946949	-2.459488	-0.212509
H	-2.768144	-0.875536	-1.939330

27
PB-2.xyz

C	1.864757	-1.251174	-0.300738
N	0.901481	-0.076794	-0.344139
C	1.678056	1.192497	-0.029939
C	3.139766	0.760728	-0.103004
C	3.096048	-0.685458	0.399339
H	1.377102	-2.084795	0.205786
H	2.081862	-1.532018	-1.333182
H	1.390763	1.495414	0.979484
H	3.502953	0.799769	-1.135659
H	3.775586	1.407640	0.504073
H	2.968661	-0.714084	1.487024
H	3.992314	-1.255720	0.148504
H	1.383031	1.971609	-0.733315
H	0.133627	-0.202184	0.332434
H	0.429043	-0.013822	-1.250534
H	-1.729805	1.059506	2.312537
C	-1.850418	0.602070	1.334515
C	-1.965408	1.405131	0.195424
C	-1.927646	-0.790670	1.219120
C	-2.161265	0.816657	-1.056909
H	-1.931471	2.486968	0.288607
C	-2.119900	-1.378679	-0.035853
H	-1.869158	-1.412826	2.107819
C	-2.238240	-0.574698	-1.172542
H	-2.283346	1.442012	-1.937173
H	-2.206695	-2.458057	-0.121825
H	-2.419335	-1.030287	-2.142084

28
PP-1.xyz

N	-3.140476	-2.223153	-2.532875
C	-4.534235	-2.728015	-2.879342
C	-3.051946	-2.066659	-1.021256
H	-2.921308	-1.318676	-2.985604
H	-2.420922	-2.873871	-2.858619

C	-5.313316	-2.598472	-1.572413
H	-4.925476	-2.142924	-3.711622
H	-4.434468	-3.770122	-3.188074
C	-4.246835	-2.859242	-0.504858
H	-3.150020	-0.999153	-0.810845
H	-2.069182	-2.404706	-0.688473
H	-4.007723	-3.927086	-0.448508
H	-4.544951	-2.526746	0.491229
H	-5.724583	-1.588853	-1.467554
H	-6.143328	-3.306464	-1.535157
C	1.349948	-1.403049	-0.924877
C	0.996538	-1.989342	-2.139866
C	0.686802	-0.254868	-0.492031
H	2.149636	-1.826972	-0.326747
C	-0.022579	-1.438296	-2.917171
H	1.530330	-2.864161	-2.498678
C	-0.344028	0.297046	-1.251949
H	0.967910	0.215727	0.445057
C	-0.689281	-0.304748	-2.458604
H	-0.268422	-1.842682	-3.896692
H	-0.870359	1.185361	-0.909490
O	-1.763871	0.136700	-3.217401
H	-1.896439	1.092170	-3.114897

28
PP-2.xyz

N	-0.549201	-0.739275	-0.794512
C	0.350600	-1.679228	-0.014588
C	-1.988442	-0.965500	-0.333620
H	-0.468966	-0.946149	-1.800073
H	-0.260104	0.235075	-0.679776
C	-0.604208	-2.776342	0.435085
H	1.164648	-1.997893	-0.667087
H	0.752367	-1.120482	0.833650
C	-1.871206	-1.993481	0.792801
H	-2.539232	-1.353073	-1.193119
H	-2.415015	-0.008527	-0.032850
H	-1.751995	-1.495488	1.760537
H	-2.761996	-2.622275	0.843851
H	-0.795768	-3.473394	-0.388589
H	-0.197325	-3.341577	1.275730
C	0.937156	-1.383694	-3.793939
C	0.302883	-2.582200	-3.448141
C	0.161136	-0.272026	-4.126987
H	2.020243	-1.326719	-3.832505
C	-1.088424	-2.668313	-3.422238
H	0.894679	-3.463869	-3.216813
C	-1.234496	-0.344358	-4.102344
H	0.639092	0.658603	-4.418504
C	-1.858071	-1.547413	-3.756667
H	-1.597024	-3.597335	-3.181036
H	-1.833550	0.523498	-4.368829
O	-3.206748	-1.683779	-3.669806
H	-3.665216	-0.955807	-4.116944

28
PP-3.xyz

N	-2.119982	0.892986	0.124470
C	-1.791854	0.076413	1.365797
C	-2.326500	-0.073137	-1.037888
H	-1.335573	1.539720	-0.088419
H	-2.950049	1.470187	0.277366
C	-1.366805	-1.276909	0.809991
H	-1.025032	0.602710	1.935479
H	-2.706456	0.003324	1.958404
C	-2.293851	-1.458967	-0.395634
H	-1.491609	0.080681	-1.722555
H	-3.259507	0.175109	-1.544187
H	-3.296552	-1.756336	-0.071325
H	-1.930339	-2.208476	-1.101399
H	-0.316715	-1.250609	0.498419
H	-1.483983	-2.062970	1.558678
C	2.584030	-1.302249	0.050272
C	2.003378	-0.985926	-1.177591
C	2.455809	-0.423602	1.126555
H	3.149464	-2.221432	0.164025
C	1.284904	0.199750	-1.331364
H	2.124643	-1.652884	-2.025717

C 1.728976 0.758625 0.988259
H 2.922297 -0.655353 2.079098
C 1.146625 1.052746 -0.241583
H 0.861494 0.486316 -2.290219
H 1.622236 1.446647 1.824377
O 0.333383 2.173797 -0.406548
H 0.740203 2.961625 -0.011815

28

PP-4.xyz

C -1.76288 -1.22031 -0.80983
N -1.06036 -1.15693 0.53260
C -1.75410 -0.08806 1.37405
C -2.86058 0.46325 0.46953
C -2.35422 0.17497 -0.94736
H -1.03468 -1.50619 -1.56976
H -2.54101 -1.98366 -0.73349
H -0.99669 0.66066 1.60881
H -3.80417 -0.05950 0.65470
H -3.02141 1.52715 0.65221
H -1.58102 0.89660 -1.23568
H -3.14737 0.19998 -1.69724
H -2.10996 -0.54454 2.29773
H -0.07253 -0.89992 0.38814
H -1.05376 -2.06789 0.99832
H 2.86941 -2.30175 0.26330
C 2.38566 -1.34027 0.12589
C 1.88650 -0.97310 -1.12757
C 2.29235 -0.44027 1.19004
C 1.27942 0.26871 -1.31422
H 1.98541 -1.65065 -1.97108
C 1.68598 0.80590 1.01554
H 2.70009 -0.70118 2.16226
C 1.17619 1.15755 -0.23886
H 0.90833 0.58081 -2.28648
H 1.62339 1.50618 1.84614
O 0.51440 2.32491 -0.46619
H 0.73740 2.99305 0.20015

28

PP-5.xyz

N 1.443738 -0.214620 0.190633
C 2.107672 0.826172 -0.705138
C 2.527266 -0.898334 0.999988
H 0.888220 -0.882033 -0.375414
H 0.759582 0.240728 0.803251
C 3.606934 0.642719 -0.461404
H 1.789123 0.648712 -1.733000
H 1.752441 1.806175 -0.381801
C 3.676553 0.100574 0.969133
H 2.784784 -1.821089 0.475241
H 2.137354 -1.140060 1.989139
H 3.511100 0.900080 1.700062
H 4.629942 -0.378049 1.200642
H 4.023151 -0.084584 -1.165579
H 4.145089 1.583499 -0.590643
C -3.333910 1.017255 0.774344
C -2.385784 1.587631 -0.073714
C -3.398062 -0.369180 0.907775
H -4.027343 1.648680 1.319723
C -1.502217 0.777463 -0.787276
H -2.346866 2.665017 -0.202476
C -2.510912 -1.190457 0.212748
H -4.139763 -0.819494 1.560055
C -1.573830 -0.605144 -0.633350
H -0.798861 1.199537 -1.501038
H -2.553696 -2.271361 0.324617
O -0.623401 -1.359107 -1.310660
H -0.955480 -2.252759 -1.490566

28

PP-6.xyz

N 1.058592 -0.832842 -0.274522
C 1.817704 -0.948146 1.025625
C 2.014210 -0.284121 -1.327643
H 0.280814 -0.168689 -0.147793
H 0.632391 -1.719301 -0.558268
C 2.831978 0.179810 0.907162
H 1.108649 -0.866617 1.850752

H 2.300539 -1.928566 1.042003
C 3.291968 0.065142 -0.551269
H 1.528394 0.587558 -1.769312
H 2.156902 -1.041656 -2.098067
H 4.029298 -0.736450 -0.653438
H 3.742599 0.985361 -0.926724
H 2.344654 1.144397 1.091778
H 3.648168 0.066964 1.622867
C -0.807346 1.883153 0.220867
C -1.226425 1.449578 -1.043666
C -1.135545 1.122227 1.345568
H -0.268342 2.818988 0.329999
C -1.944692 0.264801 -1.187027
H -1.006610 2.048187 -1.923343
C -1.857848 -0.067036 1.215338
H -0.842763 1.460273 2.335854
C -2.268789 -0.492720 -0.053033
H -2.295173 -0.074948 -2.156832
H -2.123801 -0.645666 2.097263
O -2.955770 -1.640736 -0.261978
H -3.290993 -2.010169 0.569219

31

PI-1.xyz

H 2.090440 -1.318848 -1.871815
N 0.763274 1.365794 0.247019
C -0.659308 1.492947 0.789047
C 0.799030 2.005806 -1.126345
H 1.051491 0.376621 0.168254
H 1.428666 1.824904 0.873081
C -1.441887 2.169452 -0.337820
H -1.018435 0.494972 1.047029
H -0.607355 2.109883 1.687786
C -0.379844 2.969147 -1.098706
H 0.641248 1.197034 -1.844989
H 1.779622 2.453877 -1.289727
H -0.115223 3.886796 -0.560937
H -0.692892 3.246022 -2.107222
H -1.888222 1.410635 -0.987941
H -2.244586 2.793533 0.059589
N 1.582463 -2.097043 1.280898
C 0.273695 -1.998535 0.857126
C 2.427688 -1.831635 0.229089
H 1.877917 -2.422131 2.191379
C 0.302622 -1.634500 -0.513748
C -0.924954 -2.187504 1.558980
C -0.916591 -1.449287 -1.195660
C 1.690633 -1.527561 -0.888407
C -2.102958 -1.634658 -0.505604
H -0.923606 -1.199720 -2.254090
C -2.106045 -2.001112 0.858909
H -3.050491 -1.518067 -1.022919
H -3.053728 -2.153023 1.365908
H -0.929710 -2.481864 2.604470
H 3.499528 -1.900390 0.355783

31

PI-2.xyz

H -0.787534 -1.943690 -2.242440
N 1.653629 0.584513 0.783926
C 1.841976 -0.917020 0.987747
C 2.515233 1.009824 -0.386355
H 1.871637 1.118045 1.628974
H 0.667851 0.787867 0.562149
C 2.809786 -1.341476 -0.121678
H 2.216367 -1.086428 1.997594
H 0.858900 -1.378493 0.880372
C 2.628556 -0.270115 -1.201662
H 3.483299 1.321615 0.013414
H 2.029308 1.848769 -0.886484
H 1.704754 -0.441392 -1.764765
H 3.461876 -0.225879 -1.905444
H 3.840804 -1.341583 0.245607
H 2.575258 -2.345992 -0.478906
N -1.730784 -1.693978 0.898114
C -1.558541 -0.361227 0.604987
C -1.445385 -2.447864 -0.219921
H -2.124521 -2.058233 1.754837

C -1.124641 -0.281562 -0.746293
C -1.717018 0.775744 1.410373
C -0.870251 0.987161 -1.304013
C -1.053506 -1.627635 -1.243197
C -1.031356 2.116780 -0.512797
H -0.571153 1.080318 -2.345207
C -1.447445 2.010760 0.834730
H -0.860226 3.101413 -0.937632
H -1.580576 2.913203 1.423269
H -2.058325 0.697671 2.438838
H -1.556786 -3.523214 -0.195864

31
PI-3.xyz

H 0.978889 -2.017090 2.209358
N -1.717814 -1.216890 -0.174663
C -1.803825 -0.315493 -1.393188
C -2.370853 -0.490536 0.998921
H -0.732288 -1.417153 0.068033
H -2.159038 -2.122480 -0.350559
C -1.967186 1.069639 -0.786909
H -0.907189 -0.458701 -1.997184
H -2.688376 -0.618905 -1.958525
C -2.901425 0.812795 0.398606
H -1.580374 -0.315546 1.730862
H -3.133557 -1.136475 1.433928
H -3.934477 0.687430 0.058289
H -2.881594 1.618206 1.135346
H -0.998474 1.448745 -0.444357
H -2.378467 1.775271 -1.511519
N 1.645845 -1.496339 -0.969079
C 1.548679 -0.187781 -0.535329
C 1.440344 -2.347620 0.095646
H 2.001433 -1.783906 -1.870991
C 1.220623 -0.223588 0.842326
C 1.728145 1.013296 -1.235603
C 1.065028 0.991788 1.538581
C 1.152020 -1.614312 1.220151
C 1.250275 2.180290 0.853985
H 0.837725 0.992990 2.601535
C 1.580260 2.189847 -0.520285
H 1.157791 3.124854 1.380767
H 1.731714 3.140377 -1.022147
H 1.999337 1.022631 -2.287626
H 1.538218 -3.417592 -0.030420

31
PI-4.xyz

H -1.582325 2.178772 1.993119
N 1.535734 -1.154009 0.467486
C 1.849031 0.017592 1.377625
C 2.244390 -0.922208 -0.863250
H 0.516370 -1.217712 0.319694
H 1.808179 -2.042961 0.894422
C 2.175453 1.129461 0.392309
H 0.987610 0.200537 2.020610
H 2.717712 -0.259965 1.979563
C 2.993686 0.399284 -0.676562
H 1.462632 -0.855180 -1.621268
H 2.882594 -1.779440 -1.078099
H 4.012942 0.217200 -0.320923
H 3.058920 0.949787 -1.616956
H 1.249279 1.539129 -0.027920
H 2.723116 1.942096 0.873589
N -1.161294 1.605608 -1.218349
C -1.292718 0.312114 -0.770231
C -1.280626 2.471354 -0.151858
H -1.135638 1.888416 -2.188329
C -1.471557 0.372372 0.638829
C -1.288791 -0.901777 -1.472881
C -1.655850 -0.828102 1.353297
C -1.450913 1.760834 1.004808
C -1.650234 -2.032520 0.662628
H -1.825533 -0.808048 2.426637
C -1.466845 -2.068151 -0.740588
H -1.816172 -2.962400 1.198032
H -1.492435 -3.022831 -1.257111
H -1.180406 -0.930328 -2.554021

H -1.238080 3.540220 -0.309759

31
PI-5.xyz

H -2.329193 -1.242320 -2.453796
N 1.296296 -0.191680 -0.096091
C 2.030237 -1.087434 0.882827
C 2.319229 0.453141 -1.017496
H 0.759041 0.536410 0.400280
H 0.587651 -0.712006 -0.625203
C 3.482904 -0.637195 0.767653
H 1.579327 -0.971086 1.869147
H 1.899613 -2.116973 0.542977
C 3.614715 -0.297294 -0.719875
H 2.379043 1.506066 -0.733508
H 1.962634 0.382254 -2.045221
H 3.677274 -1.211812 -1.319425
H 4.489652 0.315061 -0.945636
H 3.660919 0.250730 1.384384
H 4.170583 -1.419620 1.094044
N -2.302342 -1.367426 0.831939
C -1.797126 -0.102393 0.648283
C -2.562193 -1.938253 -0.393725
H -2.539670 -1.780460 1.723207
C -1.731975 0.123768 -0.754693
C -1.357646 0.848382 1.580336
C -1.236291 1.356196 -1.224269
C -2.215224 -1.068632 -1.393023
C -0.801502 2.301311 -0.306289
H -1.208047 1.566267 -2.290178
C -0.856393 2.047582 1.084960
H -0.434745 3.262156 -0.654411
H -0.528660 2.814803 1.779899
H -1.425152 0.668388 2.649803
H -2.990354 -2.929183 -0.455435

Table S2. M062X/6-31+G* optimized geometries for the minima of monohydrated complexes shown in Figure 3.

1H₂O

30
PB-1W-1.xyz

N	0.971460	0.316660	0.029652
C	1.445809	-0.396598	-1.213985
C	1.533654	-0.418369	1.234789
H	-0.055825	0.318709	0.065942
H	1.288403	1.301239	0.019125
C	1.737515	-1.806323	-0.720557
H	0.675810	-0.314862	-1.981905
H	2.356823	0.109598	-1.543941
C	2.381795	-1.548579	0.645112
H	0.682428	-0.791960	1.806401
H	2.094796	0.290512	1.844578
H	3.418981	-1.221831	0.518844
H	2.380307	-2.426569	1.293603
H	0.802852	-2.368425	-0.610896
H	2.388464	-2.350898	-1.407230
C	-2.081185	-0.752895	1.168052
C	-2.189259	0.635094	1.286961
C	-2.026404	-1.344230	-0.097042
H	-2.065109	-1.374406	2.059107
C	-2.246576	1.432129	0.139725
H	-2.252706	1.093177	2.269792
C	-2.087309	-0.547416	-1.243710
H	-1.967458	-2.425227	-0.189271
C	-2.197026	0.840668	-1.125702
H	-2.351323	2.509266	0.232171
H	-2.073506	-1.009771	-2.227115
H	-2.264383	1.458009	-2.016914
O	2.403890	2.735768	-0.074731
H	2.527683	3.296349	-0.855130
H	2.756340	3.243438	0.671270

30
PB-1W-2.xyz

N	-2.225741	0.803915	0.867290
C	-3.197796	0.925117	-0.299757
C	-1.891954	-0.658816	1.049168
H	-1.342352	1.295895	0.607276
H	-2.591023	1.223294	1.724660
C	-3.359830	-0.507138	-0.821944
H	-4.124401	1.376880	0.054258
H	-2.726939	1.585144	-1.029868
C	-2.085384	-1.217126	-0.353394
H	-2.607767	-1.083330	1.757102
H	-0.878758	-0.736396	1.448182
H	-1.230400	-0.947719	-0.985092
H	-2.179114	-2.305046	-0.346107
H	-4.241584	-0.979004	-0.377454
H	-3.481346	-0.520812	-1.906385
C	3.295783	0.778507	-0.199420
C	2.968334	0.345935	1.086963
C	2.766430	0.123227	-1.314669
H	3.977823	1.612953	-0.334753
C	2.114988	-0.744817	1.260262
H	3.393141	0.846192	1.952084
C	1.907547	-0.965879	-1.141174
H	3.034274	0.448902	-2.315499
C	1.585377	-1.400534	0.147074
H	1.886316	-1.098647	2.262085
H	1.513542	-1.488580	-2.008448
H	0.948107	-2.272085	0.279497
O	0.047139	1.712144	-0.313117
H	0.478739	2.579187	-0.319568
H	0.753851	1.067758	-0.506725

31

PP-1W-1.xyz

N	-3.198423	-2.091829	-2.406523
C	-4.325304	-2.845314	-3.088463
C	-3.605375	-1.819076	-0.976344
H	-2.954997	-1.207509	-2.873406
H	-2.337821	-2.671319	-2.372994
C	-5.441203	-2.902122	-2.043000
H	-4.593806	-2.329495	-4.010438
H	-3.946417	-3.839138	-3.334602
C	-4.682331	-2.863274	-0.712988
H	-4.009210	-0.804302	-0.935636
H	-2.717228	-1.896223	-0.347715
H	-4.220821	-3.833999	-0.498949
H	-5.312957	-2.590539	0.135312
H	-6.095953	-2.029045	-2.133051
H	-6.054926	-3.796803	-2.163450
C	1.721102	-1.706677	-1.809814
C	1.221060	-1.727382	-3.114367
C	1.055842	-0.972043	-0.825175
H	2.634689	-2.240177	-1.566891
C	0.062588	-1.022511	-3.437168
H	1.742864	-2.281303	-3.888746
C	-0.109356	-0.271168	-1.134949
H	1.444440	-0.941135	0.188102
C	-0.590485	-0.297215	-2.443099
H	-0.324216	-1.002650	-4.451974
H	-0.631393	0.298625	-0.369391
O	-1.768752	0.334935	-2.798029
H	-1.888496	1.153117	-2.291073
O	-1.045769	-3.600681	-1.542512
H	-0.874501	-4.551811	-1.485426
H	-0.173009	-3.167346	-1.544384

31
PP-1W-2.xyz

N	-2.771065	-2.845992	-0.816113
C	-2.929011	-4.280043	-1.269658
C	-3.449984	-2.691849	0.530311
H	-3.210434	-2.222219	-1.522250
H	-1.776352	-2.591891	-0.768355
C	-4.062945	-4.811211	-0.399302
H	-3.117729	-4.283502	-2.344022
H	-1.987523	-4.795408	-1.063614
C	-3.805552	-4.119393	0.942603
H	-4.340781	-2.080192	0.373023
H	-2.775286	-2.172034	1.211327
H	-2.962815	-4.591480	1.458955
H	-4.667125	-4.139853	1.612536
H	-5.033817	-4.510418	-0.809069
H	-4.045189	-5.900685	-0.333729
C	0.563299	-2.498680	-1.137196
C	0.128140	-2.939399	-2.391834
C	0.243330	-1.205999	-0.714140
H	1.169957	-3.144023	-0.509731
C	-0.626613	-2.104592	-3.213353
H	0.393267	-3.933163	-2.741498
C	-0.513750	-0.360710	-1.528550
H	0.593900	-0.843901	0.247870
C	-0.936088	-0.814513	-2.778273
H	-0.957509	-2.422877	-4.197515
H	-0.757444	0.646736	-1.199388
O	-1.703764	-0.045326	-3.616102
O	-1.632881	0.894614	-3.386728
O	-3.985763	-1.439168	-2.875920
H	-3.419547	-0.837496	-3.396740
H	-4.883693	-1.379965	-3.231164

31
PP-1W-3.xyz

N	1.754074	-0.317597	-0.088429
C	1.317439	0.221535	1.258776
C	1.684706	0.814528	-1.097727
H	1.136157	-1.097295	-0.366906
H	2.723426	-0.671701	-0.030742
C	0.606930	1.528598	0.925453
H	0.694650	-0.526424	1.751577
H	2.223760	0.386846	1.846730
C	1.420411	2.062831	-0.257017

H -3.937403 -1.959313 0.067851
H -3.402120 -3.410656 0.123084
31
PP-1W-8.xyz
N -0.466510 -0.745226 -0.803418
C 0.312955 -1.813245 -0.060754
C -1.923145 -0.815893 -0.348152
H -0.411243 -0.917866 -1.817832
H -0.064708 0.182805 -0.651893
C -0.767220 -2.799578 0.361177
H 1.080025 -2.207903 -0.728120
H 0.781316 -1.336198 0.803306
C -1.927553 -1.879123 0.750931
H -2.512636 -1.117976 -1.216458
H -2.236485 0.176333 -0.022763
H -1.743849 -1.425978 1.730607
H -2.887684 -2.396676 0.791097
H -1.045609 -3.439606 -0.483273
H -0.429362 -3.436443 1.180914
C 0.926410 -1.299179 -3.854285
C 0.335651 -2.522722 -3.520350
C 0.108219 -0.196986 -4.114435
H 2.004902 -1.214759 -3.939578
C -1.050768 -2.641572 -3.429990
H 0.957714 -3.396799 -3.346322
C -1.282604 -0.300983 -4.027179
H 0.551972 0.753905 -4.395481
C -1.866615 -1.530721 -3.689574
H -1.525239 -3.590046 -3.194574
H -1.920365 0.555244 -4.232265
O -3.199817 -1.688862 -3.544589
H -3.687565 -0.944655 -3.962759
O -4.357142 0.434738 -4.870758
H -4.406450 0.319950 -5.831777
H -5.199386 0.835044 -4.608708

34
PI-1W-1.xyz
H 2.668296 -1.506825 2.026285
N -1.464532 -0.059846 -0.256613
C -2.151780 -0.144329 1.085055
C -2.527013 -0.019454 -1.336882
H -0.866423 -0.900908 -0.369165
H -0.844359 0.760057 -0.297456
C -3.539293 -0.668711 0.739735
H -1.555537 -0.784521 1.736419
H -2.190148 0.866554 1.498953
C -3.850784 0.055932 -0.573953
H -2.440035 -0.944607 -1.910288
H -2.331568 0.827488 -1.995630
H -4.121144 1.098706 -0.377393
H -4.664393 -0.403690 -1.138154
H -3.507802 -1.753529 0.586683
H -4.261946 -0.457017 1.530087
N 2.698627 -0.618674 -1.139942
C 1.935845 0.401933 -0.623134
C 3.062805 -1.475665 -0.128446
H 3.008706 -0.691046 -2.098884
C 1.796672 0.160231 0.769556
C 1.382885 1.528505 -1.247371
C 1.090650 1.089541 1.555844
C 2.519100 -1.049839 1.057529
C 0.555268 2.215676 0.947490
H 0.994408 0.941116 2.628076
C 0.698150 2.431832 -0.443876
H 0.039186 2.959291 1.547686
H 0.289339 3.335281 -0.886623
H 1.515181 1.710011 -2.310189
H 3.704993 -2.321658 -0.333624
O -0.072532 -2.432390 -0.087870
H -0.173512 -3.341494 -0.403629
H 0.843310 -2.338370 0.236410

34
PI-1W-2.xyz
H 0.973764 2.392126 -2.073544
N -1.494604 0.034014 -0.393466
C -1.976149 0.053156 1.034659

C -2.707091 -0.060512 -1.301165
H -0.899839 -0.812480 -0.509415
H -0.905637 0.851345 -0.610198
C -3.329346 -0.638795 0.952240
H -1.230876 -0.447738 1.655153
H -2.073201 1.098991 1.338331
C -3.908629 -0.077296 -0.350515
H -2.615737 -0.990500 -1.865499
H -2.697232 0.778828 -1.997053
H -4.284891 0.938466 -0.191819
H -4.725975 -0.679060 -0.752213
H -3.191505 -1.723854 0.884656
H -3.949870 -0.425316 1.824639
N 0.883090 1.747695 1.150935
C 1.569740 0.634160 0.710608
C 0.595561 2.561293 0.075632
H 0.774254 2.015941 2.119556
C 1.678972 0.736056 -0.699475
C 2.112757 -0.437556 1.431319
C 2.356226 -0.274375 -1.407198
C 1.040363 1.969751 -1.080117
C 2.909110 -1.329322 -0.699653
H 2.466381 -0.211954 -2.485954
C 2.790623 -1.408821 0.707715
H 3.460501 -2.101217 -1.227600
H 3.256398 -2.236094 1.235079
H 2.036561 -0.493335 2.513574
H 0.113610 3.518208 0.225427
O -0.189034 -2.358983 -0.133751
H -0.265766 -3.187885 -0.628379
H 0.759108 -2.251016 0.068688

34
PI-1W-3.xyz
H -0.670467 -1.971134 -2.277252
N 1.533025 0.666606 0.910383
C 1.740484 -0.828117 1.089970
C 2.366755 1.118400 -0.268176
H 1.827784 1.177122 1.758725
H 0.539585 0.875733 0.743678
C 2.828536 -1.192643 0.079621
H 2.005162 -1.019508 2.130751
H 0.794177 -1.320000 0.857980
C 2.627224 -0.168470 -1.040585
H 3.289755 1.537380 0.140487
H 1.816730 1.887449 -0.811325
H 1.753587 -0.430949 -1.647366
H 3.493123 -0.074942 -1.699076
H 3.823454 -1.081486 0.523653
H 2.719405 -2.224676 -0.259773
N -1.800220 -1.749606 0.803069
C -1.658033 -0.412055 0.514880
C -1.424358 -2.495056 -0.293782
H -2.226262 -2.125485 1.638713
C -1.149995 -0.319618 -0.808985
C -1.907769 0.719784 1.302994
C -0.909935 0.955164 -1.356078
C -1.004865 -1.663210 -1.296229
C -1.161796 2.079949 -0.583314
H -0.549030 1.055518 -2.376832
C -1.653326 1.962610 0.737125
H -1.001623 3.068767 -1.002702
H -1.855874 2.860872 1.312202
H -2.305082 0.631812 2.310223
H -1.497877 -3.573681 -0.271949
O 2.968221 1.903376 2.999132
H 3.035355 2.852507 3.181114
H 3.399557 1.462319 3.745876

34
PI-1W-4.xyz
H 2.108616 -1.379750 -1.874396
N 0.875569 1.283890 0.355547
C -0.524284 1.407429 0.937663
C 0.868101 1.928830 -1.007718
H 1.175357 0.301720 0.278533
H 1.543946 1.795195 0.953480
C -1.323420 2.177880 -0.118327

H	-0.909955	0.406741	1.140206
H	-0.431978	1.958354	1.875923
C	-0.256173	2.948772	-0.901503
H	0.634085	1.143259	-1.731556
H	1.857799	2.339899	-1.211114
H	0.085670	3.827814	-0.343452
H	-0.598363	3.277902	-1.884593
H	-1.842687	1.473355	-0.775233
H	-2.069862	2.827552	0.342725
N	1.518640	-2.312377	1.221581
C	0.222950	-2.124351	0.788901
C	2.390705	-2.030398	0.195872
H	1.783955	-2.698765	2.116856
C	0.289385	-1.684718	-0.557815
C	-0.993028	-2.293472	1.464812
C	-0.909424	-1.401252	-1.241514
C	1.685313	-1.627789	-0.910270
C	-2.113207	-1.564368	-0.576692
H	-0.889227	-1.089307	-2.283041
C	-2.153693	-2.007618	0.764080
H	-3.046145	-1.369191	-1.096814
H	-3.114874	-2.141216	1.250549
H	-1.026384	-2.647315	2.491141
H	3.455995	-2.159087	0.330712
O	2.388977	3.276179	1.650372
H	3.325623	3.490591	1.526425
H	2.099980	3.803740	2.409796

34

PI-1W-5.xyz

H	1.236165	-1.878694	-2.292910
N	4.299380	0.426112	0.785887
C	3.684709	-0.964686	0.754867
C	4.917835	0.701938	-0.573762
H	4.994990	0.511878	1.529032
H	3.554494	1.138936	0.954879
C	4.244780	-1.588842	-0.518219
H	3.932584	-1.486848	1.679483
H	2.601236	-0.828924	0.687182
C	4.330472	-0.388943	-1.463801
H	6.000717	0.602258	-0.475152
H	4.665254	1.722641	-0.862301
H	3.327569	-0.103327	-1.802589
H	4.956261	-0.568724	-2.340155
H	5.238639	-2.015279	-0.341209
H	3.588505	-2.379226	-0.886260
N	0.025539	-1.782576	0.762832
C	-0.181102	-0.473242	0.391758
C	0.600497	-2.468276	-0.285422
H	-0.323490	-2.209139	1.609668
C	0.327267	-0.324132	-0.924815
C	-0.798828	0.576589	1.083570
C	0.211447	0.927969	-1.558711
C	0.819970	-1.612114	-1.330630
C	-0.412230	1.968570	-0.883725
H	0.569840	1.066818	-2.575316
C	-0.913306	1.791881	0.427833
H	-0.540548	2.928011	-1.375876
H	-1.414764	2.619164	0.920930
H	-1.199644	0.437557	2.083410
H	0.794793	-3.529119	-0.202082
O	2.351786	2.305980	0.673650
H	1.547699	2.101086	0.157236
H	2.100391	3.017910	1.279728

34

PI-1W-6.xyz

H	1.241816	-1.582584	-2.293326
N	0.277626	3.356607	0.103762
C	-0.949411	2.471393	0.002781
C	0.246483	4.351077	-1.048714
H	1.107077	2.740085	-0.014007
H	0.339188	3.818504	1.012679
C	-1.323350	2.579737	-1.468130
H	-0.686300	1.469105	0.345726
H	-1.722414	2.891503	0.650820
C	-1.067976	4.058653	-1.775197
H	1.115663	4.131276	-1.670901

H	0.330083	5.362945	-0.652083
H	-1.875811	4.677489	-1.370852
H	-0.983374	4.268473	-2.843069
H	-0.670110	1.934637	-2.067483
H	-2.356717	2.273387	-1.640143
N	1.326663	-1.520416	0.991559
C	0.013379	-1.156375	0.789799
C	1.939004	-1.721574	-0.221905
H	1.754043	-1.693390	1.890400
C	-0.199412	-1.107128	-0.611337
C	-1.007684	-0.894068	1.713829
C	-1.486061	-0.804055	-1.095035
C	1.049717	-1.462226	-1.235632
C	-2.500609	-0.553821	-0.186215
H	-1.682316	-0.792755	-2.164062
C	-2.262098	-0.596047	1.205799
H	-3.504672	-0.344950	-0.543797
H	-3.083984	-0.413999	1.891679
H	-0.832325	-0.952095	2.784232
H	2.966373	-2.056910	-0.268368
O	2.055928	1.525149	-0.831527
H	1.780585	0.589697	-0.926217
H	3.014382	1.534214	-0.968191

34

PI-1W-7.xyz

H	-0.676275	-1.965234	-2.271221
N	1.629360	0.539221	0.799609
C	1.895841	-0.952308	0.963539
C	2.492766	1.042610	-0.331302
H	1.784214	1.060041	1.666242
H	0.640723	0.687669	0.547525
C	2.775100	-1.330793	-0.237935
H	2.381732	-1.108760	1.927094
H	0.927355	-1.455095	0.959390
C	2.594596	-0.178171	-1.234280
H	3.462608	1.319065	0.090128
H	2.012017	1.917267	-0.772152
H	1.668890	-0.301302	-1.805652
H	3.425878	-0.090195	-1.936490
H	3.822798	-1.408362	0.067280
H	2.469893	-2.292208	-0.654809
N	-1.609715	-1.857553	0.883259
C	-1.508042	-0.513335	0.624998
C	-1.291468	-2.557682	-0.255391
H	-1.984183	-2.241959	1.750561
C	-1.090921	-0.365532	-0.727137
C	-1.712643	0.585772	1.473228
C	-0.906789	0.934895	-1.241250
C	-0.950585	-1.690278	-1.262027
C	-1.111694	2.025873	-0.406967
H	-0.621002	1.080915	-2.280116
C	-1.507404	1.851842	0.940911
H	-0.988113	3.031848	-0.796901
H	-1.672428	2.726045	1.563166
H	-2.034373	0.443168	2.500901
H	-1.343765	-3.637860	-0.264739
O	-2.916065	-2.198219	3.412811
H	-2.702982	-2.643190	4.245566
H	-3.882803	-2.150800	3.380736

34

PI-1W-8.xyz

H	2.125183	-1.306132	-1.922180
N	0.798804	1.379932	0.185622
C	-0.587901	1.491972	0.814177
C	0.735630	1.995804	-1.196815
H	1.100107	0.394030	0.102983
H	1.494720	1.859663	0.760671
C	-1.452294	2.134843	-0.272459
H	-0.911850	0.493116	1.111553
H	-0.491235	2.126087	1.697224
C	-0.454534	2.940732	-1.109065
H	0.544757	1.170995	-1.888820
H	1.696149	2.455502	-1.431434
H	-0.172243	3.869522	-0.599990
H	-0.834411	3.199416	-2.099267
H	-1.921348	1.356064	-0.881704

H	-2.241506	2.750172	0.163559
N	1.732270	-1.964296	1.277693
C	0.413532	-1.929715	0.884217
C	2.533718	-1.716652	0.192869
H	2.040322	-2.256756	2.205661
C	0.386822	-1.623240	-0.501984
C	-0.755646	-2.129470	1.633058
C	-0.860077	-1.503939	-1.149563
C	1.758467	-1.485361	-0.920122
C	-2.016103	-1.696464	-0.412243
H	-0.910700	-1.296474	-2.216066
C	-1.963863	-2.008071	0.965929
H	-2.983014	-1.630218	-0.902072
H	-2.891027	-2.168591	1.507583
H	-0.706463	-2.378578	2.689149
H	3.610666	-1.744345	0.290002
O	1.924852	-3.078675	3.906704
H	1.903218	-4.045993	3.945550
H	2.238358	-2.787194	4.774706

Table S3. M062X/6-31+G* optimized geometries for the minima of dihydrated complexes shown in Figure 4.

2H₂O

33
PB-2W-1.xyz

N	-0.362229	0.039359	-0.181927
C	-0.704945	1.020888	-1.286153
C	-0.912863	0.577337	1.116062
H	-0.834842	-0.863161	-0.379747
H	0.649082	-0.124403	-0.118588
C	-1.365970	2.196816	-0.566041
H	0.208084	1.272263	-1.826735
H	-1.397012	0.509240	-1.958222
C	-2.002218	1.541200	0.663787
H	-0.098323	1.096466	1.626780
H	-1.251864	-0.262596	1.724319
H	-2.908668	0.988352	0.390622
H	-2.257889	2.257175	1.447698
H	-0.611764	2.929475	-0.258521
H	-2.088285	2.703709	-1.208845
C	2.778754	0.939802	0.707306
C	2.586122	-0.196637	1.498296
C	2.905321	0.812856	-0.678342
H	2.855714	1.919195	1.171467
C	2.516546	-1.458433	0.903391
H	2.508878	-0.100485	2.577756
C	2.837230	-0.450236	-1.273854
H	3.081354	1.693443	-1.290180
C	2.642169	-1.585078	-0.483139
H	2.383277	-2.342900	1.519608
H	2.954893	-0.551372	-2.349005
H	2.605641	-2.568046	-0.943695
O	-2.233024	-1.917112	-0.577759
H	-2.256071	-2.829957	-0.896099
H	-3.140652	-1.686720	-0.285280
O	-4.654024	-0.926353	0.312715
H	-5.383680	-0.745228	-0.297938
H	-5.066769	-1.213331	1.140577

33
PB-2W-2.xyz

N	-2.056006	-0.401112	0.363563
C	-2.598001	0.801411	1.112566
C	-1.579213	0.063645	-0.992011
H	-2.778227	-1.131095	0.260328
H	-1.239016	-0.771207	0.880520
C	-2.574805	1.938280	0.091081
H	-3.587793	0.560646	1.502034
H	-1.915940	0.988708	1.944132
C	-1.395526	1.565502	-0.812415
H	-2.368533	-0.165309	-1.712263
H	-0.670917	-0.484992	-1.249326
H	-0.443592	1.771106	-0.308062
H	-1.400330	2.092443	-1.768998
H	-3.504950	1.957978	-0.486478
H	-2.455682	2.908667	0.576547
C	3.696240	-0.648602	0.741009
C	3.231899	-1.456438	-0.298561
C	3.372124	0.710135	0.770122
H	4.323976	-1.072604	1.519474
C	2.445536	-0.906723	-1.312310
H	3.495450	-2.509482	-0.326451
C	2.581914	1.260129	-0.242815
H	3.743941	1.341662	1.571554
C	2.121040	0.451060	-1.284540
H	2.105004	-1.532028	-2.132920
H	2.346742	2.320885	-0.230649
H	1.533707	0.887344	-2.089222
O	0.400341	-0.594879	1.566861

H	0.796797	-1.138291	2.263116
H	1.153175	-0.205003	1.086011
O	-4.284270	-2.020158	-0.286433
H	-4.279916	-2.885075	-0.722591
H	-5.197671	-1.876661	0.002123

33
PB-2W-3.xyz

N	2.297696	-0.810331	0.801790
C	2.762213	0.622634	0.947201
C	3.175973	-1.494685	-0.234448
H	1.311010	-0.778552	0.432246
H	2.300220	-1.302382	1.696614
C	3.472922	0.884397	-0.373897
H	1.892354	1.256492	1.129669
H	3.452106	0.671273	1.792928
C	4.206936	-0.435384	-0.628532
H	2.522215	-1.759613	-1.067564
H	3.601337	-2.401627	0.195305
H	5.095053	-0.505262	0.007965
H	4.523990	-0.557972	-1.665823
H	2.736964	1.076015	-1.163221
H	4.142829	1.743913	-0.308464
C	-3.203307	0.996723	-0.537550
C	-3.211404	-0.139480	-1.348239
C	-3.053689	0.868147	0.844787
H	-3.341639	1.977909	-0.983874
C	-3.072845	-1.405872	-0.774094
H	-3.343067	-0.041218	-2.421667
C	-2.907783	-0.395640	1.418666
H	-3.086192	1.748729	1.482085
C	-2.918481	-1.533143	0.609081
H	-3.102351	-2.292056	-1.401549
H	-2.810461	-0.496213	2.495730
H	-2.828835	-2.519065	1.056108
O	0.051233	-0.332450	-0.538701
H	-0.139971	0.628353	-0.498913
H	-0.811164	-0.782370	-0.575365
O	0.052675	2.390055	-0.083778
H	0.180809	3.036859	-0.793580
H	-0.713551	2.702063	0.420821

33
PB-2W-4.xyz

N	-2.225117	0.674128	0.865824
C	-3.163351	0.899221	-0.310258
C	-2.049100	-0.813720	1.050470
H	-1.281279	1.069286	0.610610
H	-2.552560	1.130079	1.719147
C	-3.507285	-0.508061	-0.808291
H	-4.024731	1.478781	0.021749
H	-2.600734	1.473923	-1.048010
C	-2.316116	-1.354061	-0.347091
H	-2.795670	-1.161240	1.768845
H	-1.043948	-0.998261	1.434883
H	-1.442509	-1.178732	-0.986290
H	-2.527621	-2.425318	-0.335190
H	-4.430862	-0.866227	-0.342380
H	-3.647918	-0.521640	-1.890499
C	3.151383	-0.089351	-0.213541
C	2.824304	-0.547515	1.064056
C	2.516524	-0.629559	-1.334836
H	3.909423	0.678222	-0.338432
C	1.865011	-1.548919	1.221399
H	3.327857	-0.136622	1.934006
C	1.551945	-1.627821	-1.176684
H	2.780861	-0.282841	-2.329488
C	1.229281	-2.088155	0.101414
H	1.631479	-1.923885	2.214333
H	1.072715	-2.061128	-2.050259
H	0.502142	-2.887981	0.221145
O	0.116873	1.389758	-0.186052
H	0.584137	2.250847	-0.119759
H	0.797578	0.718441	-0.367798
O	1.310310	3.870721	-0.012631
H	1.841704	4.237908	0.707511
H	1.442716	4.451290	-0.775267

PP-2W-1.xyz
 C 1.991218 -0.989603 1.221757
 N 1.455551 -0.282083 -0.003089
 C 2.627686 0.199450 -0.829252
 C 3.830804 -0.523573 -0.228894
 C 3.468944 -0.610042 1.256854
 H 1.411242 -0.679231 2.091853
 H 1.849142 -2.060402 1.059027
 H 2.697618 1.281670 -0.695137
 H 3.930177 -1.526431 -0.658297
 H 4.759637 0.018455 -0.416699
 H 3.604315 0.363331 1.741269
 H 4.061050 -1.346544 1.803424
 H 2.430747 -0.018830 -1.879589
 H 0.862491 0.513929 0.263320
 H 0.856493 -0.931013 -0.555394
 H 0.301799 3.438137 0.669447
 C -0.265112 2.566829 0.356878
 C -0.396495 2.259279 -1.002125
 C -0.904062 1.763028 1.361530
 C -1.144792 1.157391 -1.409259
 H 0.074055 2.890963 -1.750376
 C -1.655919 0.653614 0.909736
 H -0.827351 2.003857 2.361749
 C -1.777320 0.357633 -0.451616
 H -1.268509 0.913986 -2.460406
 H -2.159060 0.028902 1.643198
 O -2.465854 -0.730196 -0.900761
 H -3.067547 -1.077984 -0.201969
 O -0.134894 -2.122434 -1.332046
 H -1.078836 -1.862529 -1.372030
 H 0.017583 -2.793546 -2.011605
 O -4.145344 -1.490031 1.120774
 H -4.323006 -2.407679 1.374643
 H -5.001871 -1.037210 1.136200

34

PP-2W-2.xyz
 C 2.148448 0.308528 -1.320281
 N 1.232466 0.499538 -0.140960
 C 2.087115 0.752981 1.086206
 C 3.528523 0.746035 0.567452
 C 3.455900 -0.139353 -0.681029
 H 1.694812 -0.402785 -2.012154
 H 2.254510 1.278391 -1.813187
 H 1.897020 -0.061877 1.787886
 H 3.842408 1.758852 0.295140
 H 4.223034 0.369625 1.320678
 H 3.398039 -1.198633 -0.403110
 H 4.305798 -0.008898 -1.353687
 H 1.769412 1.694924 1.534725
 H 0.671594 -0.348340 0.001861
 H 0.566379 1.292072 -0.287635
 H 0.673609 -3.031747 1.452872
 C -0.041622 -2.403645 0.931031
 C -0.794959 -1.455197 1.631863
 C -0.242399 -2.556794 -0.442330
 C -1.734288 -0.663980 0.974822
 H -0.659921 -1.337134 2.703286
 C -1.184400 -1.772874 -1.113279
 H 0.321530 -3.301051 -0.997331
 C -1.935365 -0.838625 -0.397660
 H -2.324495 0.074854 1.508474
 H -1.349537 -1.907999 -2.179996
 O -2.883557 -0.055443 -0.995731
 H -3.049168 -0.340616 -1.907114
 O -0.389789 2.692603 -0.259915
 H -1.328253 2.643856 0.040433
 H -0.286623 3.530255 -0.731319
 O -2.970114 2.286748 0.501232
 H -3.356897 1.632442 -0.106032
 H -3.664563 2.913318 0.747475

34

PP-2W-3.xyz
 C 1.368089 -1.480930 -1.372322
 N 0.584775 -0.899962 -0.212892
 C 1.232579 -1.348226 1.070931

C 2.658028 -1.676392 0.644906
 C 2.448437 -2.345225 -0.717507
 H 0.688028 -2.027749 -2.026480
 H 1.791545 -0.636612 -1.920378
 H 0.700441 -2.235809 1.423745
 H 3.241859 -0.754511 0.539191
 H 3.161120 -2.320870 1.368406
 H 2.090596 -3.371633 -0.584731
 H 3.355097 -2.379731 -1.324357
 H 1.135070 -0.548206 1.806530
 H -0.406975 -1.164689 -0.239041
 H 0.634023 0.146484 -0.257129
 H -2.887249 -2.465710 0.907096
 C -2.632396 -1.454883 0.604852
 C -2.173110 -0.529002 1.548005
 C -2.797888 -1.055809 -0.723293
 C -1.873907 0.777549 1.170409
 H -2.063721 -0.821903 2.588407
 C -2.497598 0.251481 -1.114303
 H -3.175233 -1.758241 -1.460636
 C -2.044130 1.163826 -0.160999
 H -1.531340 1.513260 1.891925
 H -2.631717 0.560307 -2.148498
 O -1.712155 2.453726 -0.477100
 H -2.064750 2.698224 -1.346703
 O 1.005847 1.772599 -0.338350
 H 0.265400 2.403238 -0.339515
 H 1.828451 2.244089 -0.089515
 O 3.451993 2.874698 0.334959
 H 4.012517 3.294243 -0.333356
 H 3.669306 3.303031 1.175137

34

PP-2W-4.xyz
 C 2.250274 -0.294903 1.062934
 N 1.600422 0.372715 -0.134693
 C 2.689440 0.984429 -0.972542
 C 3.889938 0.098348 -0.667739
 C 3.759227 -0.124122 0.842710
 H 1.881199 0.181340 1.972037
 H 1.936720 -1.340619 1.050424
 H 2.848132 2.007676 -0.622432
 H 3.805861 -0.850989 -1.209164
 H 4.831063 0.572500 -0.952582
 H 4.126992 0.751810 1.386124
 H 4.314655 -0.995380 1.194422
 H 2.372104 1.001602 -2.016118
 H 0.877347 1.053468 0.156317
 H 1.108748 -0.360548 -0.684651
 H -3.099702 -3.110891 -0.251204
 C -2.635153 -2.150732 -0.050223
 C -1.778946 -1.998933 1.042934
 C -2.915446 -1.048372 -0.862597
 C -1.198783 -0.760860 1.316019
 H -1.571136 -2.842935 1.693959
 C -2.334853 0.192250 -0.603985
 H -3.592441 -1.153638 -1.705224
 C -1.476338 0.328576 0.489230
 H -0.559673 -0.618454 2.183132
 H -2.544648 1.050535 -1.236710
 O -0.825374 1.507503 0.759927
 H -1.333966 2.272591 0.402845
 O 0.457161 -1.857044 -1.342485
 H -0.437267 -2.075951 -1.023034
 H 0.544490 -2.267447 -2.214714
 O -2.467975 3.456564 -0.227607
 H -2.221611 4.338570 -0.542049
 H -3.296483 3.567501 0.262348

34

PP-2W-5.xyz
 C 1.956014 -0.274443 1.060759
 N 1.621905 0.301589 -0.300607
 C 2.827875 0.133012 -1.191815
 C 3.632239 -0.965036 -0.506163
 C 3.439619 -0.635700 0.976666
 H 1.710590 0.467730 1.821934
 H 1.328405 -1.158519 1.193639

H	3.369121	1.082258	-1.201862
H	3.206047	-1.947202	-0.738707
H	4.678055	-0.958606	-0.819296
H	4.061003	0.219970	1.261421
H	3.686811	-1.468501	1.637712
H	2.491882	-0.100627	-2.202988
H	1.337935	1.294312	-0.209565
H	0.833180	-0.237125	-0.699455
H	-2.810100	-2.718450	1.177574
C	-2.604549	-1.721422	0.801462
C	-1.726263	-0.876786	1.485792
C	-3.239873	-1.257957	-0.352512
C	-1.479058	0.414337	1.024723
H	-1.247907	-1.218227	2.399633
C	-2.997587	0.031243	-0.827080
H	-3.938319	-1.897097	-0.884625
C	-2.121572	0.861306	-0.130979
H	-0.828337	1.094964	1.568209
H	-3.498249	0.388817	-1.723880
O	-1.845242	2.140143	-0.545906
H	-2.436537	2.408604	-1.265536
O	-0.004161	-1.757465	-1.196231
H	-0.869100	-1.895978	-0.769944
H	-0.049747	-2.210772	-2.050238
O	0.685252	2.843672	0.362372
H	1.047267	3.721405	0.548330
H	-0.233199	2.959799	0.054898

34

PP-2W-6.xyz

C	1.615410	-0.121420	-1.313930
N	2.121474	0.355296	0.032545
C	1.700689	-0.649155	1.079962
C	1.364848	-1.901802	0.278628
C	0.734460	-1.328389	-0.993041
H	1.090984	0.702976	-1.799442
H	2.489610	-0.392839	-1.909537
H	0.814834	-0.242533	1.572853
H	2.275466	-2.465954	0.045145
H	0.686427	-2.558608	0.828090
H	-0.292648	-1.009770	-0.789922
H	0.713769	-2.039547	-1.821534
H	2.507145	-0.762110	1.805841
H	1.721982	1.288670	0.251870
H	3.150561	0.417944	0.009229
H	-2.870891	-2.799664	0.698112
C	-2.677404	-1.757606	0.465080
C	-2.075985	-0.924404	1.409172
C	-3.053450	-1.234956	-0.771520
C	-1.844190	0.419860	1.122641
H	-1.806814	-1.315385	2.386875
C	-2.821342	0.106581	-1.074666
H	-3.534838	-1.870305	-1.508697
C	-2.217128	0.923568	-0.122044
H	-1.410535	1.091544	1.858622
H	-3.118017	0.512130	-2.039439
O	-1.947299	2.253469	-0.362560
H	-2.404252	2.562394	-1.159617
O	4.932337	-0.008953	-0.134172
H	5.641983	0.649663	-0.161129
H	5.372719	-0.871404	-0.135285
O	0.659657	2.655661	0.507312
H	0.872276	3.518048	0.890272
H	-0.263077	2.702610	0.183555

37

PI-2W-1.xyz

N	1.072171	-0.830102	-0.194156
C	1.787305	-1.076545	1.105038
C	2.013272	-1.167119	-1.329606
H	0.827105	0.188984	-0.246452
H	0.194465	-1.362770	-0.243440
C	3.255681	-0.951362	0.718424
H	1.430162	-0.354043	1.840948
H	1.539145	-2.087603	1.439593
C	3.295979	-1.649845	-0.645183
H	2.169431	-0.247065	-1.896966
H	1.542527	-1.908691	-1.976309

H	3.274120	-2.736617	-0.513613
H	4.181912	-1.398873	-1.231289
H	3.530537	0.105555	0.619935
H	3.914544	-1.411297	1.457513
N	-2.479791	1.294419	-1.130938
C	-2.199438	0.051320	-0.617163
C	-2.485480	2.219562	-0.113978
H	-2.691862	1.495895	-2.097853
C	-2.002202	0.207443	0.781095
C	-2.127162	-1.197266	-1.249810
C	-1.736445	-0.932883	1.562181
C	-2.182946	1.603279	1.073683
C	-1.679147	-2.174306	0.944844
H	-1.607581	-0.844092	2.637630
C	-1.871975	-2.304863	-0.451019
H	-1.506812	-3.065695	1.540867
H	-1.842917	-3.292195	-0.902459
H	-2.297357	-1.302430	-2.317503
H	-2.723829	3.254533	-0.318721
H	-2.148306	2.076773	2.045157
O	0.711067	1.846729	-0.320144
H	1.446557	2.459511	-0.110150
H	-0.100033	2.189357	0.093545
O	2.999185	3.348043	0.126422
H	3.282860	3.791993	0.938294
H	3.352019	3.875881	-0.604343

37

PI-2W-2.xyz

N	-1.687138	0.398846	-0.124904
C	-2.694971	-0.724499	-0.207297
C	-2.434657	1.714497	-0.125963
H	-1.054745	0.332708	-0.945829
H	-1.101909	0.297251	0.716137
C	-3.968665	-0.035277	-0.682327
H	-2.300704	-1.490106	-0.876612
H	-2.805899	-1.138382	0.797786
C	-3.902312	1.318699	0.030762
H	-2.247527	2.192919	-1.089766
H	-2.041180	2.347948	0.670098
H	-4.157119	1.204370	1.089983
H	-4.568991	2.068598	-0.399159
H	-3.946251	0.099576	-1.769642
H	-4.859515	-0.613044	-0.428681
N	2.544931	0.097480	-0.593088
C	1.655314	-0.125377	0.427268
C	2.625167	-1.027901	-1.372234
H	3.116807	0.937755	-0.680555
C	1.137237	-1.439888	0.269567
C	1.281854	0.706158	1.493129
C	0.226624	-1.932272	1.223754
C	1.767750	-1.993036	-0.897602
C	-0.134251	-1.121003	2.290315
H	-0.165169	-2.942585	1.140461
C	0.387237	0.189463	2.422382
H	-0.809506	-1.500829	3.051600
H	0.102483	0.790564	3.280992
H	1.705263	1.700764	1.599769
H	3.310513	-1.066106	-2.208608
H	1.650355	-2.992099	-1.294534
O	-0.357633	-0.258936	-2.440159
H	-0.282581	0.080295	-3.343096
H	0.433504	-0.807594	-2.272659
O	4.030005	2.517675	-0.177937
H	4.137046	3.345557	-0.667542
H	4.823634	2.430859	0.370059

37

PI-2W-3.xyz

N	-1.468201	-0.146772	0.244191
C	-1.950319	0.505869	-1.029896
C	-2.649691	-0.818706	0.912686
H	-1.091353	0.584244	0.877756
H	-0.720293	-0.822021	0.045860
C	-3.453114	0.635284	-0.815070
H	-1.407303	1.442531	-1.166511
H	-1.718510	-0.180322	-1.849490
C	-3.797673	-0.666963	-0.085849

H -2.843777 -0.273996 1.839006
H -2.382985 -1.849749 1.149309
H -3.807216 -1.506324 -0.789415
H -4.765054 -0.637150 0.419354
H -3.670320 1.502564 -0.181813
H -3.988400 0.754430 -1.759174
N 2.790061 0.465310 1.002045
C 1.993794 -0.582776 0.604708
C 3.171258 1.194402 -0.099077
H 3.111585 0.631608 1.945278
C 1.845234 -0.488535 -0.804174
C 1.425838 -1.624371 1.351750
C 1.109755 -1.480863 -1.479373
C 2.601980 0.659932 -1.227350
C 0.556734 -2.523131 -0.747051
H 1.003642 -1.446758 -2.560256
C 0.715477 -2.593305 0.657571
H 0.015661 -3.313102 -1.259367
H 0.289590 -3.432838 1.199147
H 1.564258 -1.691526 2.426955
H 3.844953 2.034067 0.007974
H 2.763619 0.996303 -2.242743
O -0.987912 2.157671 1.623987
H -0.940633 2.561772 2.500743
H -0.457898 2.699712 1.003495
O 0.350780 2.884391 -0.612984
H 1.159582 2.359563 -0.763374
H 0.469247 3.719714 -1.087656

37

PI-2W-4.xyz

C -0.330024 1.612242 -1.159028
N -0.948479 0.888719 0.012024
C -0.675622 1.697073 1.265170
C 0.031359 2.959851 0.767705
C 0.730275 2.491476 -0.511587
H 0.047826 0.878516 -1.871585
H -1.121399 2.206375 -1.624030
H -0.547979 -0.054781 0.098731
H -1.974658 0.780258 -0.126478
H -0.031862 1.091207 1.904576
H -1.624577 1.876122 1.722218
H -0.698516 3.743412 0.537796
H 0.720876 3.352443 1.517667
H 1.618449 1.892489 -0.276691
H 1.031883 3.312554 -1.165282
C 1.966560 -0.891230 0.621244
C 1.686411 -1.144027 -0.748427
C 0.550652 -1.908804 -1.080184
C -0.262889 -2.384950 -0.061810
C 0.034333 -2.117101 1.295442
C 1.149653 -1.372702 1.653851
C 3.591004 0.048984 -0.612381
C 2.734957 -0.526281 -1.510945
H 0.326870 -2.136967 -2.118923
H -1.133650 -2.986114 -0.304749
H -0.611479 -2.517520 2.070747
H 1.389489 -1.189488 2.697990
H 4.513008 0.588475 -0.779679
H 2.854670 -0.535698 -2.585241
N 3.123926 -0.149666 0.669301
H 3.624481 0.099604 1.510665
O -3.699543 0.883606 -0.225777
H -4.289802 1.633202 -0.381404
H -4.254319 0.074018 -0.266125
O -5.180461 -1.441670 -0.303631
H -5.704780 -1.767571 0.441552
H -5.562643 -1.836576 -1.100069

37

PI-2W-5.xyz

C 1.257990 -0.734418 -0.597672
N 1.092597 0.436844 0.343032
C 1.096067 -0.092895 1.763183
C 1.402203 -1.584726 1.618319
C 0.825772 -1.927996 0.242103
H 0.660503 -0.558033 -1.492652
H 2.319391 -0.786149 -0.858784

H 0.221258 0.946204 0.143298
H 1.892402 1.085702 0.220010
H 0.101651 0.083770 2.175635
H 1.838186 0.465021 2.334960
H 2.484355 -1.753385 1.631485
H 0.957844 -2.163167 2.430920
H -0.268804 -1.983788 0.278393
H 1.205669 -2.867478 -0.164726
C -2.371696 0.047424 0.357105
C -2.042676 0.126547 -1.022281
C -1.558330 1.345300 -1.536396
C -1.412049 2.428046 -0.680482
C -1.743641 2.323987 0.691119
C -2.228889 1.138635 1.225415
C -2.833109 -1.936699 -0.588859
C -2.340181 -1.155146 -1.597708
H -1.323998 1.441199 -2.593344
H -1.058388 3.378167 -1.068949
H -1.639721 3.194267 1.331967
H -2.509069 1.069531 2.273312
H -3.192339 -2.956209 -0.612880
H -2.232908 -1.447783 -2.632783
N -2.835114 -1.226145 0.592310
H -3.237388 -1.550825 1.460356
O 3.628838 1.439200 0.292131
H 4.237570 0.898891 -0.253711
H 4.078567 2.271585 0.492054
O 4.937484 -0.422422 -1.267068
H 5.634483 -0.984002 -0.897207
H 5.189011 -0.260990 -2.188330

37

PI-2W-6.xyz

C -1.720424 -1.360834 -1.018269
N -1.252898 -0.597879 0.192263
C -2.462010 -0.249092 1.035501
C -3.633391 -0.945240 0.339801
C -3.193794 -0.986255 -1.126644
H -1.104951 -1.067932 -1.870602
H -1.587895 -2.427386 -0.816200
H -0.809706 0.298826 -0.136068
H -0.545555 -1.122626 0.724223
H -2.561565 0.839611 1.013668
H -2.289528 -0.573375 2.062481
H -3.761320 -1.961851 0.726548
H -4.569585 -0.405480 0.494470
H -3.294879 0.001674 -1.589702
H -3.754649 -1.706313 -1.725803
C 1.946654 -0.731008 -0.481626
C 1.915792 -0.358604 0.885645
C 2.264690 0.956994 1.242922
C 2.649586 1.839579 0.247318
C 2.682712 1.442754 -1.109595
C 2.322742 0.159623 -1.495282
C 1.354229 -2.540749 0.718820
C 1.527173 -1.528766 1.629583
H 2.261384 1.263238 2.285121
H 2.952462 2.848567 0.509860
H 3.014266 2.150874 -1.863449
H 2.359161 -0.146285 -2.536924
H 1.110925 -3.583031 0.876293
H 1.442938 -1.622418 2.703816
N 1.572433 -2.058068 -0.553855
H 1.631268 -2.632124 -1.383771
O -0.546723 1.752231 -0.877362
H -0.948306 2.504647 -0.395982
H 0.401372 1.940314 -0.984725
O -2.137022 3.470975 0.596628
H -2.768119 4.021137 0.109690
H -1.868282 3.995493 1.365019

Table S4. M062X/6-31+G* optimized geometries for the minima of trihydrated complexes shown in Figure 4.

3H₂O

36
PB-3W-1.xyz

N	-0.139608	0.522339	0.446583
C	0.616659	0.645719	-0.863175
C	-0.651948	1.892535	0.828084
H	0.518404	0.188144	1.178918
H	-0.912427	-0.147563	0.358480
C	0.699792	2.150677	-1.112041
H	1.588158	0.159639	-0.756283
H	0.023647	0.138594	-1.626693
C	-0.585298	2.682994	-0.472306
H	0.040766	2.288016	1.574701
H	-1.646588	1.789966	1.262471
H	1.577472	2.568507	-0.606774
H	0.778901	2.376388	-2.177365
H	-1.453256	2.453533	-1.101686
H	-0.566222	3.759387	-0.290426
C	-2.934115	-0.414153	-1.305531
C	-2.209707	-1.609386	-1.309469
C	-3.488295	0.062264	-0.115447
H	-3.087175	0.131092	-2.232995
C	-2.032290	-2.322956	-0.122330
H	-1.799064	-1.992645	-2.239465
C	-3.315738	-0.653961	1.072148
H	-4.071878	0.978984	-0.117001
C	-2.585849	-1.844896	1.069457
H	-1.479945	-3.257968	-0.127620
H	-3.762737	-0.293829	1.994503
H	-2.463611	-2.408505	1.989783
O	2.058841	0.306308	2.000180
H	2.848150	0.235522	1.413789
H	2.329180	0.053862	2.893191
O	3.885772	0.223698	0.007790
H	4.491148	0.969735	-0.105800
H	4.407761	-0.579134	-0.207080
O	5.418311	-2.004952	-0.599999
H	6.015231	-2.467691	0.004552
H	5.618691	-2.333857	-1.487396

36
PB-3W-2.xyz

N	1.494194	-0.546993	-0.089796
C	2.146363	0.536670	-0.923269
C	0.891570	0.096014	1.136702
H	2.212329	-1.236546	0.192153
H	0.733689	-0.990490	-0.629800
C	2.125581	1.770999	-0.023770
H	3.147034	0.209147	-1.210547
H	1.526836	0.672526	-1.812476
C	0.841821	1.579244	0.787361
H	1.570361	-0.099411	1.970146
H	-0.079871	-0.363687	1.329602
H	2.998053	1.771553	0.638869
H	2.136061	2.693823	-0.607065
H	-0.037495	1.793216	0.167681
H	0.794272	2.204989	1.681323
C	-4.262448	-0.821707	-0.716214
C	-3.859472	-1.298620	0.532211
C	-3.920309	0.472743	-1.115023
H	-4.857021	-1.451197	-1.371897
C	-3.117271	-0.480923	1.385368
H	-4.136328	-2.300826	0.845235
C	-3.173169	1.290721	-0.262721
H	-4.246227	0.848825	-2.080290
C	-2.774150	0.812900	0.988288
H	-2.822485	-0.845770	2.365404
H	-2.922559	2.303801	-0.565083
H	-2.218236	1.459292	1.663237

O	-0.904931	-0.935226	-1.385068
H	-1.312698	-1.623220	-1.930280
H	-1.646979	-0.396042	-1.056500
O	3.837770	-1.575584	0.863932
H	4.163663	-2.328600	1.375773
H	4.605285	-1.183580	0.398449
O	5.600199	-0.127231	-0.696064
H	6.111351	-0.507878	-1.425477
H	6.166190	0.555108	-0.305870

36
PB-3W-3.xyz

N	0.156872	-0.280320	-0.250894
C	0.317284	-1.530865	0.590218
C	0.080458	-0.693212	-1.702082
H	1.005396	0.315283	-0.113711
H	-0.678691	0.245604	0.029783
C	0.572424	-2.640922	-0.427507
H	1.133328	-1.373435	1.298197
H	-0.620337	-1.683169	1.128050
C	-0.232819	-2.183304	-1.646610
H	1.067959	-0.507221	-2.131409
H	-0.664329	-0.078398	-2.208096
H	1.638579	-2.691289	-0.674314
H	0.261809	-3.615049	-0.044341
H	-1.305046	-2.342342	-1.481525
H	0.051955	-2.691681	-2.570009
C	-3.232145	-0.427572	0.328077
C	-2.774451	0.083735	1.545493
C	-3.170495	0.356755	-0.825780
H	-3.657256	-1.426626	0.283157
C	-2.248312	1.375613	1.606999
H	-2.842486	-0.517319	2.448065
C	-2.649226	1.651954	-0.764201
H	-3.547490	-0.032986	-1.767524
C	-2.185802	2.160666	0.451382
H	-1.903606	1.777450	2.555235
H	-2.620306	2.269265	-1.657553
H	-1.792737	3.171737	0.503176
O	2.679488	0.574013	-0.040168
H	3.173211	0.107679	0.660628
H	3.211240	1.343276	-0.328319
O	3.507750	-1.168656	1.979955
H	4.150898	-1.866648	1.787549
H	3.695274	-0.883265	2.886183
O	4.209795	2.741677	-0.895274
H	4.255204	3.632165	-0.520531
H	4.851569	2.715855	-1.618472

36
PB-3W-4.xyz

N	2.640381	-0.416996	-0.033098
C	2.062656	0.271608	1.180460
C	2.592786	0.554636	-1.196546
H	2.027918	-1.223208	-0.257348
H	3.606806	-0.735194	0.136858
C	1.202913	1.374253	0.580730
H	1.507600	-0.455328	1.774764
H	2.896710	0.675675	1.760309
C	2.051475	1.856055	-0.599459
H	1.907940	0.130850	-1.933246
H	3.592278	0.636056	-1.624642
H	0.255615	0.948591	0.230683
H	0.982815	2.158289	1.308520
H	2.873056	2.488809	-0.247501
H	1.481610	2.424678	-1.337514
C	-4.200225	-0.268687	0.578934
C	-3.614118	0.985060	0.771941
C	-3.792032	-1.074302	-0.485952
H	-4.984874	-0.608893	1.248382
C	-2.616049	1.430054	-0.099991
H	-3.943396	1.619393	1.589781
C	-2.796048	-0.628892	-1.355401
H	-4.259627	-2.041753	-0.643439
C	-2.206794	0.621219	-1.161797
H	-2.171242	2.411260	0.042440
H	-2.489219	-1.247259	-2.194144
H	-1.440637	0.970517	-1.849353

O 0.391983 -1.828278 -0.584335
H -0.258586 -1.610238 0.121905
H 0.054910 -2.600060 -1.058920
O -0.987212 -0.909200 1.581896
H -1.350909 -1.514277 2.244753
H -1.721408 -0.313255 1.344518
O 5.447242 -0.780093 0.212519
H 6.033947 -0.326717 0.835386
H 5.992538 -1.454420 -0.218664

37

PP-3W-1.xyz

C 1.927203 -0.210466 -1.609217
N 1.534554 0.439750 -0.310428
C 2.787857 0.637789 0.519071
C 3.927549 0.122784 -0.365158
C 3.240346 -0.904036 -1.271070
H 1.118406 -0.867259 -1.933021
H 2.069546 0.584112 -2.346162
H 2.671519 0.043532 1.427782
H 4.345532 0.937055 -0.966124
H 4.735801 -0.303739 0.231928
H 3.044280 -1.834032 -0.723835
H 3.817606 -1.147905 -2.164958
H 2.859602 1.692429 0.787232
H 0.883835 -0.172080 0.195830
H 1.044458 1.352216 -0.457554
H 1.117045 -2.469341 2.273388
C 0.347153 -1.899151 1.762761
C -0.155431 -0.722200 2.328468
C -0.173927 -2.347624 0.546899
C -1.159463 0.001898 1.689692
H 0.230341 -0.367612 3.280011
C -1.184664 -1.634508 -0.103708
H 0.196249 -3.267828 0.102944
C -1.683920 -0.463478 0.477150
H -1.555335 0.916674 2.120330
H -1.601650 -1.989519 -1.042946
O -2.671817 0.269059 -0.103634
H -3.089384 -0.215517 -0.851682
O 0.382794 2.910245 -0.467263
H -0.523701 3.024827 -0.093595
H 0.553354 3.669199 -1.040810
O -2.123090 2.901127 0.567247
H -2.604016 2.107437 0.265003
H -2.770281 3.595455 0.749613
O -3.823978 -1.227751 -2.087853
H -4.080193 -0.872620 -2.951652
H -4.552380 -1.801205 -1.806019

37

PP-3W-2.xyz

C -2.447705 -1.091301 -1.310333
N -1.968625 -0.288553 -0.119987
C -3.175556 0.209023 0.638809
C -4.316188 -0.661930 0.122257
C -3.954604 -0.843697 -1.355149
H -1.901730 -0.770098 -2.198207
H -2.211122 -2.137205 -1.103352
H -3.318288 1.260192 0.375505
H -4.323646 -1.628768 0.637933
H -5.287675 -0.187928 0.274535
H -4.178480 0.069466 -1.917316
H -4.483390 -1.671854 -1.830754
H -2.973259 0.131943 1.708103
H -1.378381 0.500960 -0.411769
H -1.383673 -0.892463 0.495704
H -0.894144 3.449779 -0.804673
C -0.332556 2.610248 -0.406645
C -0.334031 2.345106 0.967311
C 0.432396 1.806076 -1.257066
C 0.406427 1.284719 1.484154
H -0.905758 2.976830 1.641567
C 1.178226 0.738520 -0.751940
H 0.458633 2.015271 -2.322887
C 1.166199 0.482900 0.624294
H 0.426106 1.074269 2.549525
H 1.781963 0.114467 -1.405426

O 1.840278 -0.563629 1.173035
H 2.509565 -0.928590 0.533639
O -0.450902 -2.041422 1.387046
H 0.470962 -1.727275 1.509310
H -0.645635 -2.672477 2.093337
O 3.590646 -1.419176 -0.650214
H 3.748549 -2.363214 -0.790486
H 4.477633 -0.998213 -0.616561
O 6.119868 -0.322222 -0.544973
H 6.615989 0.056208 -1.284033
H 6.641383 -0.157828 0.252924

37

PP-3W-3.xyz

N -1.197677 -0.618996 0.361858
C -1.799086 -0.785949 1.740304
C -2.293263 -0.771354 -0.658836
H -0.435973 -1.285907 0.188075
H -0.796657 0.351082 0.274083
C -3.264133 -1.145505 1.484004
H -1.236791 -1.544285 2.286498
H -1.693326 0.174453 2.249314
C -3.559138 -0.477293 0.137242
H -2.273410 -1.801788 -1.023796
H -2.095025 -0.088516 -1.486953
H -3.683652 0.604989 0.258488
H -4.450615 -0.872521 -0.353684
H -3.383914 -2.231028 1.401713
H -3.910804 -0.794837 2.290628
C 1.186454 -2.619275 -0.878203
C 0.949973 -1.685809 -1.893528
C 1.804124 -2.201627 0.304013
H 0.920994 -3.662359 -1.018889
C 1.313767 -0.351962 -1.726828
H 0.492772 -2.003015 -2.826780
C 2.171682 -0.866339 0.483908
H 2.010595 -2.920854 1.091671
C 1.929339 0.056480 -0.538872
H 1.152369 0.382159 -2.510733
H 2.655617 -0.538209 1.400195
O 2.234258 1.377863 -0.414278
H 2.867673 1.522410 0.325593
O -0.417624 1.960236 0.210246
H 0.503243 2.109116 -0.077400
H -1.000502 2.591536 -0.259009
O 4.079765 1.584071 1.604569
H 4.090520 2.294195 2.262797
H 5.000717 1.454347 1.333359
O -2.374109 3.528760 -0.987692
H -2.766077 4.236630 -0.456285
H -2.400645 3.839731 -1.903881

37

PP-3W-4.xyz

C 2.502947 0.253278 -0.853616
N 1.837772 -0.569367 0.229777
C 2.903463 -1.026583 1.194262
C 4.063401 -0.072541 0.934185
C 4.001404 0.112934 -0.584427
H 2.177413 -0.120170 -1.825499
H 2.162234 1.283039 -0.724964
H 3.163762 -2.056245 0.937063
H 3.890021 0.881362 1.444514
H 5.013225 -0.482877 1.282477
H 4.403694 -0.769555 -1.093413
H 4.554510 0.986898 -0.933895
H 2.500640 -0.999237 2.207646
H 1.326094 -1.371784 -0.184812
H 1.161038 0.033562 0.733091
H -1.411257 3.774133 -0.583343
C -1.529461 2.696827 -0.525633
C -0.780649 1.857954 -1.355787
C -2.455002 2.132921 0.356793
C -0.949611 0.476076 -1.305862
H -0.076742 2.285199 -2.064874
C -2.630636 0.750745 0.421210
H -3.055736 2.774086 0.995534
C -1.878880 -0.075000 -0.418126

H -0.401469 -0.184180 -1.973606
H -3.354039 0.311469 1.102540
O -2.011419 -1.432805 -0.405052
H -2.797963 -1.712921 0.115680
O 0.600078 1.483166 1.613936
H -0.119534 1.941301 1.141491
H 0.409717 1.589507 2.556748
O 0.403367 -2.513500 -1.145124
H 0.539903 -3.406747 -1.489348
H -0.553111 -2.398965 -0.969435
O -4.291704 -2.060160 0.981315
H -4.364111 -2.703534 1.701169
H -5.117118 -2.122050 0.478209

37

PP-3W-5.xyz

C 1.409980 0.408304 -1.054768
N 2.206190 0.514014 0.231158
C 2.331144 -0.867797 0.810225
C 2.290098 -1.761512 -0.422181
C 1.208715 -1.096786 -1.282296
H 0.474610 0.956026 -0.923157
H 2.000763 0.882774 -1.840490
H 1.461493 -1.031863 1.450974
H 3.261559 -1.751522 -0.931008
H 2.050277 -2.795682 -0.166128
H 0.216783 -1.399902 -0.935532
H 1.291966 -1.354518 -2.340083
H 3.245529 -0.924237 1.403017
H 1.743447 1.167942 0.894294
H 3.149896 0.868254 0.012390
H -2.063281 -3.702156 0.107781
C -1.991090 -2.621276 0.172017
C -1.393043 -2.019546 1.279604
C -2.512143 -1.819937 -0.843768
C -1.313974 -0.630691 1.376073
H -1.004464 -2.633744 2.087652
C -2.434020 -0.429782 -0.765172
H -2.985551 -2.276941 -1.707718
C -1.839200 0.158632 0.352362
H -0.879873 -0.149182 2.248563
H -2.838060 0.198584 -1.554678
O -1.727562 1.520757 0.474523
H -2.358914 1.983264 -0.121743
O 4.821862 1.138582 -0.710423
H 5.267211 1.998283 -0.733080
H 5.486478 0.489637 -0.984131
O 0.586136 2.107087 1.793914
H 0.637271 2.758612 2.506194
H -0.326692 2.116235 1.436471
O -3.639408 2.619019 -1.156550
H -3.590595 3.458508 -1.636177
H -4.550208 2.542313 -0.835814

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PP-3W-6.xyz

C -3.160431 0.665113 -0.996993
N -1.737009 0.317188 -0.611924
C -1.649968 0.277388 0.894549
C -3.088299 0.008046 1.314866
C -3.888070 0.872042 0.334795
H -3.153665 1.540643 -1.646531
H -3.558851 -0.188295 -1.548935
H -1.306091 1.261104 1.226504
H -3.323129 -1.053161 1.175868
H -3.264389 0.269381 2.360205
H -3.846196 1.924426 0.634791
H -4.938563 0.583708 0.263476
H -0.925224 -0.486471 1.185277
H -1.030471 0.972493 -0.978100
H -1.516237 -0.637352 -0.958359
H 3.748318 -2.450524 0.347460
C 3.105170 -1.605713 0.120473
C 2.305734 -1.616148 -1.025633
C 3.089670 -0.486711 0.957749
C 1.507540 -0.517613 -1.339588
H 2.317202 -2.475757 -1.689421
C 2.291425 0.615443 0.657148

H 3.709030 -0.467770 1.849560
C 1.513784 0.600087 -0.503571
H 0.914390 -0.499808 -2.250025
H 2.278673 1.488847 1.303504
O 0.714190 1.657336 -0.853789
H 1.036930 2.488917 -0.436689
O -1.552585 -2.387702 -0.836700
H -0.920847 -2.667837 -0.139163
H -1.620873 -3.106711 -1.479286
O 0.181077 -2.485066 1.264257
H 1.102544 -2.273011 1.028971
H 0.220241 -3.086031 2.022123
O 1.887689 3.843106 0.305928
H 1.482173 4.683740 0.563463
H 2.751803 4.066162 -0.071575

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PI-3W-1.xyz

N -1.515803 -0.549042 0.334205
C -2.525811 -0.873826 -0.737183
C -2.230549 -0.487268 1.664460
H -1.093821 0.381447 0.109977
H -0.755237 -1.241409 0.339771
C -3.859948 -0.522473 -0.089458
H -2.274841 -0.299526 -1.629920
H -2.446916 -1.942242 -0.954214
C -3.650659 -0.965183 1.361963
H -2.215120 0.555609 1.989144
H -1.688441 -1.095557 2.389726
H -4.032087 0.558733 -0.141563
H -4.695232 -1.026745 -0.579197
H -3.713064 -2.056091 1.438865
H -4.376038 -0.535373 2.055394
N 2.491244 0.769366 0.043637
C 1.858311 -0.440268 -0.086635
C 2.435790 1.436214 -1.154102
H 2.995689 1.056669 0.880369
C 1.363647 -0.528211 -1.416349
C 1.700216 -1.476840 0.844643
C 1.740905 0.690687 -2.076286
H 2.916540 2.398790 -1.267049
C 0.699048 -1.702737 -1.817926
C 1.046773 -2.625522 0.415871
H 2.102908 -1.387780 1.849449
C 0.551689 -2.738596 -0.906287
H 0.330638 -1.806202 -2.835137
H 1.565660 0.956019 -3.109806
H 0.069343 -3.662020 -1.213750
H 0.933911 -3.462033 1.099420
O -0.765283 1.893160 -0.533860
H 0.072491 1.937277 -1.027050
H -1.046809 2.806970 -0.323317
O 3.872862 0.701066 2.557268
H 3.839980 1.195094 3.388778
H 4.753333 0.299382 2.524641
O -1.744669 4.434738 0.015764
H -1.471024 5.087486 0.675028
H -2.279710 4.911672 -0.634099

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PI-3W-2.xyz

N -1.338665 0.977193 0.211317
C -0.741409 1.807344 -0.899378
C -2.574843 1.682802 0.725436
H -0.647543 0.900938 0.985083
H -1.557935 0.030038 -0.119102
C -1.329284 3.192558 -0.658613
H 0.346718 1.739033 -0.838734
H -1.091175 1.381162 -1.844100
C -2.760524 2.874764 -0.214649
H -2.356657 2.002177 1.746638
H -3.406922 0.977142 0.737683
H -0.779671 3.699723 0.142026
H -1.285693 3.813613 -1.555533
H -3.372185 2.591047 -1.077764
H -3.252898 3.708295 0.289843
N 1.253145 -2.357959 1.087723
C 0.003105 -2.196961 0.539986

C 2.204535 -2.229960 0.101905
H 1.443783 -2.615098 2.045743
C 0.180272 -1.927227 -0.842605
C -1.265181 -2.305565 1.127367
C 1.596144 -1.945705 -1.093335
H 3.252258 -2.370265 0.331914
C -0.957701 -1.776179 -1.657267
C -2.367782 -2.160667 0.297999
H -1.383092 -2.527679 2.184046
C -2.217278 -1.897624 -1.084555
H -0.849912 -1.598171 -2.723824
H 2.090743 -1.824623 -2.047393
H -3.102568 -1.816939 -1.708346
H -3.364939 -2.270908 0.713573
O 0.605190 1.446030 2.042920
H 0.838847 1.357268 2.976003
H 1.424832 1.343402 1.504020
O 2.339156 1.061122 0.048163
H 2.362437 0.134678 -0.247174
H 3.225415 1.437727 -0.134155
O 4.896383 2.013187 -0.506521
H 5.152454 2.448338 -1.331695
H 5.566203 2.256270 0.147724

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PI-3W-3.xyz

N -0.491451 0.841213 -0.117090
C -0.800086 -0.109128 1.020981
C -0.825486 0.142736 -1.419492
H 0.492441 1.138211 -0.097054
H -1.097988 1.677427 -0.030064
C -0.899624 -1.467949 0.341410
H -0.016249 -0.024250 1.773785
H -1.765758 0.193427 1.433679
C -1.570470 -1.118300 -0.989315
H 0.120457 -0.092802 -1.910933
H -1.407264 0.827820 -2.036571
H -2.633232 -0.900419 -0.835802
H -1.484538 -1.906782 -1.740187
H 0.101809 -1.884532 0.177699
H -1.475941 -2.172971 0.944523
N 2.767584 -1.694923 -0.853064
C 2.695919 -0.346585 -0.588851
C 2.788662 -2.391302 0.336872
H 2.930051 -2.103845 -1.762433
C 2.635016 -0.198294 0.821795
C 2.692098 0.753168 -1.458790
C 2.563246 1.098478 1.366584
C 2.691367 -1.518150 1.385107
C 2.552645 2.190156 0.510619
H 2.535892 1.241096 2.443667
C 2.618251 2.017932 -0.892276
H 2.514468 3.195193 0.919399
H 2.629391 2.892081 -1.535854
H 2.764776 0.624418 -2.535574
H 2.874984 -3.469079 0.336319
H 2.687870 -1.781636 2.433532
O -2.760626 2.319449 -0.108006
H -3.421282 1.767913 0.368361
H -3.119122 3.213726 -0.185718
O -4.162329 0.391325 1.202879
H -4.627503 0.530273 2.039642
H -4.737728 -0.186197 0.657098
O -5.631895 -1.227403 -0.501421
H -6.279562 -0.860199 -1.119958
H -5.929320 -2.126448 -0.301967

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PI-3W-4.xyz

N 1.837433 0.790626 -0.030782
C 3.132384 0.226086 0.504664
C 2.091342 2.202763 -0.509316
H 1.134152 0.780379 0.734551
H 1.469415 0.196052 -0.786618
C 4.006684 1.456916 0.714646
H 2.909966 -0.347412 1.405442
H 3.540164 -0.438514 -0.260875
C 3.611128 2.353149 -0.462919

H 1.598899 2.877533 0.194424
H 1.645794 2.329386 -1.496758
H 3.761995 1.940556 1.667139
H 5.068084 1.201701 0.724693
H 4.061079 1.984534 -1.391169
H 3.907695 3.395817 -0.333145
N -1.988191 -0.942810 0.539805
C -0.962127 -1.117360 -0.352095
C -1.745053 -1.702305 1.653768
H -2.833348 -0.402339 0.330867
C -0.021383 -2.008492 0.234123
C -0.794418 -0.585887 -1.639377
C -0.541518 -2.358515 1.527158
H -2.465826 -1.737389 2.460188
C 1.112278 -2.387208 -0.511102
C 0.331014 -0.981804 -2.350558
H -1.536477 0.084061 -2.064127
C 1.275455 -1.879313 -1.792343
H 1.832842 -3.088944 -0.099252
H -0.116756 -3.052632 2.239328
H 2.127970 -2.188975 -2.389956
H 0.478430 -0.617964 -3.363298
O 0.472365 0.535683 2.335871
H 0.007444 -0.323734 2.369982
H -0.013295 1.137258 2.917451
O -4.087842 0.483062 -0.669014
H -4.709050 -0.050852 -1.183101
H -4.569455 1.303441 -0.438239
O -5.543819 2.784660 -0.029116
H -6.259234 2.813697 0.621241
H -5.685536 3.534195 -0.623735

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PI-3W-5.xyz

N -1.355638 0.208426 -0.515778
C -1.633677 -0.257867 0.896724
C -1.064491 -1.011239 -1.367319
H -0.566412 0.868434 -0.537180
H -2.197794 0.684726 -0.886223
C -1.041193 -1.659543 0.934129
H -1.187948 0.449159 1.596604
H -2.720905 -0.277423 1.017776
C -1.384561 -2.195680 -0.457291
H -0.006020 -0.975431 -1.630448
H -1.674550 -0.954968 -2.269194
H -2.449603 -2.446006 -0.519108
H -0.808283 -3.080159 -0.736267
H 0.044874 -1.604454 1.074299
H -1.465531 -2.254204 1.746010
N 2.582055 -0.749894 0.560901
C 2.014080 0.392662 0.054191
C 2.441576 -0.750010 1.928224
H 3.130356 -1.405764 0.006898
C 1.472520 1.124174 1.145995
C 1.944245 0.856261 -1.268213
C 0.839585 2.356805 0.889595
C 1.754863 0.365900 2.331088
C 0.762250 2.816938 -0.417401
H 0.435667 2.948548 1.707113
C 1.310818 2.071197 -1.488873
H 0.293408 3.774371 -0.623593
H 1.251452 2.468147 -2.497776
H 2.387227 0.288489 -2.082391
H 2.852419 -1.557924 2.518408
H 1.509386 0.628354 3.350742
O -3.917389 0.617811 -1.370601
H -4.565332 0.336758 -0.692142
H -4.395839 1.133783 -2.033813
O -5.278630 -0.387702 0.812734
H -5.731423 0.166508 1.465286
H -5.806265 -1.196689 0.741041
O 4.122560 -2.020452 -1.515464
H 4.995196 -1.623250 -1.651803
H 4.182571 -2.915570 -1.878541

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PI-3W-6.xyz

N 0.780901 -0.054560 0.253027

C	0.543249	-1.309168	-0.553855
C	0.702023	-0.414587	1.721270
H	0.093071	0.671065	0.014333
H	1.741494	0.301930	0.044481
C	-0.159065	-2.238391	0.426362
H	-0.036019	-1.055749	-1.442106
H	1.526762	-1.693132	-0.842183
C	0.570222	-1.937899	1.738439
H	-0.182484	0.076623	2.130329
H	1.597563	-0.034792	2.214226
H	1.561481	-2.404443	1.737807
H	0.031996	-2.282757	2.623900
H	-1.220997	-1.974109	0.499201
H	-0.084253	-3.283510	0.118286
N	-3.451543	-0.490944	0.768164
C	-2.662183	0.568531	0.384871
C	-3.712973	-1.283962	-0.328569
H	-3.878219	-0.603569	1.676859
C	-2.399194	0.416031	-1.002300
C	-2.170928	1.652165	1.125671
C	-1.619613	1.389007	-1.657089
C	-3.075773	-0.777044	-1.427802
C	-1.128485	2.462462	-0.927813
H	-1.423734	1.309453	-2.723145
C	-1.401356	2.591520	0.454298
H	-0.543078	3.229374	-1.425713
H	-1.019909	3.452761	0.994295
H	-2.400229	1.766997	2.181882
H	-4.344653	-2.156406	-0.233497
H	-3.110589	-1.187761	-2.427119
O	3.435657	0.214483	0.002807
H	3.829600	-0.527072	-0.494086
H	4.098593	0.931512	0.060200
O	3.929187	-2.181170	-1.348319
H	4.141729	-2.225332	-2.292018
H	4.459268	-2.874164	-0.928262
O	5.320570	2.259230	0.228247
H	5.902271	2.382482	0.991067
H	5.555969	2.946783	-0.409836

Table S5. SAPT(DFT) energy decomposition in kcal/mol for non-hydrated complexes formed by pyrrolidinium cation and benzene, phenol and indole.

	E_{elec}	E_{exch}	E_{ind}	$E_{exch-ind}$	E_{disp}	$E_{exch-ind}$	δHF
PB-1	-10.70	12.37	-10.94	4.38	-8.99	1.10	-2.32
PB-2	-11.18	12.24	-11.02	4.44	-8.04	1.00	-2.55
PP-1	-15.39	15.63	-12.06	5.08	-8.33	1.09	-2.46
PP-2	-12.01	13.47	-11.33	4.68	-10.03	1.23	-2.26
PP-3	-17.66	19.34	-12.84	5.64	-11.01	1.47	-3.13
PP-4	-12.25	14.12	-11.43	4.95	-10.78	1.34	-2.28
PP-5	-15.40	15.43	-12.40	5.00	-7.14	0.96	-2.62
PP-6	-11.24	12.48	-11.31	4.49	-9.07	1.10	-2.39
PI-1	-14.65	15.82	-13.40	5.74	-11.62	1.46	-3.06
PI-2	-15.43	16.44	-13.25	5.57	-12.78	1.62	-2.79
PI-3	-14.76	17.28	-13.61	5.89	-12.79	1.65	-3.33
PI-4	-15.46	16.67	-13.14	5.52	-12.78	1.63	-3.00
PI-5	-15.39	14.55	-13.51	5.38	-9.65	1.22	-3.11

In the manuscript $E_{rep} = E_{exch}$; $E_{ind} = E_{exch-ind} + E_{ind} + \delta HF$; $E_{disp} = E_{exch-disp} + E_{disp}$
The PBE0/aug-cc-pVDZ ionization potential and HOMO values employed for calculating the shift factor in SAPT calculations are the following (in a. u.):

ipBz=0.35761049
homoBz=-0.267285
ipPh=0.32821696
homoPh=-0.240820
ipId=0.29825484
homold=-0.220040
ipPy+=0.62899926
homoPy+=-0.527359

Table S6. Pair energy contributions to monohydrated complexes as obtained with M062X/6-31+G*.

	Pyrr...π	Pyrr...H₂O	H₂O...π	3-body
PB-1W-1	-15.92	-17.20	0.44	1.62
PB-1W-2	-5.81	-17.09	-2.69	-1.85
PP-1W-1	-16.95	-17.04	-2.16	1.05
PP-1W-2	-16.55	-16.99	-3.38	0.47
PP-1W-3	-19.62	-17.25	0.54	1.68
PP-1W-4	-17.62	-17.23	0.47	1.61
PP-1W-5	-10.56	-17.18	-3.95	-1.66
PP-1W-6	-10.13	-17.13	-2.49	-1.20
PP-1W-7	-19.47	-5.59	-7.22	-1.88
PP-1W-8	-17.51	-4.08	-7.64	-1.85
PI-1W-1	-20.47	-16.83	-2.33	1.18
PI-1W-2	-18.59	-16.56	-2.58	0.91
PI-1W-3	-22.32	-17.22	0.62	1.93
PI-1W-4	-21.04	-17.26	0.52	1.97
PI-1W-5	-12.10	-16.90	-2.83	-1.55
PI-1W-6	-12.39	-17.19	-2.67	-1.49
PI-1W-7	-22.57	-3.80	-6.04	-1.30
PI-1W-8	-21.11	-3.65	-6.02	-1.47

Table S7. NBO charges for the units forming the complexes with benzene as obtained at the M06-2X/6-31+G* level of calculation.

	Benzene	Pyrrolidinium	(H₂O)_n
PB-1	0.030	0.970	
PB-2	0.036	0.964	
PB-1W-1	0.025	0.940	0.035
PB-1W-2	0.018	0.943	0.039
PB-2W-1	0.023	0.929	0.048
PB-2W-2	0.015	0.924	0.061
PB-2W-3	0.013	0.925	0.062
PB-2W-4	0.015	0.924	0.061
PB-3W-1	0.022	0.925	0.053
PB-3W-2	0.015	0.917	0.068
PB-3W-3	0.021	0.915	0.064
PB-3W-4	0.015	0.920	0.065

Table S8. NBO charges for the units forming the complexes with phenol as obtained at the M06-2X/6-31+G* level of calculation.

	Phenol	Pirrolidinium	(H₂O)_n
PP-1	0.038	0.963	
PP-2	0.028	0.972	
PP-3	0.046	0.954	
PP-4	0.027	0.973	
PP-5	0.040	0.960	
PP-6	0.031	0.969	
PP-1W-1	0.037	0.932	0.031
PP-1W-2	0.043	0.929	0.028
PP-1W-3	0.037	0.928	0.035
PP-1W-4	0.025	0.940	0.035
PP-1W-5	0.037	0.936	0.027
PP-1W-6	0.023	0.942	0.035
PP-1W-7	0.019	0.939	0.042
PP-1W-8	-0.005	0.969	0.036
PP-2W-1	0.012	0.922	0.066
PP-2W-2	0.034	0.918	0.048
PP-2W-3	0.036	0.911	0.053
PP-2W-4	0.011	0.915	0.074
PP-2W-5	0.030	0.915	0.055
PP-2W-6	0.034	0.914	0.052
PP-3W-1	0.004	0.917	0.079
PP-3W-2	-0.003	0.921	0.082
PP-3W-3	0.006	0.900	0.094
PP-3W-4	0.002	0.907	0.091
PP-3W-5	0.002	0.911	0.087
PP-3W-6	0.009	0.910	0.081

Table S9. NBO charges for the units forming the complexes with indole as obtained at the M06-2X/6-31+G* level of calculation.

	Indole	Pirrolidinium	(H₂O)_n
PI-1	0.036	0.964	
PI-2	0.030	0.970	
PI-3	0.041	0.959	
PI-4	0.032	0.968	
PI-5	0.037	0.963	
PI-1W-1	0.048	0.926	0.026
PI-1W-2	0.046	0.917	0.037
PI-1W-3	0.028	0.938	0.034
PI-1W-4	0.033	0.935	0.032
PI-1W-5	0.026	0.935	0.039
PI-1W-6	0.034	0.944	0.022
PI-1W-7	0.009	0.966	0.025
PI-1W-8	0.013	0.961	0.026
PI-2W-1	0.042	0.903	0.055
PI-2W-2	0.025	0.923	0.052
PI-2W-3	0.046	0.919	0.035
PI-2W-4	0.029	0.921	0.050
PI-2W-5	0.030	0.924	0.046
PI-2W-6	0.041	0.891	0.068
PI-3W-1	0.020	0.909	0.071
PI-3W-2	0.042	0.912	0.046
PI-3W-3	0.028	0.923	0.049
PI-3W-4	0.017	0.920	0.063
PI-3W-5	0.007	0.925	0.068
PI-3W-6	0.028	0.909	0.063