

SUPPLEMENTARY INFORMATION

All clusters given in the main text have been optimized at the MP2/aug-cc-pVDZ level and the structural and spectroscopic results are presented in Table S1. The labeling of atoms is given in the main text.

Table S1. The MP2/aug-cc-pVDZ level calculation results for $\text{HNO}_3 \cdot \text{HCl} \cdot (\text{H}_2\text{O})_n$, with $n=1$ to 6. The frequencies, Freq, in cm^{-1} and IR intensities, I, km/Mole .

System	Bond distances of HNO_3 (Å)	Bond distances of H_2O (Å)	Bond distances of HCl (Å)	Bond distances of H_3O^+ (Å)	Freqs/I
Monomer HNO_3	0.977 O-H 1.416 N-O 1.222 N-O2 1.211 N-O3	-	-	-	878/207 N-O 1320/196 NO_2 sym 1348/107 NOH bend 1861/258 NO_2 asym 3704/90 O-H
Monomer HCl	-	-	1.29	-	3023/42 H-Cl
Monomer H_2O	-	0.965 O-H	-	-	1622/67 H_2O bend 3803/4 H_2O sym 3937/64 H_2O asym
Monomer H_3O^+	-	-	-	0.982 O-H	905/416 H_3O^+ umbrella 1669/94 H_3O^+ bend 1670/94 H_3O^+ bend 3550/34 H_3O^+ sym 3678/459 H_3O^+ asym 3679/460 H_3O^+ asym
NC1W-1	1.00 O-H 1.37 N-O 1.23 N-O2 1.21 N-O3 1.94 O2...H3	0.97 O1-H1 0.97 O1-H2 1.68 O1...H	1.30 H3-Cl	-	2865/433 H3-Cl 3195/1214 O-H
NC1W-2	1.00 O-H 1.40 N-O 1.22 N-O2 1.21 N-O3	0.97 O1-H1 0.97 O1-H2 1.67 O1...H	1.30 H3-Cl	-	2879/265 H3-Cl 3139/1109 O-H
NC1W-3	0.99 O-H 1.38 N-O 1.23 N-O2 1.21 N-O3	0.97 O1-H1 0.97 O1-H2 1.68 O1...H3	1.33 H3-Cl 2.23 H...Cl	-	2345/1345 H3-Cl 3473/726 O-H
NC1W-4	0.98 O-H 1.42 N-O 1.22 N-O2 1.21 N-O3	0.97 O1-H1 0.97 O1-H2 1.75 O1...H3	1.32 H3-Cl 2.38 H...Cl	-	2570/965 H3-Cl 3562/385 O-H
NC2W-1	1.01 O-H 1.40 N-O 1.22 N-O2 1.22 N-O3	0.97 O1-H1 0.97 O1-H2 0.97 O4-H4 0.97 O4-H5 1.60 O1...H 1.66 O4...H3	1.34 H3-Cl	-	2367/1360 H3-Cl 2952/1509 O-H

NC2W-2	1.02 O-H 1.36 N-O 1.24 N-O2 1.22 N-O3	0.98 O1-H1 0.96 O1-H2 0.97 O4-H4 0.97 O4-H5 1.58 O1...H 1.87 O2...H3	1.30 H3-Cl	-	2788/596 H3-Cl 2910/1690 O-H
NC2W-3	1.02 O-H 1.40 N-O 1.22 N-O2 1.22 N-O3	0.98 O1-H1 0.97 O1-H2 0.97 O4-H4 0.97 O4-H5 1.57 O1...H	1.31 H3-Cl	-	2725/782 H3-Cl 2852/1591 O-H
NC2W-4	1.01 O-H 1.36 N-O 1.24 N-O2 1.22 N-O3	0.97 O1-H1 0.97 O1-H2 0.97 O4-H3 0.97 O4-H4 1.62 O1...H 1.67 O4...H3	1.33 H3-Cl	-	2407/1448 H3-Cl 3406/1451 O-H
NC2W-5	0.99 O-H 1.38 N-O 1.23 N-O2 1.21 N-O3	0.98 O1-H1 0.97 O1-H2 0.97 O4-H3 0.96 O4-H4 1.57 O1...H3	1.35 H3-Cl 2.16 H...Cl	-	2122/2307 H3-Cl 3378/775 O-H
NC2W-6	0.99 O-H 1.42 N-O 1.22 N-O2 1.21 N-O3	0.99 O1-H1 0.97 O1-H2 0.97 O4-H3 0.96 O4-H4 1.57 O1...H3	1.35 H3-Cl 2.18 H...Cl	-	2125/2118 H3-Cl 3409/482 O-H
NC3W-1	1.01 O-H 1.36 N-O 1.24 N-O2 1.22 N-O3	0.97 O1-H1 0.98 O1-H2 0.99 O4-H4 0.97 O4-H5 0.97 O5-H6 0.96 O5-H7 1.60 O1...H 1.57 O4...H3	1.35 H3-Cl	-	2125/2324 H3-Cl 2978/1625 O-H
NC3W-2	1.04 O-H 1.37 N-O 1.23 N-O2 1.22 N-O3 1.98 O2...H3	0.99 O1-H1 0.97 O1-H2 0.98 O4-H4 0.96 O4-H5 0.97 O5-H6 0.97 O5-H7 1.51 O1...H	1.30 H3-Cl	-	2598/1698 O-H 2900/546 H3-Cl
NC3W-3	1.05 O-H 1.38 N-O 1.23 N-O2 1.22 N-O3	0.98 O1-H1 0.98 O1-H2 0.97 O4-H4 0.97 O4-H5 0.97 O5-H6 0.96 O5-H7 1.47 O1...H	1.30 H3-Cl	-	2367/2152 O-H 2754/759 H3-Cl
NC3W-4	1.04 O-H 1.35 N-O 1.23 N-O2 1.23 N-O3	0.97 O1-H1 0.97 O1-H2 0.97 O5-H6 0.97 O5-H7	1.74 H3...Cl 1.87 H...Cl	1.07 O4-H3 1.00 O4-H4 1.01 O4-H5	2582/2425 O-H

NC4W-1	1.03 O-H 1.38 N-O 1.22 N-O2 1.22 N-O3	0.99 O1-H1 0.97 O1-H2 0.97 O4-H4 0.96 O4-H5 0.97 O5-H6 0.98 O5-H7 0.97 O6-H8 0.97 O6-H9 1.52 O1...H 1.52 O5...H3	1.37 H3-Cl	-	1715/1605 H3-Cl 2662/2040 O-H
NC4W-2	1.09 O-H 1.36 N-O 1.23 N-O2 1.23 N-O3	0.99 O1-H1 0.98 O1-H2 0.98 O4-H4 0.96 O4-H5 0.97 O5-H6 0.97 O5-H7 0.97 O6-H8 0.97 O6-H9 1.37 O1...H	1.30 H3-Cl	-	1874/2249 O-H 2781/558 H3-Cl
NC4W-3	1.60 O...H 1.27 N-O 1.28 N-O2 1.24 N-O3 1.48 O2...H3	0.97 O4-H4 0.99 O4-H5 0.98 O5-H6 0.97 O5-H7 0.98 O6-H8 0.97 O6-H9	1.38 H3-Cl	1.01 O1-H 1.05 O1-H1 1.01 O1-H2	1847/1415 H3-Cl
NC4W-4	1.39 O...H 1.32 N-O 1.25 N-O2 1.23 N-O3 1.76 O...H3	0.99 O4-H4 0.96 O4-H5 0.97 O5-H6 0.97 O5-H7 0.98 O6-H8 0.97 O6-H9	1.32 H3-Cl	1.09 O1-H 1.02 O1-H1 1.00 O1-H2	2510/1126 H3-Cl
NC4W-5	1.05 O-H 1.36 N-O 1.23 N-O2 1.22 N-O3 1.94 O2...H3	0.99 O1-H1 0.97 O1-H2 0.99 O4-H4 0.96 O4-H5 0.98 O5-H6 0.97 O5-H7 0.97 O6-H8 0.96 O6-H9 1.48 O1...H	1.30 H3-Cl	-	2457/2101 O-H 2846/634 H3-Cl
NC5W-1	1.03 O-H 1.37 N-O 1.23 N-O2 1.22 N-O3	1.00 O1-H1 0.97 O1-H2 0.99 O5-H6 0.97 O5-H7 0.97 O6-H8 0.98 O6-H9 0.97 O7-H10 0.97 O7-H11	1.93 H3...Cl 1.90 H...Cl	1.02 O4-H3 1.08 O4-H4 0.99 O4-H5	2752/2265 O-H
NC5W-2	1.48 O...H 1.31 N-O 1.24 N-O2 1.23 N-O3	0.98 O1-H1 0.96 O1-H2 0.98 O5-H5 0.96 O5-H6 0.99 O7-H10 0.97 O7-H11	1.92 H3...Cl 1.95 H8...Cl	1.04 O4-H 1.02 O4-H3 1.01 O4-H4 1.01 O6-H7 1.02 O6-H8 1.05 O6-H9	-

NC6W	1.43 O...H 1.32 N-O 1.25 N-O2 1.24 N-O3	0.98 O1-H1 0.97 O1-H2 0.98 O5-H5 0.96 O5-H6 0.99 O6-H7 0.96 O6-H8 0.99 O8-H12 0.97 O8-H13	1.92 H3...Cl 1.93 H10...Cl	1.06 O4-H 1.01 O4-H3 1.00 O4-H4 1.02 O7-H9 1.01 O7-H10 1.04 O7-H11	-
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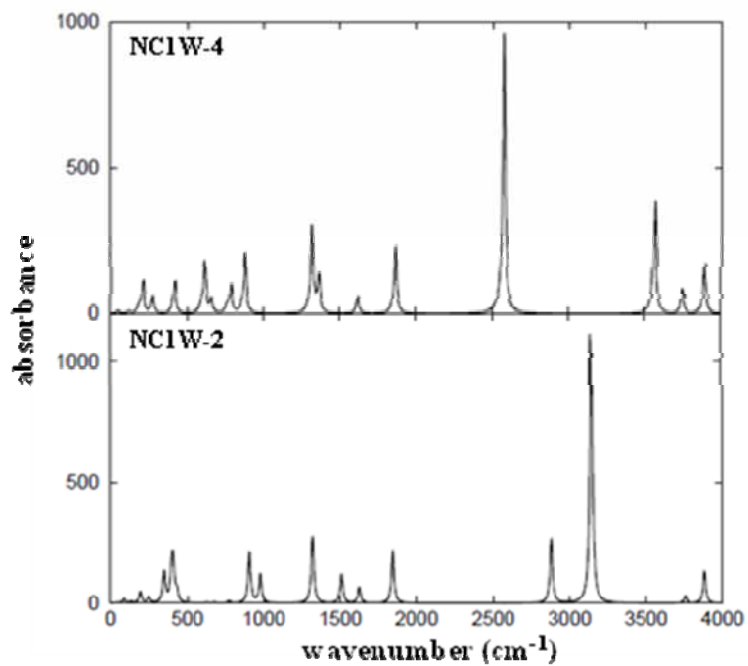


Figure S1. IR Spectrum of NC1W-2,4 clusters. Bands are represented by Lorentzian curves with a hwhm of 10 cm⁻¹.

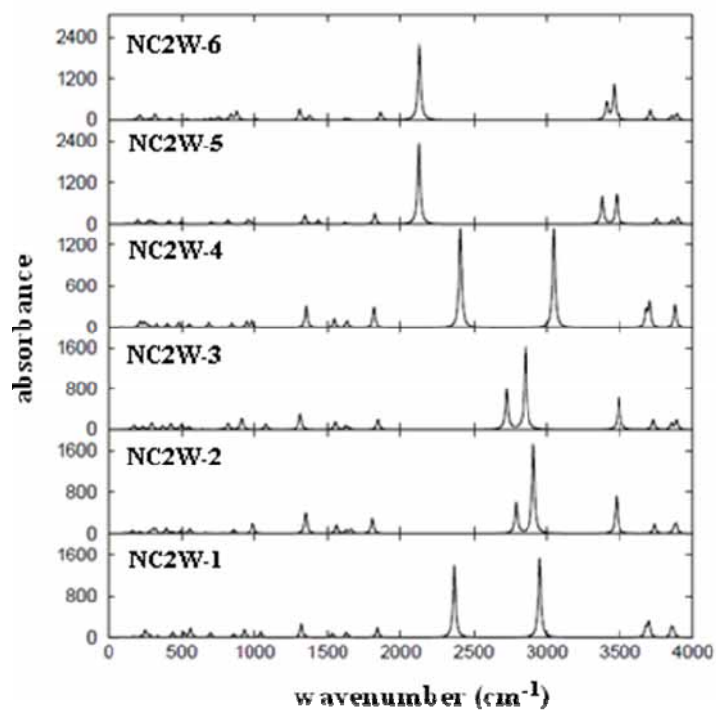


Figure S2. IR Spectrum of NC2W-1,2,3,4,5,6 clusters. Bands are represented by Lorentzian curves with a hwhm of 10 cm⁻¹.

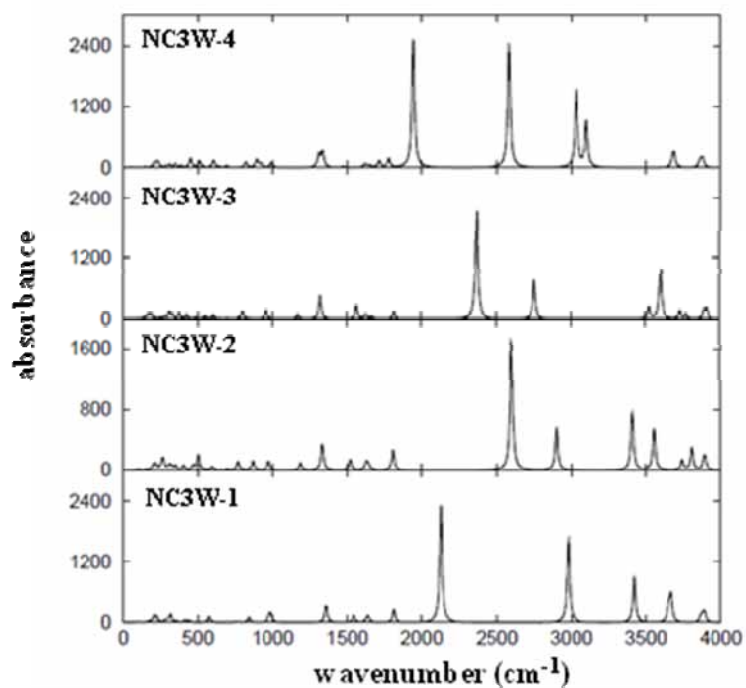


Figure S3. IR Spectrum of NC3W-1,2,3,4 clusters. Bands are represented by Lorentzian curves with a hwhm of 10 cm⁻¹.

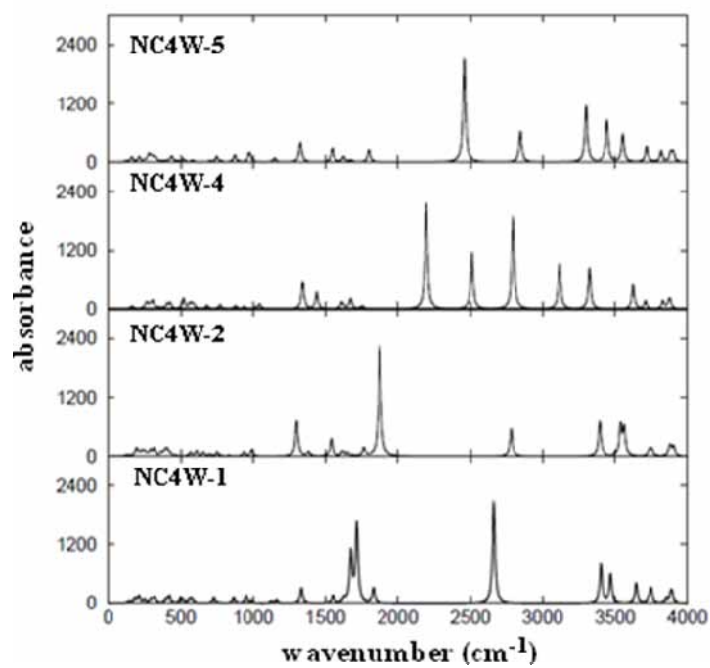


Figure S4. IR Spectrum of NC4W-1,2,4,5 clusters. Bands are represented by Lorentzian curves with a hwhm of 10 cm⁻¹.

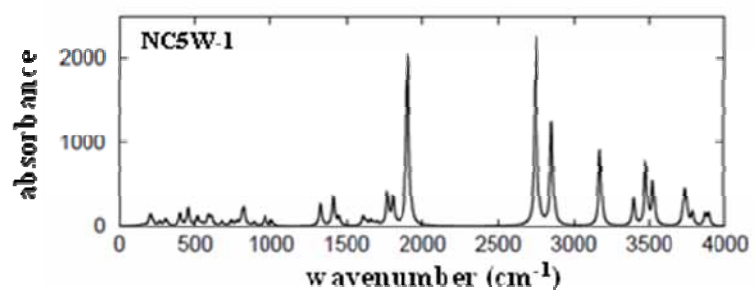


Figure S5. IR Spectrum of NC5W-1 cluster. Band is represented by Lorentzian curves with a hwhm of 10 cm⁻¹.

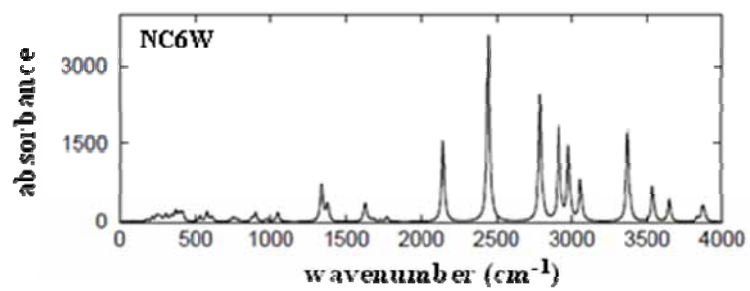


Figure S6. IR Spectrum of NC6W cluster. Band is represented by Lorentzian curves with a hwhm of 10 cm⁻¹.