Electronic Supplementary Information (ESI)

Structure, Stability and Spectral Signatures of Monoprotic Carborane Acid – Water Clusters ($CBW_{n,}$ Where n= 1–6)

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(1) **Table S1** Calculated O-H Stretching Frequencies of CBW_{nFm} (where n=3 and 4) Clusters, at B3LYP/6-31+G* Level. Along with Red Shift and Experimental Values (cm^{-1})

(2) **Table S2** Calculated O-H Stretching Frequencies of CBW_{nFm} (where n=5 and 6) Clusters, at B3LYP/6-31+G* Level. Along with Red Shift and Experimental Values (cm^{-1})

(3) **Fig. S1** Optimized geometries of CBW_{nFm} (where n= 3; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

(4) **Fig. S2** Optimized geometries of CBW_{nFm} (where n= 4; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

(5) **Fig. S3** Optimized geometries of CBW_{nFm} (where n= 5 and 6; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

Table S1 Calculated O-H Stretching Frequencies of CBW_{nFm} (where n=3 and 4) Clusters, at B3LYP/6-31+G* Level. Along with Red Shift and Experimental Values (cm^{-1})

CBW_{nFm} n = 3 and 4; m = 0, 5, and10	Description of O-H Stretching	ν_{calc} and (red shift)	ν_{expt} [a]
CBW_{3F0a}	H^+ oscillation between CB and *AD* water	1439	
	E_{as} stretch to *AD* water	2988	2889
	E_{ss} stretch to *AD* water	3042	
CBW_{3F5a}	E_{as} stretch to *AD* water	2531, 2685	2665, 2700
	E_{ss} stretch to *AD* water	2851	2420
CBW_{3F10a}	E_{as} stretch to *AD* water	2168, 2518	2100
CBW_{3F0b}	H^+ oscillation between CB and *AD* water	2115	
	$O\text{-}H_W$ (*AD*) Stretch to *AD* water	3043 (714)	
CBW_{3F5b}	E_{as} stretch to *AD* water	2260	2100
	E_{ss} stretch to *AD* water	2465	2420
CBW_{3F10b}	E_{as} stretch to *AD* water	2220	
CBW_{3F0c}	$O\text{-}H_{CB}$ Stretch to *AD* type water	2596 (1039)	
	$O\text{-}H_{CB}$ Stretch to *A* type water	3024 (611)	
	$O\text{-}H_W$ (*AD*) Stretch to *AD* water	3298 (459)	3195
	$O\text{-}H_W$ (*AD*) Stretch to *B-H in CB*	3561 (196)	
CBW_{3F5c}	$O\text{-}H_{CB}$ Stretch to *AD* type water	1964 (1620)	
CBW_{3F10c}	$O\text{-}H_{CB}$ and Bending Mode of water	1793	1756
	$O\text{-}H_{CB}$ Stretch to *A* type water	2772 (802)	
CBW_{4F0a}	E_{as} stretch to *AD* water	2951	2860
	E_{ss} stretch to *AD* water	2720	
	E Stretch to CB	2053	
CBW_{4F5a}	E_{as} stretch to *AD* water	2512	
	E_{ss} stretch to *AD* water	2578	
CBW_{4F10a}	E_{as} stretch to *AD* water	2677	2665
	E_{ss} stretch to *AD* water	2435	2420
CBW_{4F0b}	H^+ oscillation between CB and *AD* water	1982	
	$O\text{-}H_W$ (*AD*) Stretch to *AD* water	2939 (818)	
CBW_{4F5b}	E_{as} stretch to *AD* water	2042	
	E_{ss} stretch to *AD* water	2496	
CBW_{4F10b}	*E* stretch to *AD* water	1999	1885
	E stretch to *A* water	2665	

	O-H_W (*AD*) Stretch to *AD* water	2941 (816)
CBW_{4F0c}	O-H_{CB} Stretch to *A* type water	2467 (1168)
	O-H_W (*AD*) Stretch to *AD* water	2735 (1022)
CBW_{4F5c}	H^+ oscillation between CB and *AD* water	1849
	E Stretch to CB	2595
CBW_{4F10c}	*E* Stretch to CB	2781
	O-H_W (*ADD*) Stretch to *AD* water	3317 (440)

[a]Experimental O-H stretching frequency value taken from references [58-62]

Table S2 Calculated O-H Stretching Frequencies of CBW_{nFm} (where n=5 and 6) Clusters, at B3LYP/6-31+G* Level. Along with Red Shift and Experimental Values (cm^{-1})

CBW_{nFm} n = 5 and 6; m = 0, 5, and 10	Description of O-H Stretching	ν_{calc} (red shift)	ν_{expt} [a]
CBW_{5F0a}	E_{as} stretch to *AD* water	2234	
	E_{ss} stretch to *AD* water	2879	
	E stretch to *AD* water	2624	2665
CBW_{5F5a}	*E* stretch to *AD* water	2463	
	E stretch to *AD* water and CB	2601	2665
CBW_{5F10a}	*E* stretch to *ADD* water	2427	2420
	E stretch to *AD* water and CB	2594	
CBW_{5F0b}	E_{as} stretch to *AD* water	2220	
	E_{ss} stretch to *AD* water	2443, 2996	2420
	O-H_W (*ADD*) Stretch to *AD* water	3457 (300)	
CBW_{5F5b}	*E* stretch to *ADD* water	2052	
CBW_{5F10b}	*E* stretch to *ADD* water	1974	
	E_{ss} stretch to *ADD* water	2402	2420
CBW_{6F0}	E_{as} stretch to *AD* water	2227	
	E_{ss} stretch to *AD* water	2549	
	O-H_W (*AAD*) Stretch to *ADD* water	1983 (1774)	
CBW_{6F5}	*E* stretch to *AD* water	2065	
	O-H_W (*AD*) Stretch to *ADD* water	2222 (1535)	
CBW_{6F10}	*E* stretch to *AAD* water	2070, 2625	
	O-H_W (*ADD*) Stretch to *AD* water	2339 (1418)	

[a]Experimental O-H stretching frequency value taken from references [58-62]

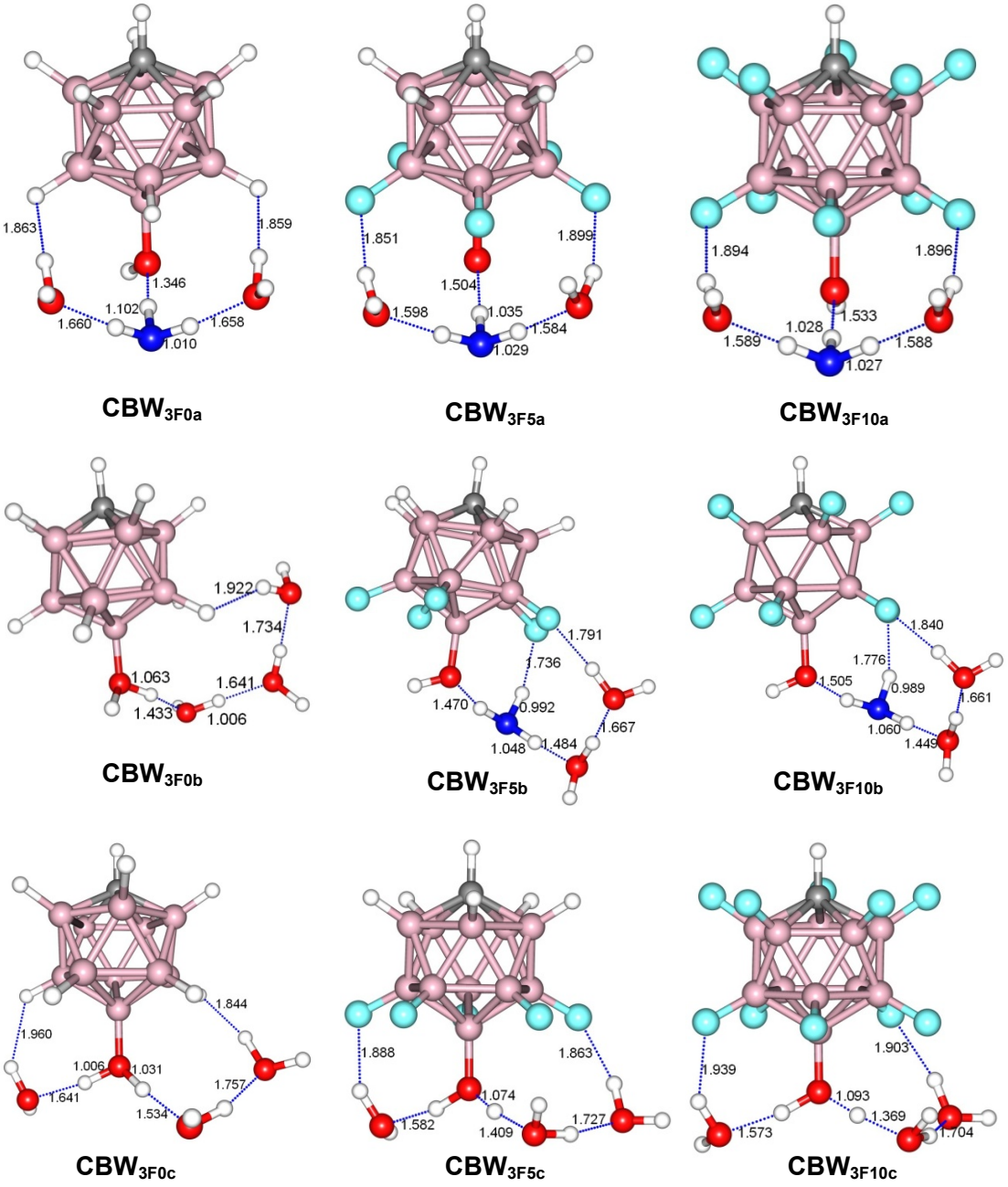

Fig. S1 Optimized geometries of CBW_{nFm} (where n= 3; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

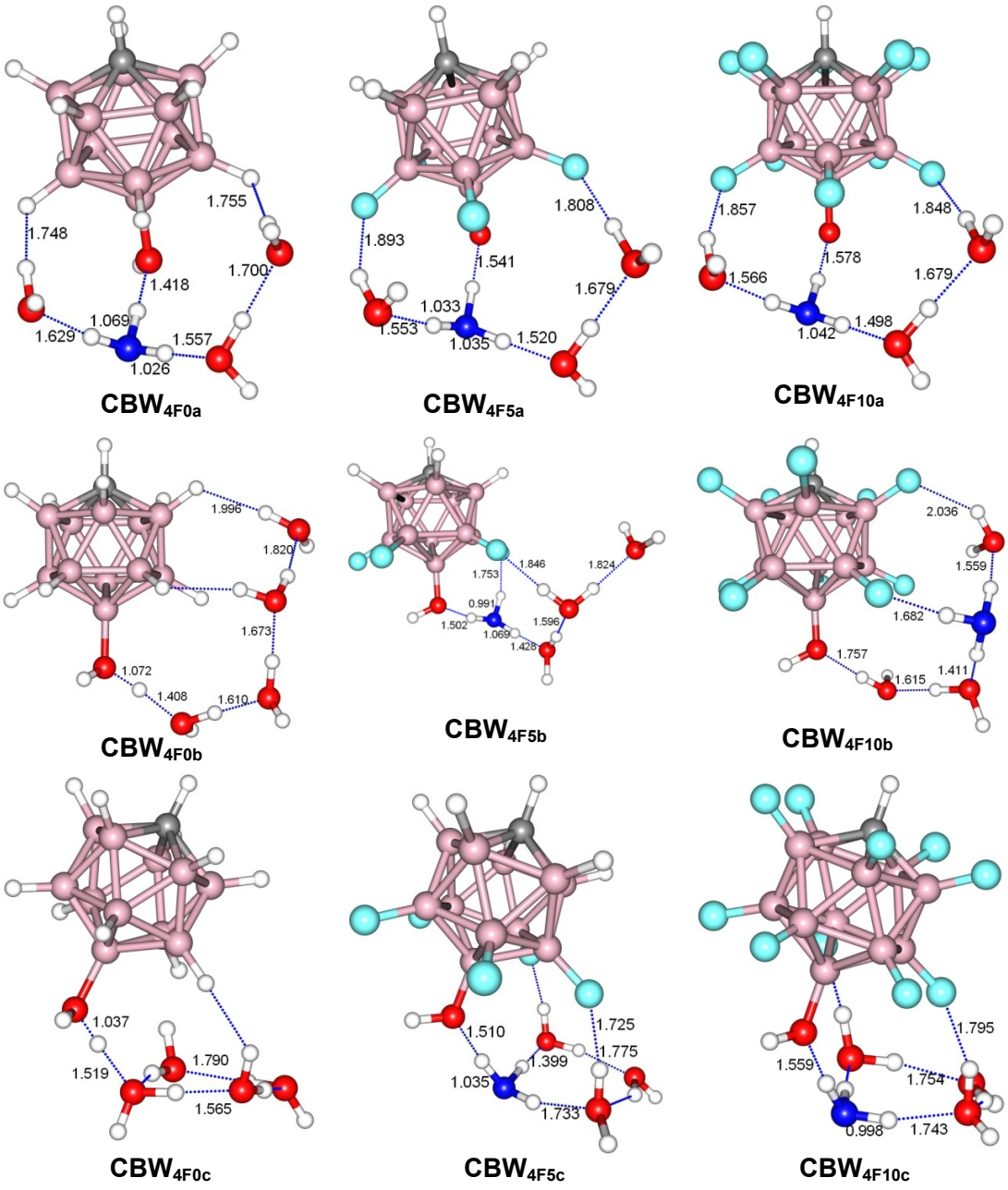

Fig. S2 Optimized geometries of CBW_{nFm} (where n= 4; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

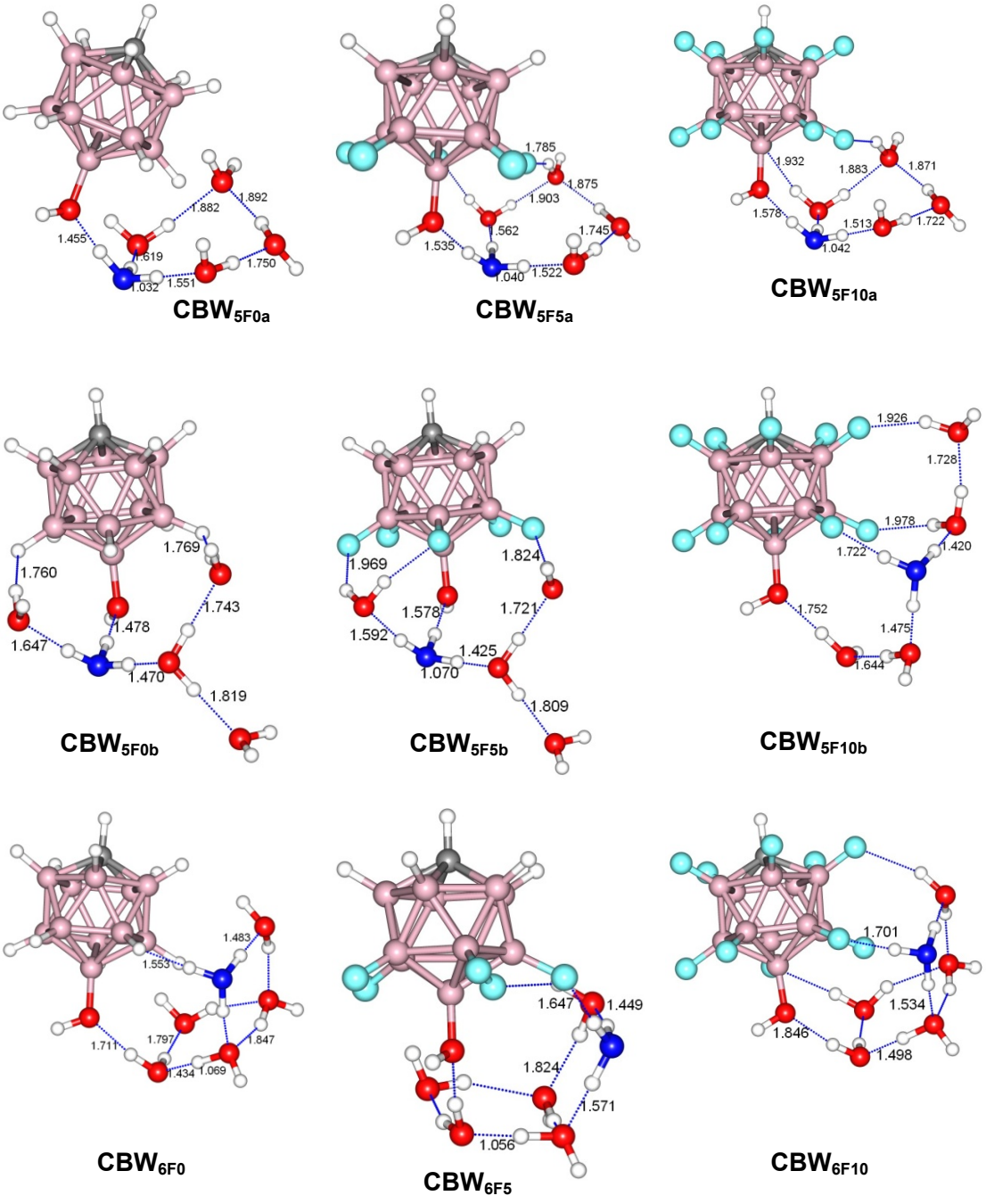

Fig. S3 Optimized geometries of CBW_{nFm} (where n= 5 and 6; m=0, 5, and 10) clusters at B3LYP/6-31+G* level. The blue color indicates the Eigen (H_3O^+) cation. Distances are in Å.

Ref 39

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