Electronic Supplementary Information

On the Synergetic Effects of Cyclic Cooperativity in Water Clusters

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Table S1: Molecular energies (in a.u.) of various species in the **HB1** energy estimation in cyclic water tetramer by the MTA-based method (*cf.* Scheme 3 in Main text), at the MP2(full)/aug-cc-pVTZ level. See main text for details.

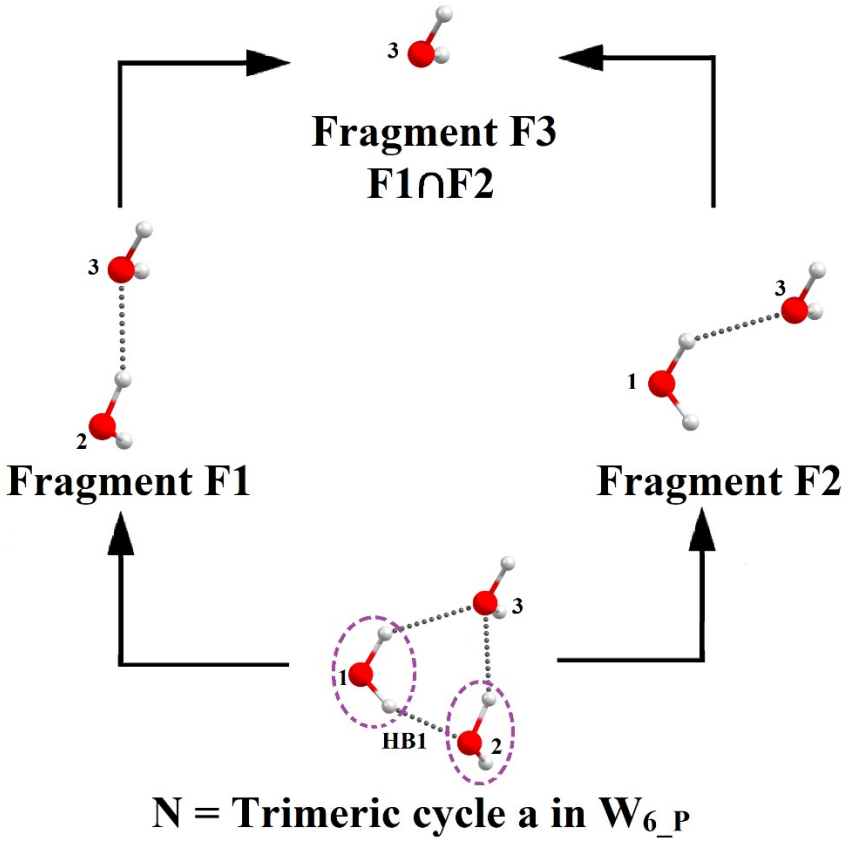
Species	Energy
Water Tetramer (E_M)	-305.415949
Fragment F1 (E_{F1})	-229.050800
Fragment F2 (E_{F2})	-229.050494
Fragment F3 (E_{F3})	-152.694193
Water dimer ($E^{dimer}_{1\ldots2}$)	-152.691954
Water monomer ($E^{monomer}_{1}$)	-76.343489
Water monomer ($E^{monomer}_{2}$)	-76.343926

Table S2: Molecular energies (in a.u.) of various species in **HB1** energy evaluation in cyclic water trimer by the MTA calculation of (*cf.* Scheme S1), at the MP2(full)/aug-cc-pVTZ level.

Species	Energy
Water Trimer (E_N)	-229.046810
Fragment F1 (E_{F1})	-152.692585
Fragment F2 (E_{F2})	-152.693753
Fragment F3 (E_{F3})	-76.343509
Water dimer ($E^{dimer}_{1\ldots2}$)	-152.691954
Water monomer 1 (E_1)	-76.343489
Water monomer 2 (E_2)	-76.343926

Table S3: Molecular energies (in a.u.) of various species in the **HB1** energy estimation in W_{6_P} cluster by the MTA-based method (cf. Scheme S2), at the MP2(full)/aug-cc-pVTZ level.

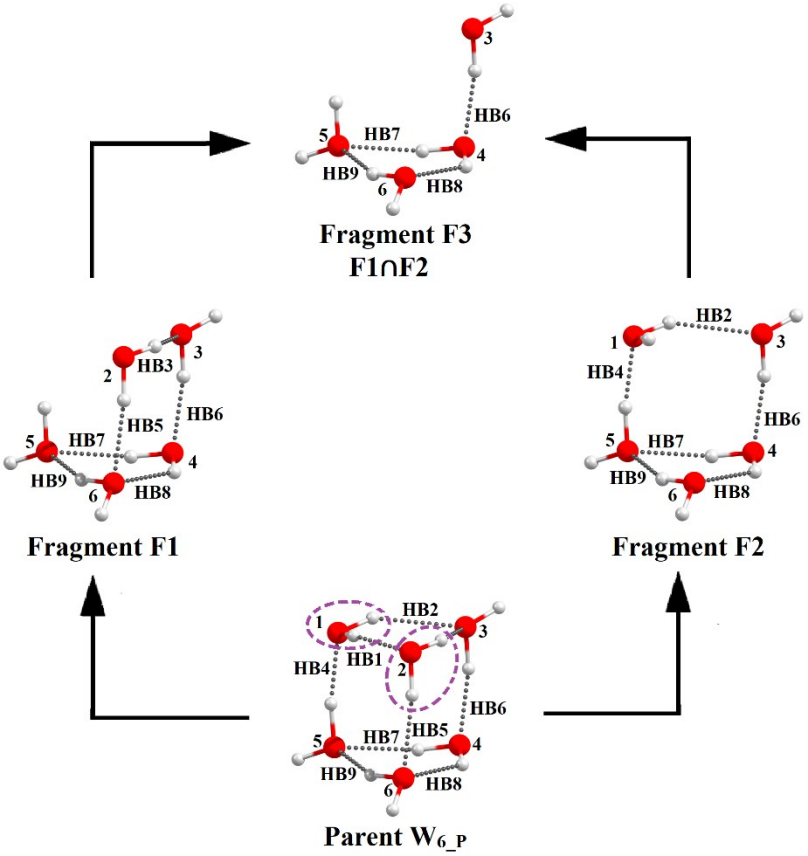
Species	Energy
Parent W_{6_P} Cluster (E_{W6_P})	-458.146736
Fragment F1 (E_{F1})	-381.766532
Fragment F2 (E_{F2})	-381.7774331
Fragment F3 (E_{F3})	-305.405370



Scheme S1. The MTA-based fragmentation for the estimation of energy of **HB1** in trimeric cycle **a** in W_{6_P} cluster.

Scheme S1 demonstrate the MTA-based fragmentation procedure for the estimation of energy of **HB1** in trimeric cycle **a** made up of water molecules 1, 2 and 3. The **HB1** is an interaction between water molecule 1 and 2. Similar to fragmentation method of tetrameric cycle (in main text) the cyclic trimer is divided into two primary fragments F1 and F2 by removing water molecules 1 and 2, respectively. Fragment F3 (water molecule 3) is a common overlap of fragments F1 and F2. Utilizing the single point (SP) energies of these fragments the E_{HB1} in this trimeric water cycle can be calculated as $E_{HB1}^{cyc\ a} = (E_{F1} + E_{F2} - E_{F3}) - E_N = 2.50$ kcal/mol at the MP2(full)/aug-cc-pVTZ level. For energies of E_{F1}, E_{F2}, E_{F3} and E_N; see Table S2 in supporting information (SI). Note that this $E_{HB1}^{cyc\ a}$ in this trimeric cycle is certainly different from that cyclic tetramer (5.55 kcal/mol; see Scheme 3 and discussion in main text). Further, $E_{HB1}^{cyc\ a}$ in this cyclic trimer includes the cooperativity contribution of water molecule 3. Recall the discussion in main text that ($E_{HB1}^{dimer} = 2.85$ kcal/mol) excludes this cooperativity effect.

Therefore, the cooperativity contribution (the difference between $E_{HB1}^{cyc\ a}$ and E_{HB1}^{dimer}) to the HB1 in cyclic trimer is $E_{coop.}^{cyc\ a} = E_{HB1}^{cyc\ a} - E_{HB1}^{dimer}$ = 2.50 - 2.85 = -0.35 kcal/mol.



Scheme S2. The MTA-based fragmentation for the estimation of energy of **HB1** in W_{6_P} cluster.

Similarly, the energy of **HB1** in actual W_{6_P} can be calculated (cf. Scheme S2) by the MTA-based by dividing the W_{6_P} cluster into two primary fragments, F1 and F2 (obtained by removing water molecules 1 and 2, respectively). A common overlapping fragment of F1 and F2 is fragment F3 consisting of four water molecules (water 3, 4, 5, and 6). The energy of **HB1** in this W_{6_P} cluster can be obtained using the SP energy of these fragments and that of the parent W_{6_P} cluster as $E_{HB1}^{W6\_P} = (E_{F1} + E_{F2} - E_{F3}) - E_{W6\_P}$ = 5.11 kcal/mol at the MP2(full)/aug-cc-pVTZ level. For details of energy of these primary fragments and that of parent W_{6_P} cluster, see Table S3 in SI.

Table S4. The BSSE corrected HB energies (in kcal/mol) in W_{6_P} cluster obtained by synergetic addition of BSSE corrected cyclic cooperativity contributions ($E^{Syn.}_{HB}$) and that by MTA-based method employing actual cluster ($E^{cluster}_{HB}$). The BSSE corrected HB energies in the respective dimer species (E^{Dimer}_{HB}) are also provided (in kcal/mol). All the calculations were performed at the MP2(full)/aug-cc-pVTZ level of theory

HB	$E^{Dimer}_{HB(BSSE)}$	$E^{Cyc.\ 1}_{coop.(BSSE)}$	$E^{Cyc.2}_{coop.(BSSE)}$	$E^{Syn.}_{HB(BSSE)}$	$E^{W_{6\_P}}_{HB(BSSE)}$	$\lvert\Delta E_{HB}\rvert$
HB1	1.84	-0.27 (-a)	2.84 (+c)	4.40	4.27	0.13
HB2	2.54	-0.27 (-a)	2.70 (+d)	6.09	6.21	0.12
HB3	1.90	-0.27 (-a)	-0.12 (-e)	2.16	1.90	0.26
HB4	3.60	3.31 (+c)	3.05 (+d)	9.96	9.97	0.01
HB5	4.47	2.49 (+c)	-1.25 (-e)	5.71	5.41	0.30
HB6	4.31	2.69 (+d)	1.01 (-e)	8.01	8.00	0.01
HB7	4.02	-0.49 (-b)	3.04 (+d)	6.57	6.73	0.16
HB8	1.31	-1.16 (-b)	-0.12 (-e)	0.03	0.46	0.43
HB9	3.9	-1.48 (-b)	2.98 (+c)	5.74	6.19	0.45

The plus/minus sign indicates positive/negative cooperativity contributions.
The labels "**a**" to "**e**" represent the trimeric or tetrameric cycles in Fig. 1.

Note on BSSE corrected HB energy Evaluation: As discussed in Scheme 2, one or two water molecules in the primary or secondary fragments are removed to estimate the HB energy. Here, instead of removing these molecules completely, ghost orbitals of these molecules are added in the fragment energy calculations. Thus-calculated energies of the fragments are used for evaluating the BSSE-corrected HB energy (as in Schemes 2, S1 and S2). The BSSE corrected cooperativity contributions from different cyclic structure are also evaluated as the difference between the BSSE-corrected HB energies in these cyclic structures and the BSSE corrected HB energy in the respective dimer. The results of BSSE-corrected HB energy in the dimer, the BSSE-corrected cooperativity contribution of cyclic structures and the BSSE-corrected HB energy obtained by synergetic cooperativity effects in W_{6_P} and W_8 clusters are now summarized in Tables S4 and S5 in ESI†, respectively. As can be seen from Tables S4 and S5, the BSSE-corrected HB energies in these clusters are smaller than their uncorrected counterparts (Tables 1 and 2 of main text). Nevertheless, the difference between the uncorrected and corrected energies is less than 1 kcal/mol. These small BSSE corrections to HB energy by MTA-based method may be attributed to the numerical addition of fragment energies (BSSE-corrected or -uncorrected) leading to the cancellation of errors. Importantly, BSSE-corrected HB energies obtained using the synergetic effects match their BSSE-corrected MTA-based counterparts in actual clusters quite well, the typical difference being less than 0.5 kcal/mol. With this understanding of small BSSE, the uncorrected HB energies in larger cluster are used for the further discussion. See discussion in main text for further details.

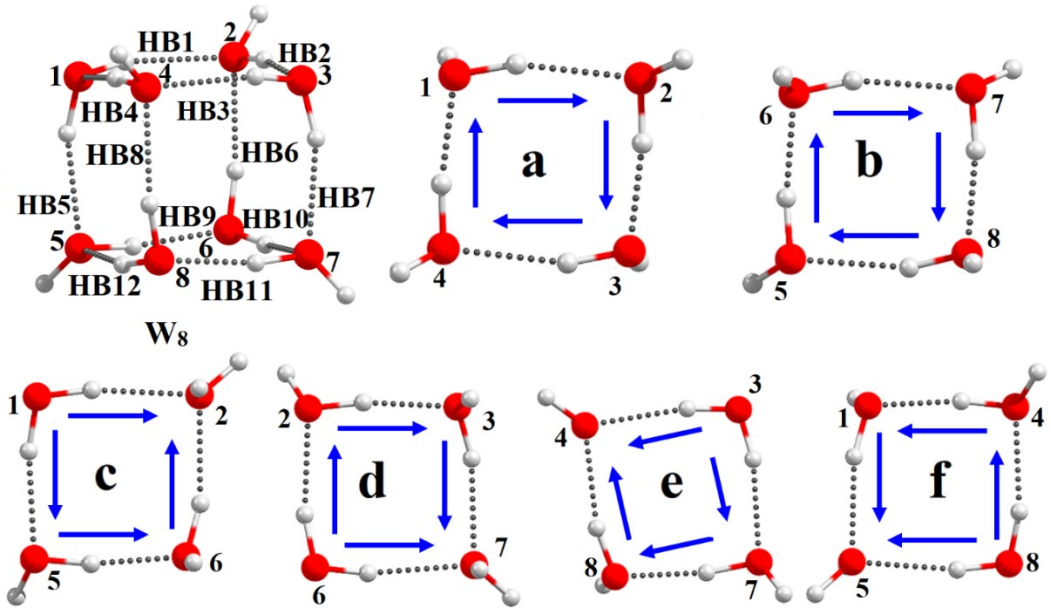


Fig. S1 Structure of W_8 cluster consisting of six tetrameric cycles denoted by labels **a** to **f**.

Table S5. The BSSE corrected HB energies (in kcal/mol) in W_8 cluster obtained by synergetic addition of BSSE corrected cyclic cooperativity contributions ($E^{Syn.}_{HB}$) and that by MTA-based method employing actual cluster ($E^{cluster}_{HB}$). The BSSE corrected HB energies in the respective dimer species (E^{Dimer}_{HB}) are also provided (in kcal/mol). All the calculations were performed at the MP2(full)/aug-cc-pVTZ level of theory

HB	$E^{Dimer}_{HB(BSSE)}$	$E^{Cyc.\ 1}_{coop.(BSSE)}$	$E^{Cyc.2}_{coop.(BSSE)}$	$E^{Syn.}_{HB(BSSE)}$	$E^{W_{6\_P}}_{HB(BSSE)}$	$\lvert\Delta E_{HB}\rvert$
HB1	4.42	3.41 (+a)	-1.45 (-c)	6.38	6.75	0.37
HB2	3.89	3.41 (+a)	1.95 (+d)*p*	9.25	9.66	0.41
HB3	4.42	3.41 (+a)	-1.45 (-e)	6.38	6.75	0.37
HB4	3.89	3.41 (+a)	1.95(+f)*p*	9.25	9.66	0.41
HB5	3.02	0.21 (-c)	0.29 (-f)	3.52	3.13	0.39
HB6	3.02	0.29 (-c)	0.21 (-d)	3.52	3.13	0.39
HB7	3.02	0.29 (-d)	0.21 (-e)	3.52	3.13	0.39
HB8	3.02	0.29 (-e)	0.21 (-f)	3.52	3.13	0.39
HB9	3.89	1.95 (+c)*p*	3.41 (+b)	9.25	9.66	0.41
HB10	4.42	-1.45 (-d)	3.41 (+b)	6.38	6.75	0.37
HB11	3.89	1.95 (+e)*p*	3.41 (+b)	9.25	9.66	0.41
HB12	4.42	-1.45 (-f)	3.41 (+b)	6.38	6.75	0.37

The plus/minus sign indicates positive/negative cooperativity contributions.

The labels "**a**" to "**f**" represent the tetrameric cycles in Fig. S1 ESI†.

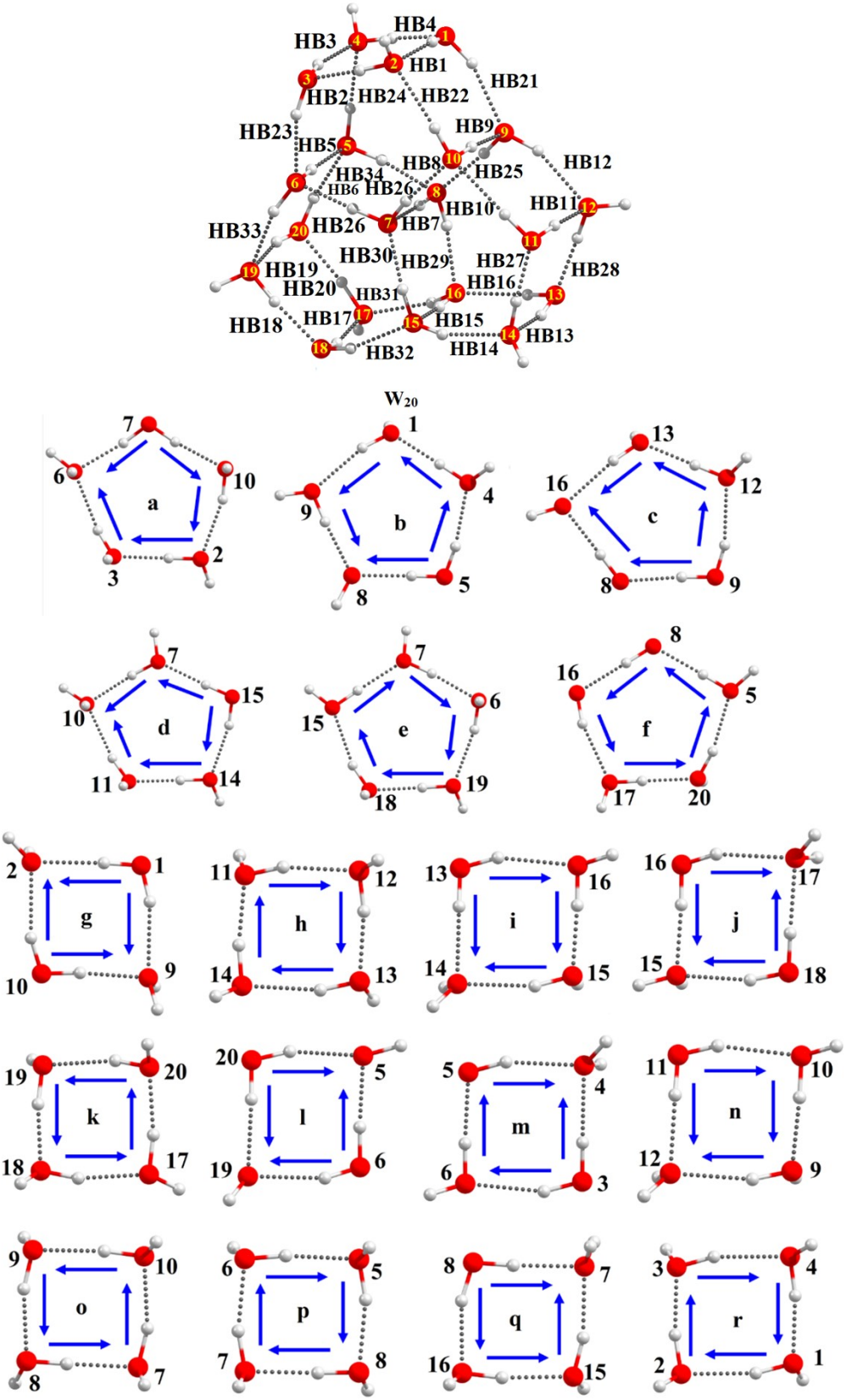


Fig. S2 Structure of W_{20} cluster consisting of six pentameric cycles denoted by labels **a** to **f** and twelve tetrameric cycles, denoted by labels **g** to **r**.

Table S6. The hydrogen bond energies (in kcal/mol) in W_{20} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer}) is also provided (kcal/mol). All the calculations were performed at the MP2/aug-cc-pVTZ level of theory. See text for details.

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_{20}				
HB1	5.05	-0.73 (-g)	3.49 (+r) [#1, #2]	-	7.81	7.41	0.40
HB2	4.70	3.42 (+r)	2.11 (+a) partial	-	10.23	10.36	0.13
HB3	5.10	3.36 (+r)	-1.29 (-m)	-	7.18	7.41	0.23
HB4	4.70	3.44 (+r)	2.25 (+b) partial	-	10.39	10.38	0.01
HB5	4.86	-1.01 (-l)	1.68 (+m) partial	3.69 (+p)	9.21	9.03	0.18
HB6	4.71	-2.26 (-a)	3.37 (+e)	3.66 (+p)	9.47	8.71	0.76
HB7	4.68	3.68 (+o)	3.54 (+p)	-1.96 (-q)	9.93	9.26	0.67
HB8	4.65	3.71 (+p)	-2.20 (-b)	3.11 (+f)	9.27	8.70	0.57
HB9	4.87	-0.94 (-g)	3.64 (+o)	1.56 (+n) partial	9.14	8.94	0.20
HB10	3.22	-0.02 (-d)	-0.20 (-n)	-	3.00	3.86	0.86
HB11	5.08	-1.36 (-n)	3.51 (+h)	-	7.20	7.47	0.27
HB12	3.74	0.20 (-n)	-0.45 (-c)	-	3.49	4.59	1.10
HB13	5.12	3.34 (+h)	-1.28 (-i)	-	7.18	7.42	0.24
HB14	3.75	0.32 (-d)	-0.50 (-i)	-	3.57	4.75	1.18
HB15	4.84	-0.95 (-j)	1.70 (+i) partial	2.49 (+q) partial	8.08	9.19	1.11
HB16	3.16	0.10 (-i)	-0.14 (-c)	-	3.12	4.02	0.90
HB17	5.04	-0.71 (-j)	3.50 (+k)	-	7.82	7.43	0.39
HB18	4.70	3.44 (+k)	3.28 (+e)	-	11.42	10.43	0.99
HB19	5.07	3.35 (+k)	-0.69 (-l)	-	7.73	7.32	0.41
HB20	4.73	3.42 (+k)	3.14 (+f)	-	11.29	10.35	0.94
HB21	4.64	-0.81 (-g)	2.16 (+b) partial	-	5.99	6.96	0.97
HB22	4.69	-0.86 (-g)	2.15 (+a) partial	-	5.98	6.91	0.93
HB23	3.18	0.09 (-m)	0.34 (-a)	-	3.60	4.04	0.44
HB24	3.90	0.30 (-m)	0.28 (-b)	-	4.48	4.87	0.39
HB25	4.11	3.60 (+o)	0.33 (-b)	-0.93 (-c)	7.11	7.00	0.11
HB26	4.12	3.59 (+o)	0.04 (-a)	-0.48 (-d)	7.27	6.76	0.51
HB27	4.69	3.41 (+h)	1.19 (+d) partial	-	9.29	10.34	1.05
HB28	4.68	3.42 (+h)	1.17 (+c) partial	-	9.27	10.34	1.07
HB29	2.70	0.16 (-q)	-0.52 (-c)	3.11 (+f)	5.45	5.40	0.05
HB30	3.91	0.36 (-q)	-0.98 (-d)	3.24 (+e)	6.53	6.85	0.32
HB31	4.62	-0.87 (-j)	2.90 (+f)	-	6.65	6.85	0.20
HB32	4.63	-0.80 (-j)	2.92 (+e)	-	6.75	6.98	0.23
HB33	4.64	-0.92 (-l)	3.15 (+e)	-	6.87	7.15	0.28
HB34	4.59	-0.79 (-l)	2.96 (+f)	-	6.76	7.07	0.31

[#1] The plus and minus sign before labels "**a**" to "**r**" indicate positive/negative cooperativity contribution

[#2] The labels **a** to **f** denote pentameric cycles and **g** to **r** denote twelve tetrameric cycles in Fig. S2.

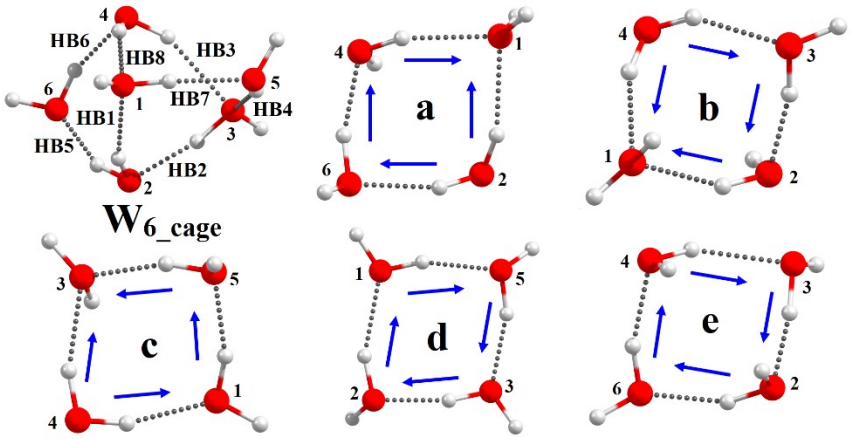


Fig. S3 Structure of W_6 (cage) cluster consisting of five tetrameric cooperative cycles denoted by labels **a** to **e**.

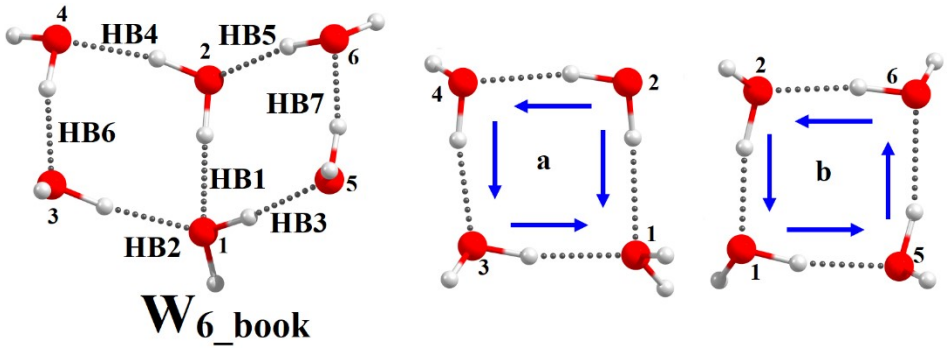


Fig. S4 Structure of W_6 (book) cluster consisting of two tetrameric cooperative cycles denoted by labels **a** and **b**.

Table S7. The hydrogen bond energies (in kcal/mol) in W_6 (book) and W_{6_cage} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E^{Syn.}_{HB}$) and that by MTA-based method employing actual cluster ($E^{cluster}_{HB}$). The hydrogen bond energy in the respective dimer species (E^{Dimer}_{HB}) is also provided (in kcal/mol). All the calculations were performed at MP2(full)/aug-cc-pVTZ level of theory. See text for details.

HB	E^{Dimer}_{HB}	$E^{Cyc.\ 1}_{coop.}$	$E^{Cyc.\ 2}_{coop.}$	$E^{Cyc.\ 3}_{coop.}$	$E^{Syn.}_{HB}$	$E^{cluster}_{HB}$	$\lvert\Delta E_{HB}\rvert$
			W_{6_book}				
HB1	5.32	-1.16 (-a)	3.09 (+b)	-	7.25	7.23	0.02
			W_{6_cage}				
HB1	4.96	-1.25 (-a) [#1, #2]	0.73 (-b)	2.81 (+d)	7.25	6.37	0.88
HB2	4.81	2.36 (+b) partial	3.20 (+d)	2.50 (+e)	12.87	10.47	2.40
HB3	4.33	0.45 (-b)	-1.08 (-c)	2.33 (+e)	6.03	5.49	0.54
HB4	5.16	0.98 (-c)	3.35 (+d)	-	9.49	8.20	1.29
HB5	4.10	0.55 (-a)	2.68 (+e)	-	7.33	5.99	1.34
HB6	5.30	1.82 (+a) partial	2.44 (+d)	-	9.56	8.27	1.29
HB7	5.21	2.10 (+c) partial	2.95 (+d)	-	10.26	8.78	1.48
HB8	3.96	0.08 (-a)	-1.17 (-b)	0.05 (-c)	2.92	3.96	1.04

[#1] The plus and minus sign before labels "**a**" to "**e**" indicate positive/negative cooperativity contribution.
[#2] The labels **a** to **e** denote the tetrameric cycles in Fig. S3.

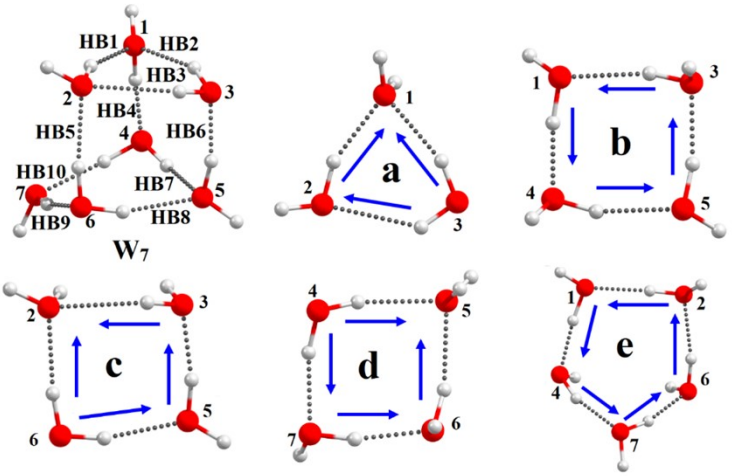


Fig. S5 Structure of W_7 cluster consisting of one trimeric (denoted by **a**), three tetrameric (denoted by **b** to **d**) and one pentameric (denoted by **e**) cooperative cycles.

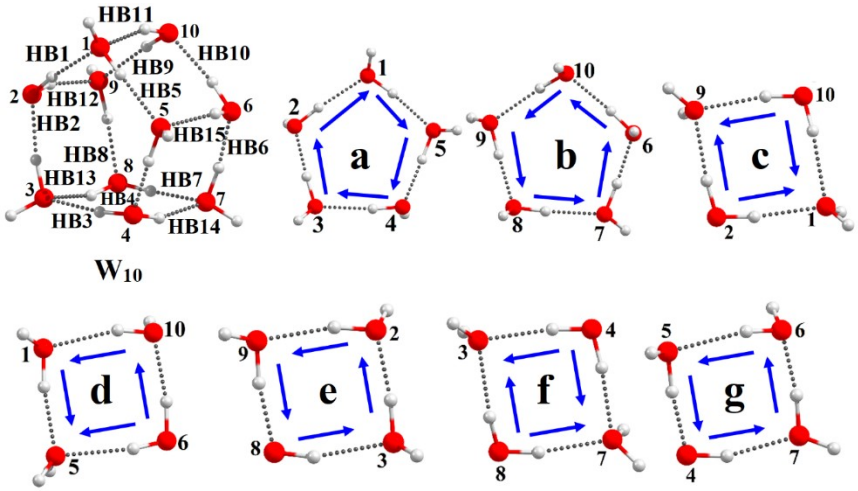


Fig. S6 Structure of W_{10} cluster consisting of two pentameric (denoted by **a** and **b**), five tetrameric (denoted by **c** to **g**) cooperative cycles.

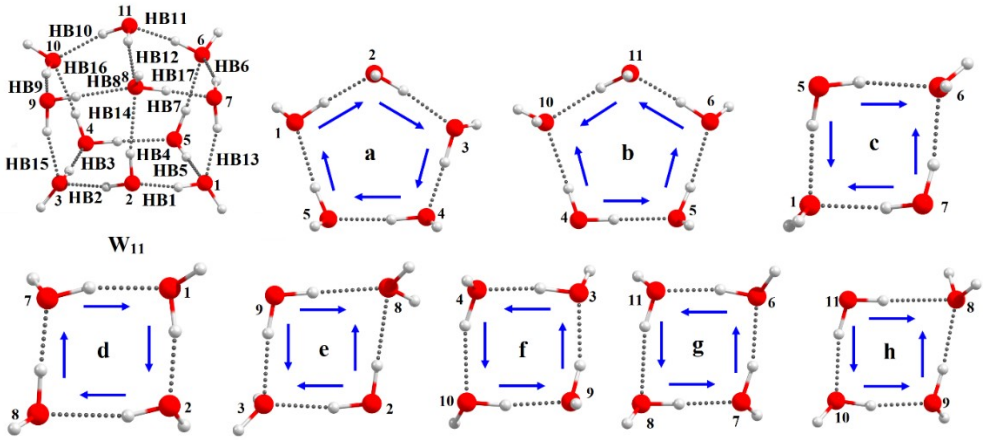


Fig. S7 Structure of W_{11} cluster consisting of two pentameric (denoted by **a** and **b**), six tetrameric (denoted by **c** to **h**) cooperative cycles

Table S8. The HB energies (in kcal/mol) in W_7, W_{10}, and W_{11} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer} **)** is also provided (in kcal/mol). All the calculations were performed at the MP2(full)/aug-cc-pVTZ level of theory.

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_7				
HB1	4.79	-0.60 (-a) [#1]	3.17 (+e)	-	7.36	7.11	0.25
HB2	4.96	-0.60 (-a) [#2]	3.30 (+b)	-	7.66	7.98	0.32
HB3	1.51	-0.60 (-a)	-0.17 (-c)	-	0.74	0.42	0.32
HB4	4.69	3.35 (+b)	3.44 (+e)	-	11.48	11.56	0.08
HB5	5.20	-1.51 (-c)	2.86 (+e)	-	6.55	6.24	0.31
HB6	5.33	3.07(+b)	1.02 (+c) partial	-	9.42	9.48	0.06
HB7	5.31	3.16 (+b)	-1.42 (-d)	-	7.05	7.25	0.20
HB8	3.97	-0.30 (-d)	0.17 (+b)	-	3.84	3.61	0.23
HB9	5.30	2.94 (+e)	1.90 (+d) partial	-	10.14	9.08	1.06
HB10	3.97	2.89 (+e)	0.31 (-d)	-	7.17	5.93	1.24
			W_{10}				
HB1	4.97	-0.75 (-c) [#1]	1.94 (+d) partial	-	6.16	6.24	0.08
HB2	4.55	3.54 (+e) [#2]	3.83 (+a)	-	11.92	10.66	1.26
HB3	4.92	-0.87 (-f)	3.89 (+a)	-	7.94	7.49	0.45
HB4	4.32	3.57 (+g)	4.27 (+a)	-	12.16	11.38	0.78
HB5	4.42	0.42 (-d)	3.89 (+a)	-	8.73	8.14	0.59
HB6	4.36	3.57 (+g)	4.03 (+b)	-	11.96	11.23	0.73
HB7	4.94	-0.87 (-f)	3.86 (+b)	-	7.93	7.48	0.45
HB8	4.56	3.54 (+e)	3.78 (+b)	-	11.88	10.62	1.26
HB9	5.00	-1.16 (-c)	3.50 (+b)	-	7.34	6.85	0.49
HB10	3.54	0.64 (-d)	3.70 (+b)	-	7.88	6.76	1.12
HB11	5.03	-0.19 (-c)	3.53 (+a)	-	8.37	6.92	1.45
HB12	4.96	-1.32 (-c)	3.60 (+e)	-	7.24	7.53	0.29
HB13	4.96	3.48 (+e)	-0.83 (-f)	-	7.61	7.22	0.39
HB14	4.95	-0.92 (-f)	3.74 (+g)	-	7.77	7.73	0.04
HB15	4.85	-0.79 (-d)	3.40 (+g)	-	7.46	6.95	0.51
			W_{11} [#3]				
HB1	4.59	3.61 (+a) [#1]	3.23 (+d)	-	11.43	9.93	1.50
HB2	4.74	3.90 (+a) [#2]	-0.71 (-e)	-	7.92	7.54	0.38
HB3	4.25	4.22 (+a)	3.59 (+f)	-	12.06	11.80	0.26
HB4	4.16	3.86 (+a)	0.68 (-b)	-	8.70	7.74	0.96
HB5	5.05	3.38 (+a)	-0.86 (-c)	-	7.57	6.68	0.89
HB6	4.81	-0.82 (-c)	3.62 (+g)	-	7.61	7.52	0.09
HB7	4.27	3.40 (+d)	3.41 (+g)	-	11.09	11.70	0.61
HB8	4.54	-0.76 (-e)	0.70 (-h)	-	4.48	5.79	1.31
HB9	4.65	3.22 (+f)	2.02 (+h) partial	-	9.89	9.59	0.30
HB10	3.30	0.70 (-b)	0.49 (-h)	-	4.49	4.15	0.34
HB11	4.58	2.43 (+b) partial	3.22 (+g)	-	10.24	9.88	0.36
HB12	4.71	3.01 (+g)	-0.92 (-h)	-	6.80	6.50	0.30
HB13	4.81	-0.83 (-c)	3.63 (+d)	-	7.62	7.55	0.07
HB14	4.67	-0.50 (-e)	2.98 (+d)	-	7.15	6.34	0.81
HB15	4.77	-0.98 (-e)	3.57 (+f)	-	7.36	7.50	0.14
HB16	5.05	-1.55 (-b)	3.23 (+f)	-	6.73	6.65	0.08
HB17	5.04	2.50 (+b) partial	-0.86 (-c)	-	6.68	6.63	0.05

[#1] The plus and minus sign before labels "**a**" to **"h"** indicate positive/negative cooperativity contribution.

[#2] The labels **a** to **h** denote the cycles of HB network in Figs. S5 to S7.

[#3] All the calculations were performed in W11 cluster at the MP2aug-cc-pVTZ level of theory.

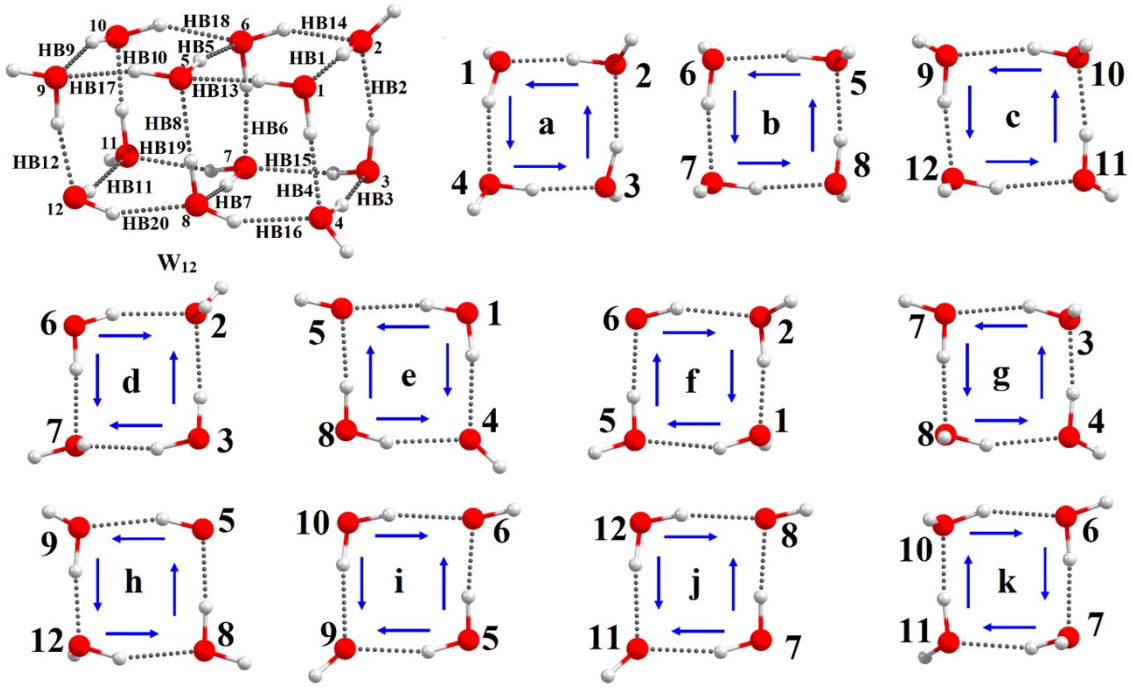


Fig. S8 Structure of W_{12} cluster consisting of eleven tetrameric (denoted by **a** and **k**) cooperative cycles.

Table S9. The HB energies (in kcal/mol) in W_{12} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer}) is also provided (in kcal/mol). All the calculations were performed at MP2/aug-cc-pVTZ level of theory.

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_{12}				
HB1	4.75	3.25 (+a) [#1]	3.13 (+f)	-	11.13	10.25	0.83
HB2	5.01	3.25 (+a) [#2]	-0.69 (-d)	-	7.57	7.10	0.47
HB3	4.75	3.25 (+a)	3.13 (+g)	-	11.13	10.25	0.88
HB4	5.01	3.25 (+a)	-0.69 (-e)	-	7.57	7.10	0.47
HB5	4.77	3.42 (+b)	2.90 (+f)	-0.90 (-i)	10.18	8.71	1.47
HB6	4.77	3.42 (+b)	-0.90 (-d)	2.90 (+k)	10.18	8.71	1.47
HB7	4.77	3.42 (+b)	2.90 (+g)	-0.90 (-j)	10.18	8.71	1.47
HB8	4.77	3.42 (+b)	-0.90 (-e)	2.90 (+h)	10.18	8.71	1.47
HB9	5.01	3.25 (+c)	-0.69 (-i)	-	7.57	7.10	0.47
HB10	4.75	3.25 (+c)	3.13(+k)	-	11.13	10.25	0.88
HB11	5.01	3.25 (+c)	-0.69 (-j)	-	7.57	7.10	0.47
HB12	4.75	3.25 (+c)	3.13 (+h)	-	11.13	10.25	0.88
HB13	4.46	-0.72 (-e)	2.93 (+f)	-	6.67	6.95	0.28
HB14	4.51	-0.87 (-d)	3.09 (+f)	-	6.73	7.08	0.35
HB15	4.46	-0.72 (-d)	2.93 (+g)	-	6.67	6.95	0.28
HB16	4.51	-0.87 (-e)	3.26 (+g)	-	6.90	7.08	0.18
HB17	4.51	3.09 (+h)	-0.87 (-i)	-	6.73	7.08	0.35
HB18	4.46	-0.72 (-d)	2.93 (+k)	-	6.67	6.95	0.28
HB19	4.51	-0.87 (-j)	3.09 (+k)	-	6.73	7.08	0.35
HB20	4.46	-0.72 (-j)	2.93 (+h)	-	6.67	6.95	0.28

[#1] The plus and minus sign before labels "**a**" to "**k**" indicate positive/negative cooperativity contribution.

[#2] The labels **a** to **k** denote the tetrameric cycles in Fig. S8.

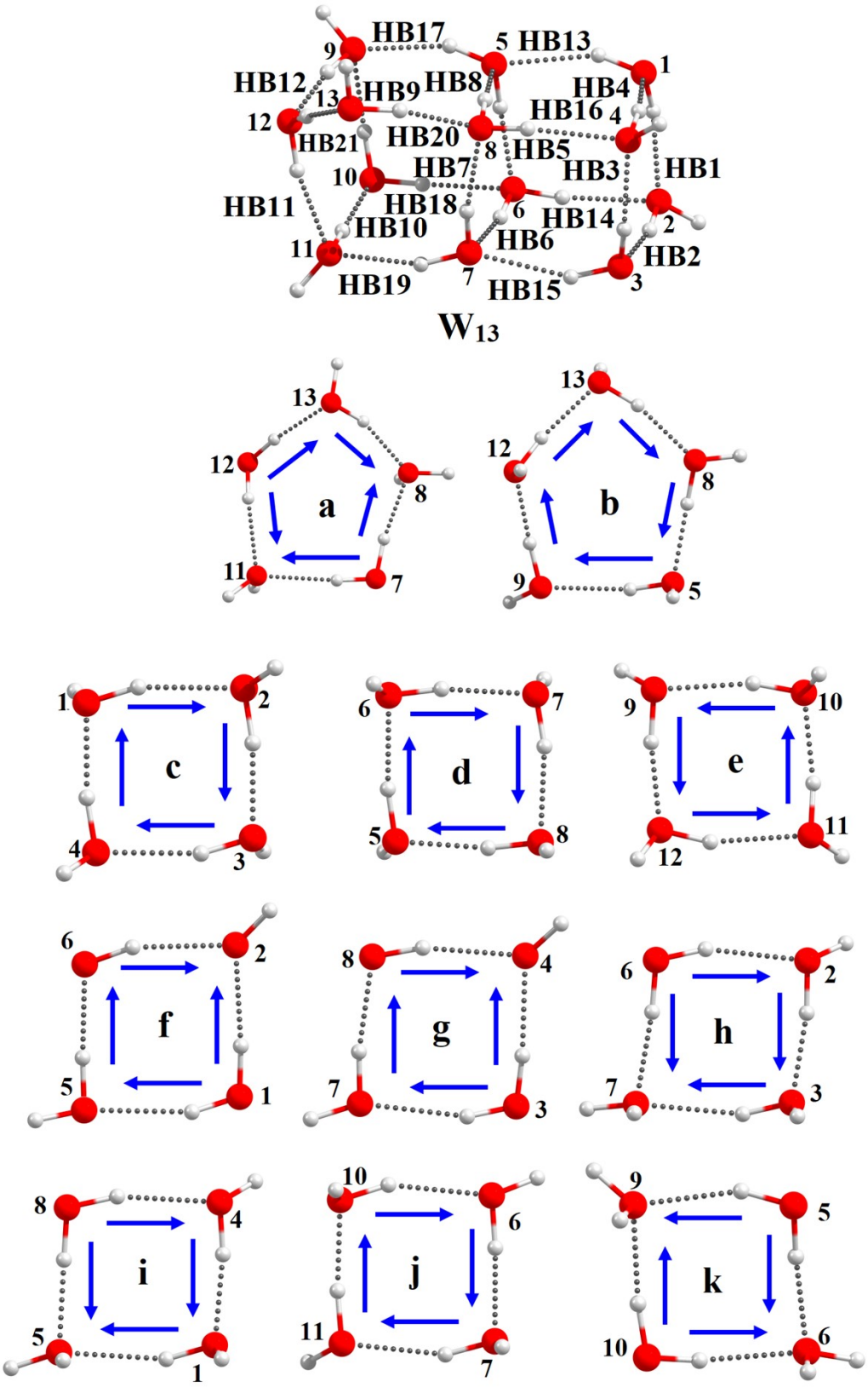


Fig. S9 Structure of W_{13} cluster consisting of two pentameric (denoted by **a** and **b**) and nine tetrameric (denoted by **c** and **k**) cooperative cycles.

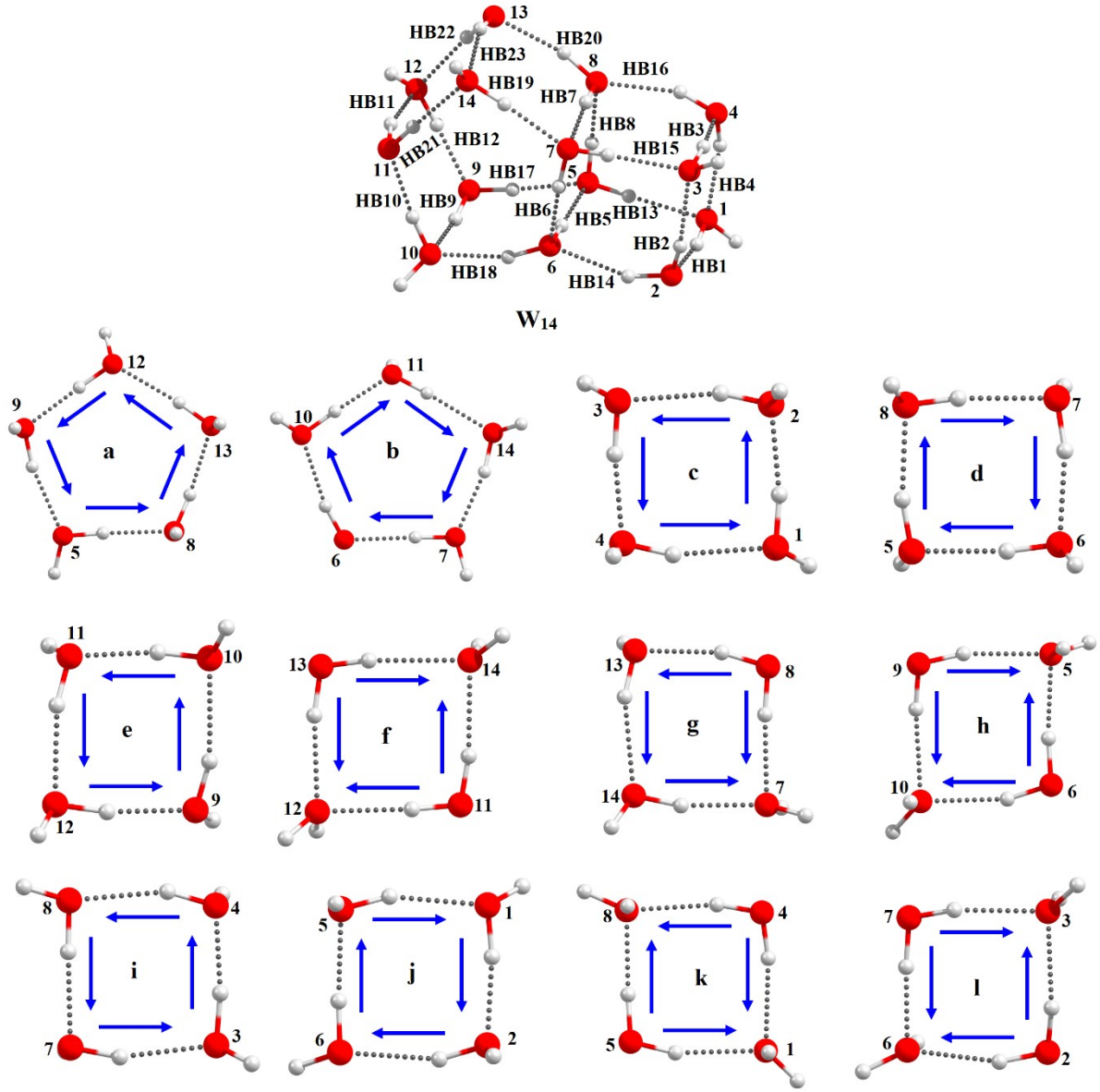


Fig. 10 Structure of W_{14} cluster consisting of two pentameric (denoted by **a** and b) and ten tetrameric (denoted by **c** to **l**) cooperative cycles.

Table S10. The HB energies (in kcal/mol) in W_{13} and W_{14} clusters obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer}) is also provided (in kcal/mol). All the calculations were performed at the MP2/aug-cc-pVTZ level of theory.

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_{13}				
HB1	5.07	3.23 (+c) [#1]	-1.37 (-f)	-	6.93	7.22	0.29
HB2	4.79	3.26 (+c) [#2]	1.44 (+h) partial	-	9.49	9.95	0.46
HB3	5.03	3.29 (+c)	-1.39 (-g)	-	6.93	7.18	0.25
HB4	4.79	3.26 (+c)	1.37 (+i) partial	-	9.42	10.01	0.59
HB5	4.68	3.66 (+d)	1.36 (+f) partial	-0.93 (-k)	8.76	8.72	0.04
HB6	4.80	3.47 (+d)	-1.71 (-h)	2.79 (+j)	9.35	8.89	0.46
HB7	4.82	3.43 (+d)	1.28 (+g) partial	-1.26 (-a)	8.27	8.12	0.15
HB8	4.59	3.60 (+d)	-1.87 (+i) partial	3.35 (+b)	9.67	9.20	0.47
HB9	4.99	3.45 (+e)	-0.72 (-k)	-	7.72	7.29	0.43
HB10	4.80	3.32 (+e)	2.96 (+j)	-	11.08	10.07	1.01
HB11	5.10	3.34 (+e)	-1.09 (-a)	-	7.35	7.03	0.32
HB12	4.49	3.48 (+e)	3.69 (+b)	-	11.66	10.84	0.82
HB13	2.81	-0.15 (-f)	-0.18 (-i)	-	2.48	2.88	0.40
HB14	3.03	0.13 (-f)	-0.23 (-h)	-	2.93	3.15	0.22
HB15	2.98	-0.21 (-g)	-0.03 (-h)	-	2.75	3.24	0.49
HB16	3.34	0.09 (-g)	-0.32 (-i)	-	3.11	3.51	0.40
HB17	4.62	-0.93 (-k)	3.30 (+b)	-	7.00	7.22	0.22
HB18	4.56	-0.73 (-k)	2.87 (+j)	-	6.70	6.79	0.09
HB19	4.83	-0.77 (-a)	2.88 (+j)	-	6.94	7.09	0.15
HB20	4.50	0.15 (-a)	2.86 (+b)	-	7.51	6.89	0.62
HB21	4.65	0.15 (-a)	3.07 (+b)	-	7.86	6.81	1.05
			W_{14}				
HB1	4.76	3.23 (+c) [#1]	3.23 (+j)	-	11.22	10.25	0.97
HB2	4.97	3.28 (+c) [#2]	-0.70 (-l)	-	7.54	7.02	0.52
HB3	4.62	3.32 (+c)	3.41 (+i)	-	11.35	10.72	0.63
HB4	4.98	3.27 (+c)	-0.71 (-k)	-	7.55	7.04	0.51
HB5	4.84	3.67 (+d)	-1.10 (-h)	3.00 (+j)	10.41	9.19	1.22
HB6	4.61	3.55 (+d)	-1.11 (-l)	3.69 (+b)	10.74	9.31	1.43
HB7	4.89	3.43 (+d)	2.88 (+i)	-1.55 (-g)	9.64	8.58	1.06
HB8	4.62	3.54 (+d)	-1.05 (-k)	3.43 (+a)	10.55	9.26	1.29
HB9	5.01	3.33 (+e)	-0.76 (-h)	-	7.58	7.11	0.47
HB10	4.57	3.45 (+e)	3.74 (+b)	-	11.76	10.70	1.06
HB11	4.96	3.57 (+e)	-0.88 (-f)	-	7.66	7.55	0.11
HB12	4.60	3.44 (+e)	3.65 (+a)	-	11.70	10.54	1.16
HB13	4.65	-0.94 (-k)	3.16 (+j)	-	6.87	7.30	0.43
HB14	4.58	3.07 (+j)	-0.77 (-l)	-	6.88	7.27	0.39
HB15	4.62	-1.04 (-l)	3.20 (+i)	-	6.78	7.67	0.89
HB16	4.50	-0.81 (+k)	3.08 (+i)	-	6.77	7.51	0.74
HB17	4.59	-0.88 (-h)	3.47 (+a)	-	7.18	7.46	0.28
HB18	4.50	-0.96 (-h)	3.60 (+b)	-	7.14	7.50	0.36
HB19	4.27	0.27 (-g)	3.50 (+b)	-	8.03	8.40	0.37
HB20	2.95	0.10 (-g)	3.38 (+a)	-	6.43	6.66	0.23
HB21	5.01	-0.79 (-f)	3.41 (+b)	-	7.63	6.97	0.66
HB22	5.02	-0.83 (-f)	3.42 (+a)	-	7.61	6.95	0.66
HB23	4.90	-0.74 (-f)	1.92 (+g) partial	-	6.07	6.28	0.21

[#1] The plus and minus sign before labels "**a**" to **"l"** indicate positive/negative cooperativity contribution.

[#2] The labels "**a**" to **"l"** denote the cycles of HB network in Figs. S9 and S10.

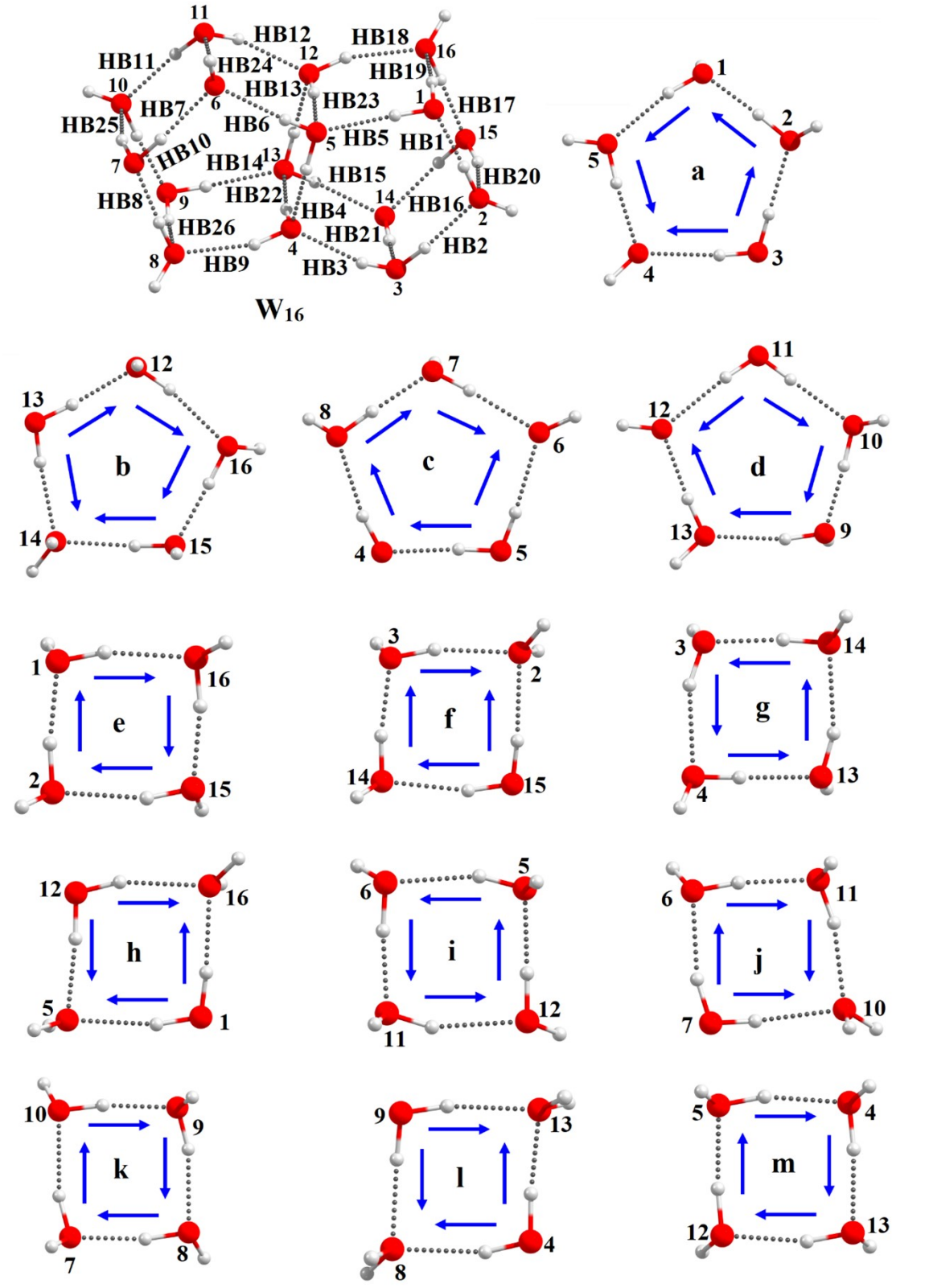


Fig. S11 Structure of W_{16} cluster consisting of four pentameric (denoted by **a** to **d**) and nine tetrameric (denoted by **e** and **m**) cooperative cycles.

Table S11. The HB energies (in kcal/mol) in W_{16} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer}) is also provided (in kcal/mol). All the calculations were performed at the MP2/aug-cc-pVTZ level of theory

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_{16}				
HB1	4.60	3.50 (+e)[#1]	2.55 (+a) partial	-	10.65	10.51	0.14
HB2	4.27	0.47 (-f)[#2]	0.78 (-a)	-	5.52	5.04	0.48
HB3	4.91	2.81 (+g)	-1.51 (-a)	-	6.21	7.03	0.82
HB4	4.22	3.59 (+m)	0.74 (-a)	0.48 (-c)	9.03	7.11	1.92
HB5	4.80	-0.93 (-h)	2.40 (+a) partial	-	6.26	7.11	0.85
HB6	5.01	2.89 (+i)	-1.66 (-c)	-	6.24	7.21	0.97
HB7	3.60	0.30 (-j)	0.71 (-c)	-	4.61	4.13	0.48
HB8	4.61	3.48 (+k)	2.39 (+c) partial	-	10.48	10.54	0.06
HB9	4.74	-0.87 (-l)	2.31 (+c) partial	-	6.17	7.02	0.85
HB10	4.60	3.50 (+k)	2.55 (+d) partial	-	10.65	10.51	0.14
HB11	4.27	0.47 (-j)	0.78 (-d)	-	5.52	5.04	0.48
HB12	4.91	2.81 (+i)	-1.51 (-d)	-	6.21	7.03	0.82
HB13	4.22	3.59 (+m)	0.74 (-b)	0.48 (-d)	9.03	7.11	1.92
HB14	4.80	-0.93 (-l)	2.40 (+d) partial	-	6.26	7.11	0.85
HB15	5.01	2.89 (+g)	0.71 (-b)	-	6.24	7.21	0.97
HB16	3.60	0.30 (-f)	4.31(-b)	-	4.61	4.13	0.48
HB17	4.61	3.48 (+e)	2.39 (+b) partial	-	10.48	10.54	0.06
HB18	4.74	-0.87 (-h)	2.31 (+b) partial	-	6.17	7.02	0.85
HB19	5.01	3.57 (+e)	-0.82 (-h)	-	7.76	7.38	0.38
HB20	4.97	3.42 (+e)	1.32 (-f)	-	7.07	7.44	0.37
HB21	4.79	2.92(+f) partial	2.10 (+g)	-	9.80	10.38	0.58
HB22	4.84	2.78 (+g)	-1.00 (-l)	3.58 (+m)	10.21	8.87	1.34
HB23	4.84	2.78 (+i)	-1.00 (-h)	3.58 (+m)	10.21	8.87	1.34
HB24	4.79	2.92 (+i)	2.10 (+j) partial	-	9.80	10.38	0.58
HB25	4.97	-1.32 (-j)	3.42 (+k)	-	7.07	7.44	0.37
HB26	5.01	3.57 (+k)	-0.82 (-l)	-	7.76	7.38	0.38

[#1] The plus and minus sign before labels "**a**" to **"m"** indicate positive/negative cooperativity contribution.

[#2] The labels **a** to **m** denote the cycles of HB network in Fig. S11.

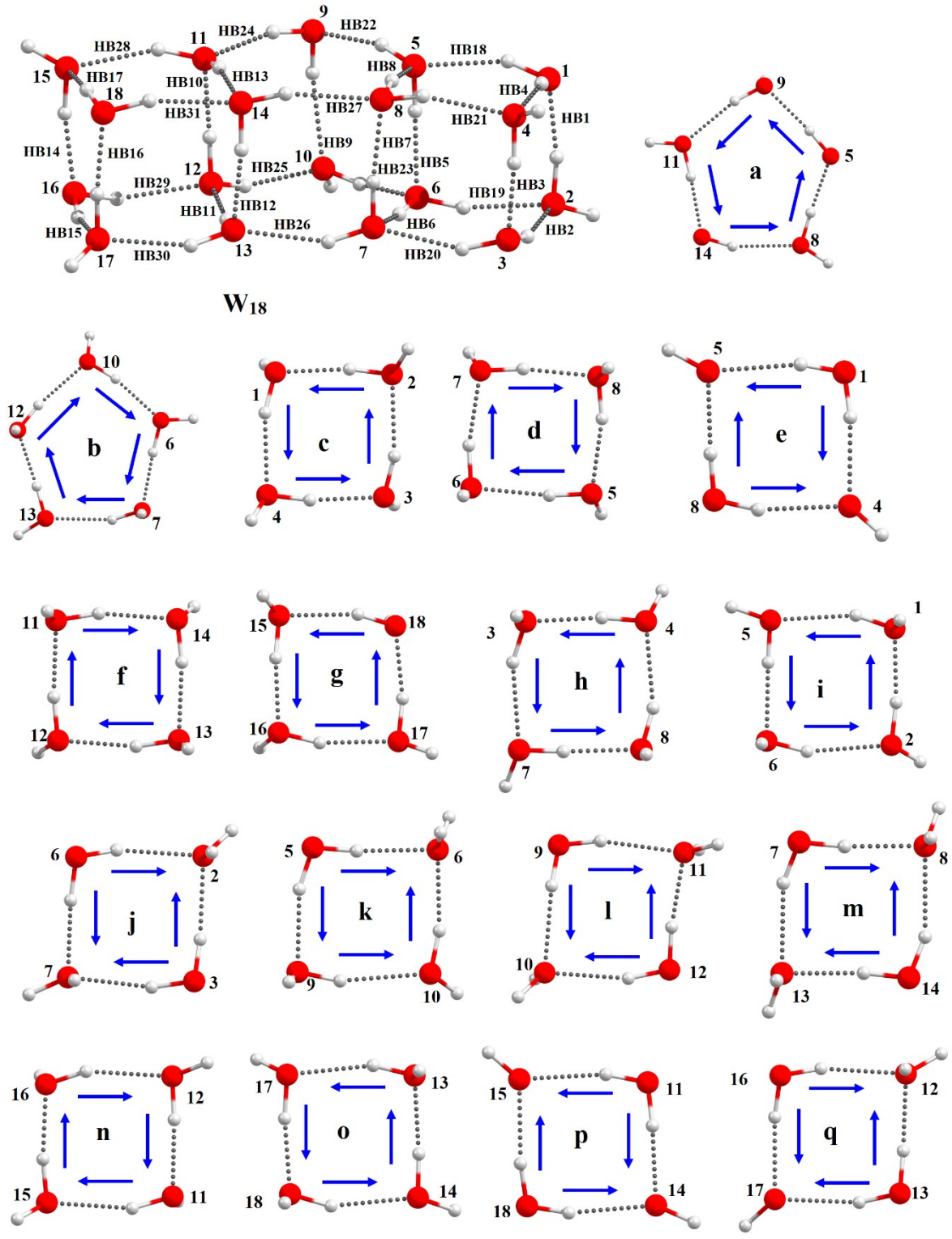


Fig. S12 Structure of W_{16} cluster consisting of two pentameric (denoted by **a** and **b**) and fifteen tetrameric (denoted by **c** and **q**) cooperative cycles.

Table S12. The HB energies (in kcal/mol) in W_{18} cluster obtained by synergetic addition of cyclic cooperativity contributions ($E_{HB}^{Syn.}$) and that by MTA-based method employing actual cluster ($E_{HB}^{cluster}$). The hydrogen bond energy in the respective dimer species (E_{HB}^{Dimer}) is also provided (in kcal/mol). All the calculations were performed at the MP2/aug-cc-pVTZ level of theory

HB	E_{HB}^{Dimer}	$E_{coop.}^{Cyc.\ 1}$	$E_{coop.}^{Cyc.\ 2}$	$E_{coop.}^{Cyc.\ 3}$	$E_{HB}^{Syn.}$	$E_{HB}^{cluster}$	$\lvert\Delta E_{HB}\rvert$
			W_{18}				
HB1	4.81	3.32 (+c)[#1]	2.84 (+i)	-	10.97	10.33	0.64
HB2	4.98	3.34 (+c)[#2]	-0.67 (-j)	-	7.64	7.11	0.53
HB3	4.78	3.35 (+c)	2.97 (+h)	-	11.10	10.12	0.98
HB4	4.99	3.34 (+c)	-0.68 (-e)	-	7.65	7.13	0.52
HB5	4.90	3.53 (+d)	2.54 (+i)	-1.50 (-k)	9.47	8.43	1.04
HB6	4.62	3.17 (+b)	3.67 (+d)	-0.97 (-j)	10.49	9.25	1.24
HB7	4.82	3.80 (+d)	2.85 (+h)	-0.88 (-m)	10.58	9.25	1.33
HB8	4.65	2.91 (+a)	3.66 (+d)	-0.93 (-e)	10.29	9.19	1.10
HB9	4.97	1.62 (+k) partial	-0.65 (-l)	-	5.94	6.02	0.08
HB10	4.80	3.65 (+f)	-0.98 (-l)	2.85 (+n)	10.32	9.08	1.24
HB11	4.78	2.88 (+b)	3.62 (+f)	-0.91 (-q)	10.38	8.84	1.54
HB12	4.90	3.57 (+f)	-0.82 (-m)	2.74 (+o)	10.39	8.81	1.58
HB13	4.76	2.81 (+a)	3.61 (+f)	-0.89 (-p)	10.29	8.72	1.57
HB14	4.78	3.33 (+g)	2.98 (+n)	-	11.09	10.14	0.95
HB15	4.99	3.33 (+g)	-0.68 (-q)	-	7.63	7.13	0.50
HB16	4.80	3.31 (+g)	2.92 (+o)	-	11.04	10.22	0.82
HB17	5.00	3.32 (+g)	-0.69 (-p)	-	7.62	7.14	0.48
HB18	4.63	-0.74 (-e)	2.67 (+i)	-	6.56	7.06	0.50
HB19	4.77	2.72 (+i)	-0.87 (-j)	-	6.61	7.27	0.66
HB20	4.66	2.88 (+h)	-0.76 (-j)	-	6.78	6.96	0.18
HB21	4.74	-0.87 (-e)	2.94 (+h)	-	6.80	7.11	0.31
HB22	3.36	2.75 (+a)	-0.02 (-k)	-	6.09	6.3	0.21
HB23	4.39	3.12 (+b)	0.24 (-k)	-	7.75	7.95	0.20
HB24	4.76	2.70 (+a)	-0.81 (-l)	-	6.64	6.6	0.04
HB25	4.74	2.75 (+b)	-0.81 (-l)	-	6.67	6.73	0.06
HB26	4.38	2.76 (+b)	-0.86 (-m)	-	6.28	7.07	0.79
HB27	4.38	2.70 (+a)	-0.84 (-m)	-	6.24	7.03	0.79
HB28	4.76	2.96 (+n)	-0.85 (-p)	-	6.87	7.15	0.28
HB29	4.69	2.88 (+n)	-0.74 (-q)	-	6.83	7.02	0.19
HB30	4.75	2.88 (+o)	-0.86 (-q)	-	6.76	7.14	0.38
HB31	4.65	2.79 (+o)	-0.73 (-p)	-	6.71	6.92	0.21

[#1] The plus and minus sign before labels "**a"** to **"q"** indicate positive/negative cooperativity contribution.

[#2] The labels **a** to **q** denote the cycles of HB network in Fig. S12.