Supporting Information

Deciphering the Structural Evolution and Electronic Properties of Magnesium Clusters: a New Aromatic Homonuclear Metal Mg_{17} Cluster

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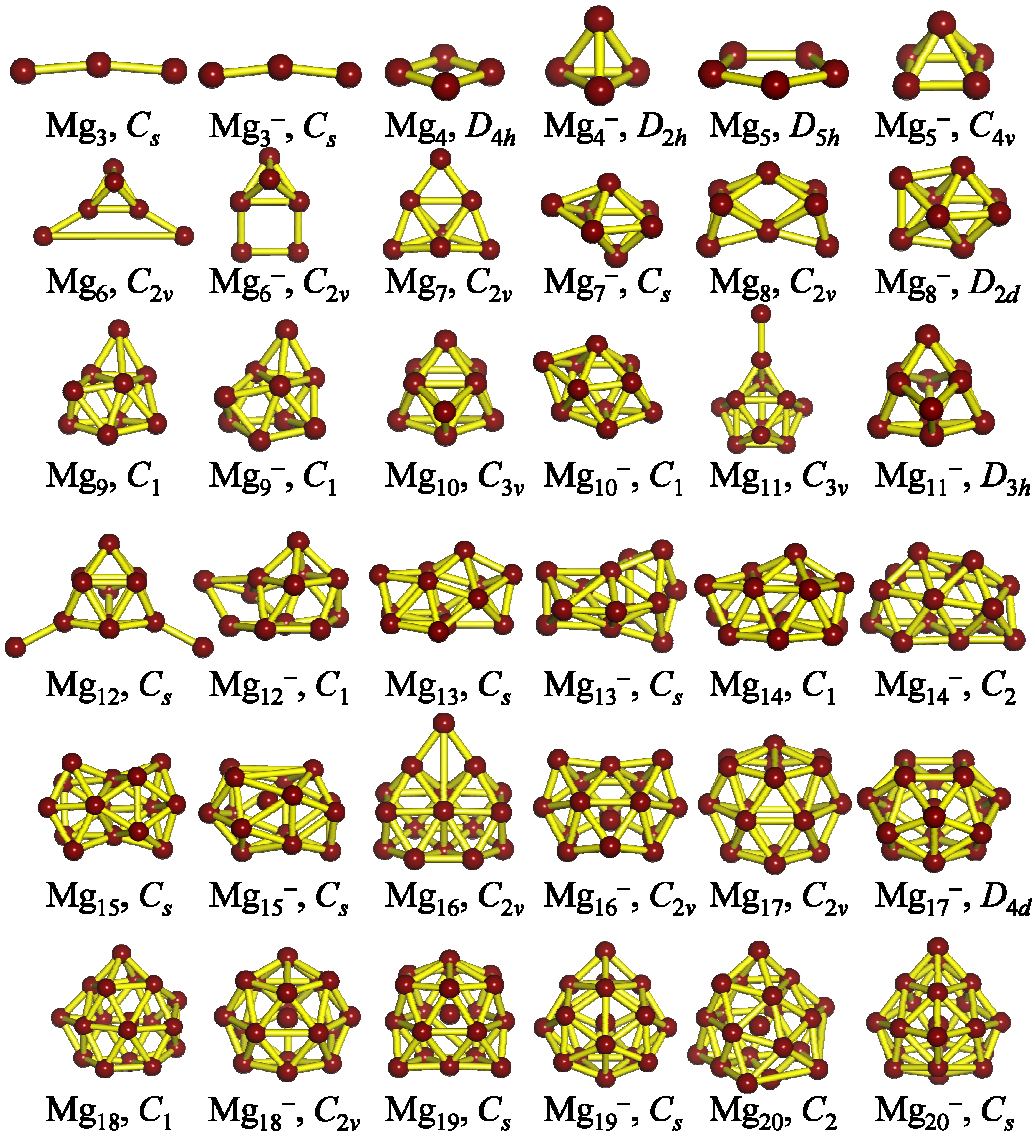

Figure S1. The low-lying structures of Mg_n^Q (n = 3–20, Q = 0, –1) clusters.

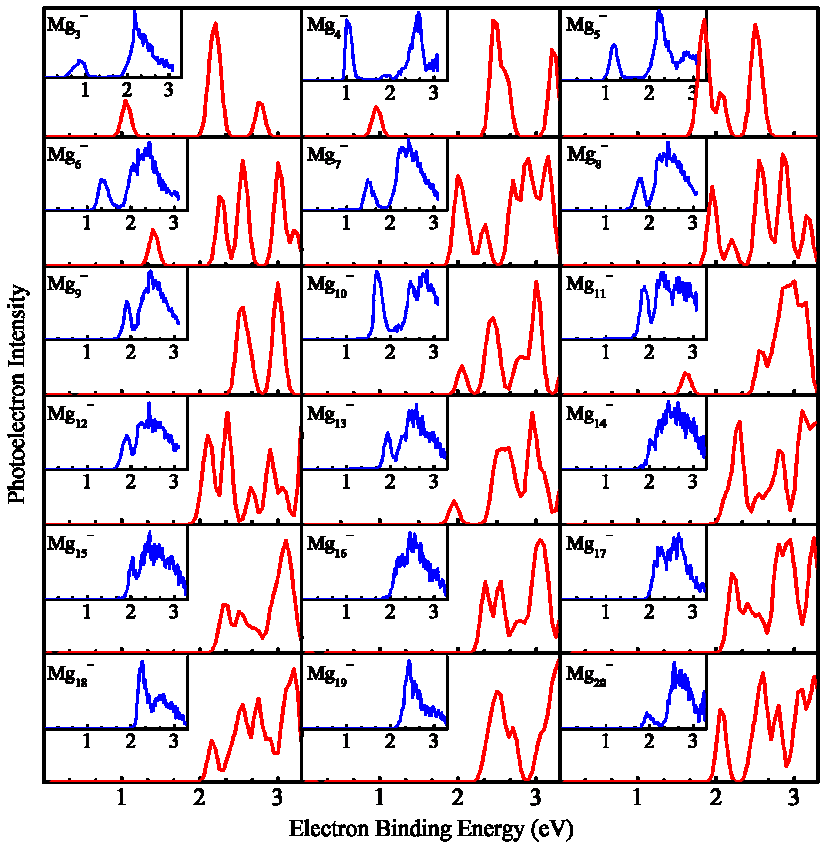

Figure S2. Comparison of the simulated photoelectron spectra (outer) with the experimental PES (inset) from reference 8 of low-ling Mg_n^- (n = 3–20) clusters.

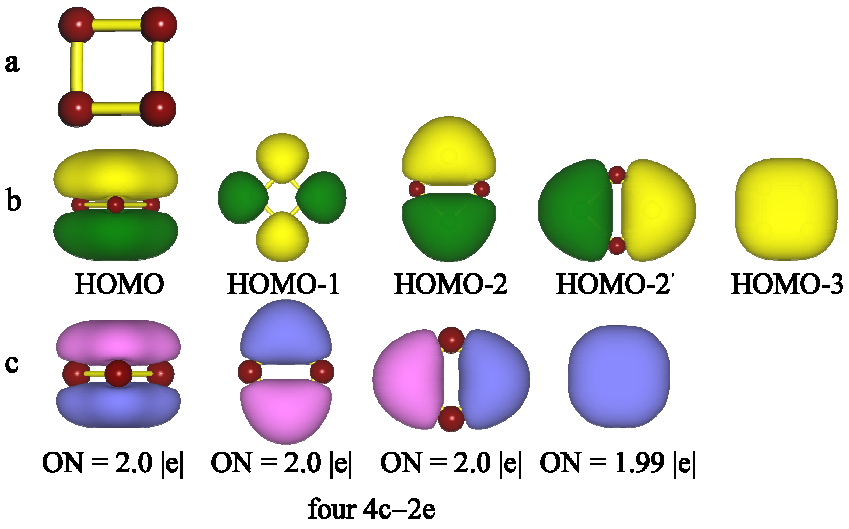

Figure S3. The low-lying structure (a), molecular orbital (b) and chemical bonding analyses (c) using the AdNDP method of neutral Mg_4 cluster.

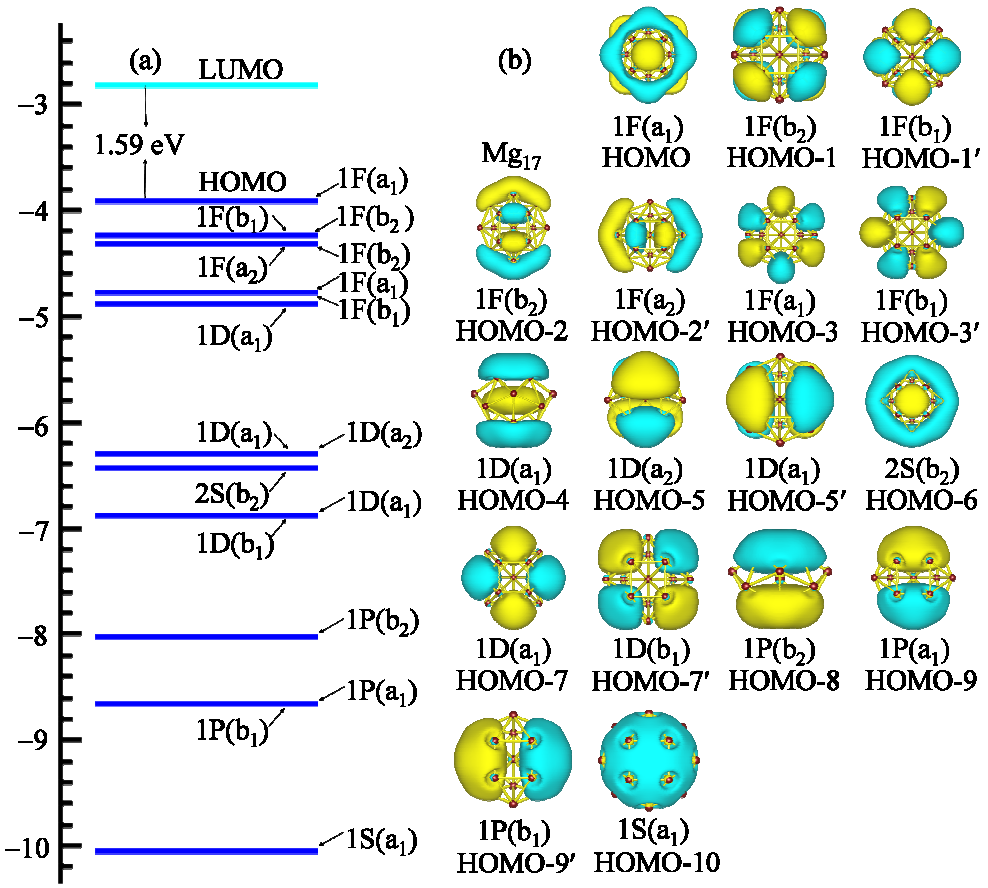

Figure S4. Molecular orbitals and energy levels of neutral Mg_{17} cluster. The HOMO−LUMO gap is indicated (in black).

Table S1. The vibrational frequency of lowest-energy Mg_n^Q (n = 3–20, Q = 0, –1) clusters.

Mg_n	Vibrational frequency
Mg_3	122, 122, 131
Mg_4	146, 146, 171, 171, 171, 191
Mg_5	81, 81, 100, 103, 103, 131, 178, 178, 204
Mg_6	34, 70, 84, 108, 115, 119, 119, 120, 127, 140, 157, 212
Mg_7	87, 87, 101, 101, 106, 106, 114, 122, 122, 137, 151, 151, 164, 164, 224
Mg_8	55, 61, 75, 89, 105, 113, 117, 124, 127, 139, 139, 146, 157, 158, 160, 175, 190, 214
Mg_9	82, 82, 105, 105, 110, 110, 129, 129, 133, 136, 150, 165, 174, 180, 188, 194, 194, 194, 194, 230, 229
Mg_{10}	60, 60, 108, 108, 114, 114, 121, 138, 138, 138, 147, 157, 157, 159, 177, 192.6544, 195, 196, 196, 220, 220, 233, 233, 244
Mg_{11}	59, 59, 65, 65, 98, 104, 104, 123, 124, 124, 129, 129, 135, 135, 138, 149, 151, 176, 191, 198, 201, 201, 206, 206, 222, 232, 232,
Mg_{12}	31, 37, 39, 68, 70, 82, 106, 109, 115, 117, 125, 132, 136, 137, 141, 142, 147, 161, 175, 188, 198, 200, 202, 205, 205, 211, 226, 232, 233, 255
Mg_{13}	7, 45, 52, 61, 72, 82, 103, 103, 113, 116, 124, 125, 133, 136, 138, 145, 145, 151, 166, 169, 171, 182, 189, 194, 199, 203, 207, 212, 218, 235, 235, 237, 244
Mg_{14}	29, 46, 59, 70, 78, 88, 91, 98, 101, 105, 112, 115, 120, 121, 123, 128, 130, 137, 138, 143, 149, 158, 165, 177, 180, 181, 186, 193, 198, 200, 209, 211, 218, 228, 232, 249
Mg_{15}	72, 72, 76, 76, 79, 94, 94, 97, 97, 104, 111, 111, 118, 118, 118, 121, 121, 130, 153, 153, 155, 160, 166, 172, 172, 193, 195, 198, 1998, 1998, 2008, 210, 224, 228, 228, 232, 232, 245, 245
Mg_{16}	52, 56, 62, 67, 73, 80, 88, 90, 94, 101, 104, 106, 109, 110, 117, 124, 127, 128, 137, 138, 142, 148, 151, 157, 162, 169, 178, 180, 185, 191, 197, 200, 204, 208, 211, 221, 224, 230, 234, 237, 241, 250
Mg_{17}	53, 53, 90, 90, 93, 93, 103, 103, 104, 104, 110, 112, 121, 124, 124, 129, 130, 133, 133, 143, 145, 153, 155, 156, 158, 158, 174, 182, 182, 205, 205, 208, 208, 211, 214, 213, 214, 228, 228, 233, 233, 235, 239, 245, 246
Mg_{18}	56, 73, 74, 82, 84, 86, 88, 88, 88, 89, 91, 98, 104, 106, 112, 115, 118, 118, 130, 142, 142, 143, 146, 152, 154, 157, 157, 167, 172, 177, 186, 192, 195, 197, 201, 209, 209, 209, 216, 219, 220, 235, 239, 242, 247, 255, 258, 287
Mg_{19}	10, 55, 81, 84, 93, 98, 98, 101, 102, 106, 107, 109, 109, 112, 114, 123, 124, 126, 126, 134, 135, 139, 141, 145, 152, 152, 158, 159, 161, 171, 174, 180, 188, 189, 202, 206, 211, 212, 213, 218, 218, 222, 225, 234, 235, 236, 238, 247, 248, 252, 269
Mg_{20}	80, 80, 83, 85, 85, 91, 91, 95, 109, 110, 110, 110, 115, 117, 117, 117, 124, 124, 131, 132, 132, 134, 134, 139, 139, 144, 151, 154, 159, 160, 171, 172, 172, 180, 194, 194, 203, 203, 204, 206, 223, 223, 224, 227, 227, 230, 235, 235, 240, 240, 241, 249, 249, 252
Mg_n^-	Vibrational frequency
Mg_3^-	155, 155, 182

Mg_4^-	131, 131, 155, 155, 155, 201
Mg_5^-	86, 86, 110, 110, 114, 115, 115, 141, 193
Mg_6^-	20, 20, 97, 113, 113, 124, 124, 169, 169, 169, 188, 188
Mg_7^-	21, 52, 62, 92, 109, 114, 134, 137, 147, 147, 151, 172, 180, 187, 207
Mg_8^-	33, 36, 41, 107, 113, 115, 123, 125, 130, 146, 153, 162, 163, 175, 178, 179, 200, 202,
Mg_9^-	95, 95, 95, 95, 122, 122, 129, 133, 133, 141, 150, 171, 183, 187, 187, 190, 203, 203, 204, 228, 228
Mg_{10}^-	60, 60, 104, 104, 118, 118, 121, 134, 134, 138, 138, 139, 142, 162, 180, 196, 197, 197, 207, 210, 210, 223, 231, 231
Mg_{11}^-	15, 35, 69, 70, 93, 100, 106, 109, 113, 120, 130, 132, 136, 137, 143, 145, 160, 175, 187, 194, 199, 199, 208, 209, 224, 2264, 232
Mg_{12}^-	21, 37, 49, 62, 77, 93, 95, 101, 106, 112, 126, 127, 131, 132, 139, 140, 150, 167, 175, 185, 189, 193, 196, 206, 206, 210, 221, 226, 238, 249
Mg_{13}^-	34, 43, 56, 61, 73, 89, 91, 107, 109, 112, 122, 124, 129, 131, 137, 140, 142, 146, 162, 168, 179, 179, 191, 192, 197, 201, 204, 207, 215, 225, 233, 238, 244
Mg_{14}^-	42, 48, 62, 74, 85, 89, 92, 98, 102, 105, 116, 118, 120, 123, 126, 131, 134, 137, 141, 144, 153, 161, 170, 177, 181, 184, 189, 192, 198, 199, 205, 212, 218, 229, 231, 245
Mg_{15}^-	67, 67, 70, 86, 87, 92, 92, 93, 93, 108, 108, 113, 119, 119, 121, 121, 124, 140, 140, 142, 155, 160, 162, 170, 170, 184, 193, 194, 196, 196, 199, 203, 218, 223, 223, 229, 229, 242, 242
Mg_{16}^-	25, 39, 64, 74, 76, 87, 89, 92, 101, 103, 104, 108, 114, 117, 121, 121.8571, 129, 130, 132, 136, 144, 145, 149, 158, 168, 177, 178, 185, 189, 190, 196, 204, 205, 210, 214, 222, 222, 223, 228, 231, 241, 245
Mg_{17}^-	27, 49, 85, 86, 89, 93, 94, 95, 102, 105, 110, 117, 117, 118, 120, 125, 129, 132, 137, 138, 138, 144, 150, 152, 156, 163, 174, 177, 178, 183, 199, 201, 207, 208, 210, 213, 215, 216, 223, 226, 227, 230, 234, 242, 245
Mg_{18}^-	20, 71, 79, 79, 85, 89, 92, 92, 96, 99, 99, 101, 108, 109, 118, 117.1876, 119, 119, 124, 127, 138, 151, 153, 153, 154, 154, 154, 156, 170 , 174, 188, 188 , 197, 201, 205, 205, 214, 214, 218, 227, 227, 228, 231, 235, 244, 245 , 245, 265
Mg_{19}^-	37, 69, 73, 75, 76, 81, 91, 94, 97, 98, 105, 106, 107, 111, 113, 115, 123, 130, 132, 132, 135, 137, 139, 148, 152, 155, 156, 162, 164, 171, 176, 177, 178, 200, 200, 204, 208, 214, 214, 215, 222, 223, 229, 231, 236, 237, 240, 246, 258, 259, 272
Mg_{20}^-	64, 78, 78, 80, 84, 86, 89, 93, 95, 105, 106, 108, 108, 114, 116, 118, 120, 122, 124, 128, 130, 132, 133, 135, 139, 144, 147, 150, 155, 159, 166, 167, 172, 176, 188, 200, 202, 205, 207, 218, 219, 221, 222, 224, 228, 231, 232, 236, 240, 242, 243, 246.6061, 251

Table S2. The second-order energy differences (Δ^2E) of the lowest-energy Mg_n^Q (n = 3–19, Q = 0, –1) clusters.

	Δ^2E	
n	Mg_n	Mg_n^-
3	–0.51	–0.16
4	0.52	0.56
5	–0.08	–0.12
6	–0.31	–0.25
7	0.09	–0.11
8	–0.58	–0.56
9	0.12	0.75
10	0.63	0.32
11	–0.09	–0.34
12	–0.28	–0.14
13	0.16	0.04
14	–0.63	–0.34
15	0.67	0.39
16	–1.00	–0.70
17	0.57	0.33
18	–0.04	0.05
19	–0.16	0.32

Table S3. The nucleus-independent chemical shift (NICS) and multicenter bond order indices calculated at B3PW91/6-311+G(d) level of theory.

cluster	R(bq) Å	NICS_zz ppm	multicenter bond order
Mg_4	0.0	–37.1083	0.0322
	0.5	–36.5795	
	1.0	–34.0287	