Supporting information for:

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Table S1 Cartesian coordinates of optimized $[Mg_3@C_{20}]^+$ at the M06-2X/def2-TZVP level.

Mg	-0.167839	-0.092710	2.194434
C	1.829586	-3.053551	0.506077
C	2.007302	-3.125159	-0.738585
C	2.059695	-2.982459	-2.043959
C	1.903746	-2.524318	-3.212699
C	1.407131	-1.573419	-3.995635
C	0.815801	-0.541154	-4.375374
C	0.115575	0.579481	-4.240587
C	-0.519336	1.529386	-3.765920
C	-1.088935	2.287418	-2.830074
C	-1.551768	2.856963	-1.827865
C	-1.882067	3.161798	-0.563415
C	-2.005124	3.132480	0.672018
C	-2.024354	2.918079	1.986699
C	-1.793464	2.346084	3.058781
C	-1.360927	1.481412	3.970477
C	-0.775822	0.462978	4.394175
C	-0.077588	-0.666842	4.424404
C	0.550355	-1.558935	3.784611
C	1.089533	-2.256226	2.809868
C	1.510812	-2.752578	1.732299
Mg	0.860724	-1.067136	-1.765671
Mg	-0.648330	1.164363	-0.474429

Table S2 Vibrational frequencies of $[Mg_3@C_{20}]^+$. Positive values indicate real frequencies (stable modes). The absence of imaginary frequencies (-i cm^{-1}) confirms that the optimized geometry corresponds to a true minimum on the potential energy surface, with no tendency for spontaneous dissociation.

Mode	Frequency cm^{-1}	Mode	Frequency cm^{-1}
1:	36.83	33:	443.68
2:	37.41	34:	452.80
3:	49.82	35:	469.09
4:	63.76	36:	492.96
5:	64.47	37:	496.49
6:	67.60	38:	502.28
7:	73.96	39:	521.71
8:	78.81	40:	534.18
9:	111.39	41:	536.07
10:	114.83	42:	544.14
11:	141.36	43:	546.28
12:	146.33	44:	559.30
13:	150.31	45:	566.44
14:	168.42	46:	627.68
15:	205.13	47:	877.79
16:	219.29	48:	883.89
17:	237.72	49:	1180.33
18:	244.64	50:	1204.13
19:	298.63	51:	1463.36
20:	301.92	52:	1476.06
21:	310.70	53:	1627.92
22:	315.53	54:	1697.95
23:	337.16	55:	1809.69
24:	346.07	56:	1941.96
25:	361.86	57:	2034.73
26:	365.91	58:	2054.49
27:	388.03	59:	2075.56
28:	401.85	60:	2152.82
29:	415.27	61:	2156.31
30:	427.00	62:	2177.95
31:	434.15	63:	2186.25
32:	434.55		

Figure S1 The bond-length (Å) of bare C_{20} ring calculated at the M06-2X/def2-TZVP level.

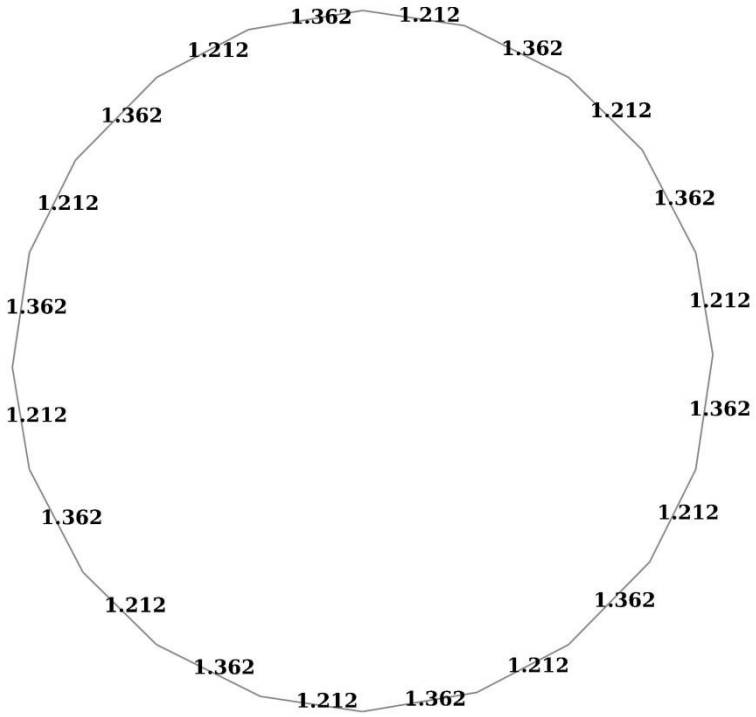


Figure S2 The bond orders of bare C_{20} ring calculated at the M06-2X/def2-TZVP level.

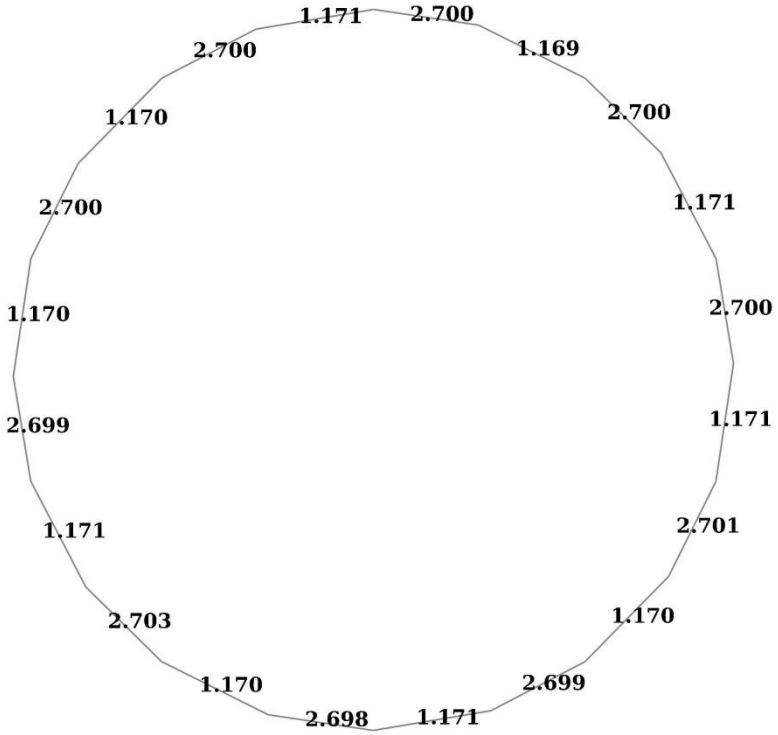
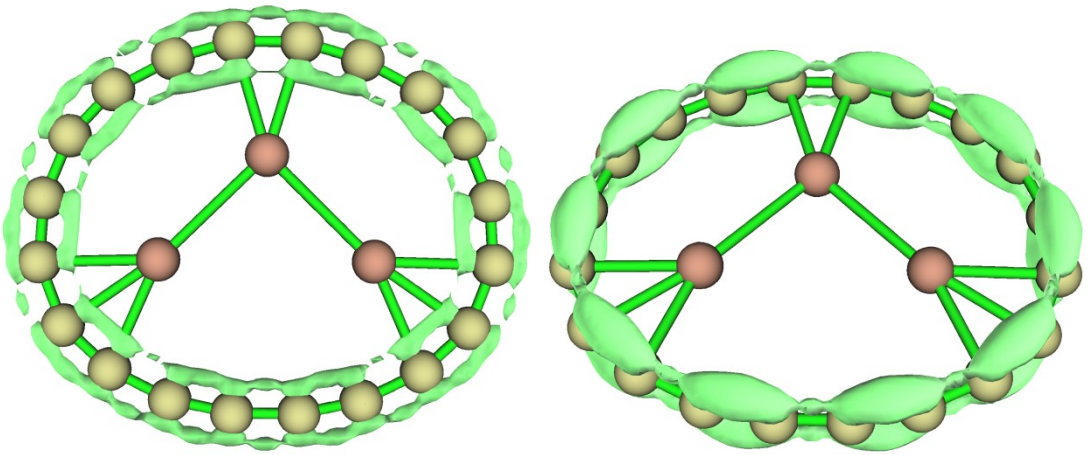


Figure S3 Two orthogonal sets of π electron delocalizations in the $[Mg_3@C_{20}]^+$. The electron density isosurface is plotted at 0.7 a.u. and 0.5 a.u., respectviely.



isovalue=0.7 a.u. isovalue=0.5 a.u.

Figure S4 The color-filled localized orbital locator (LOL) map of $[Mg_3@C_{20}]^+$.

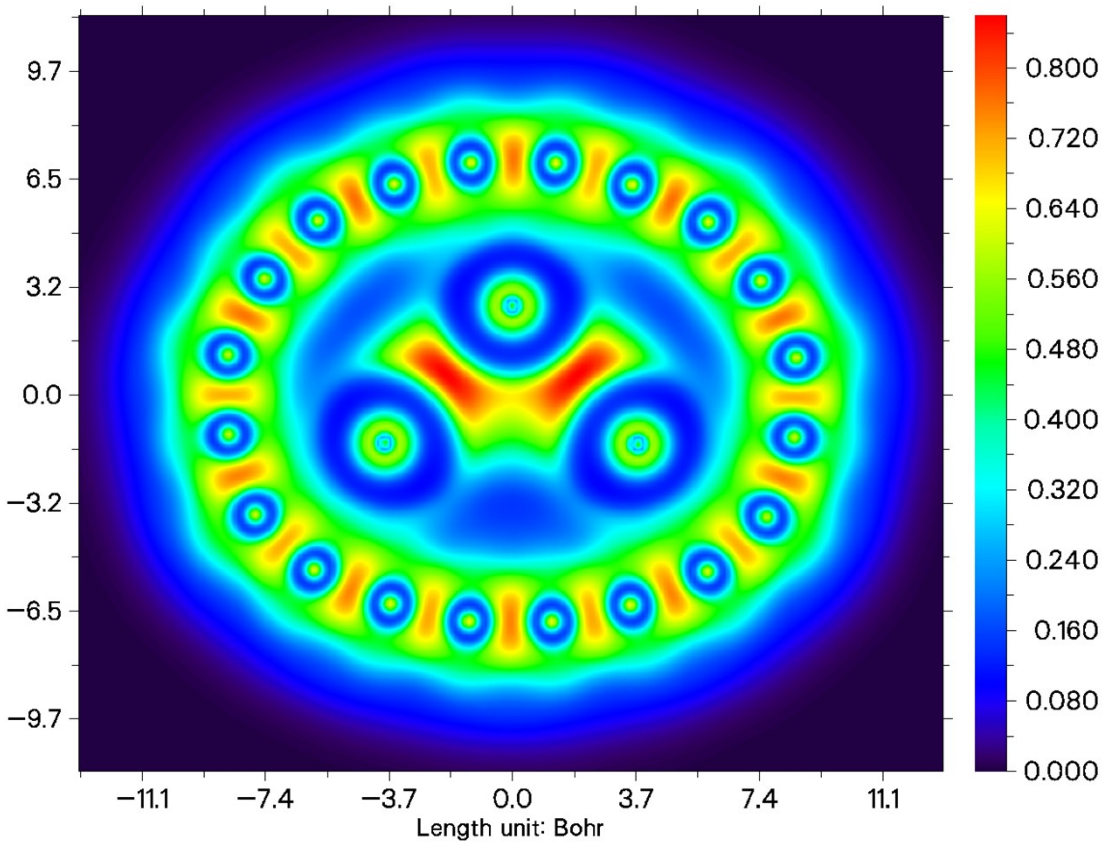


Table S3 Natural atomic orbital occupancies.

Spin orbitals		Natural Electron Configuration
Alpha	Mg1	[core]3S(0.38)3p(0.36)3d(0.02)
	Mg2	[core]3S(0.54)3p(0.12)3d(0.01)
	Mg3	[core]3S(0.54)3p(0.12)3d(0.01)
Beta	Mg1	[core]3S(0.48)3p(0.15)3d(0.01)
	Mg2	[core]3S(0.15)3p(0.09)3d(0.01)
	Mg3	[core]3S(0.15)3p(0.09)3d(0.01)

Figure S5 Molecular orbital diagrams for $[Mg_3@C_{20}]^+$ (isovalue=0.05 a.u.). Dotted and solid lines represent unoccupied and occupied orbitals, respectively.

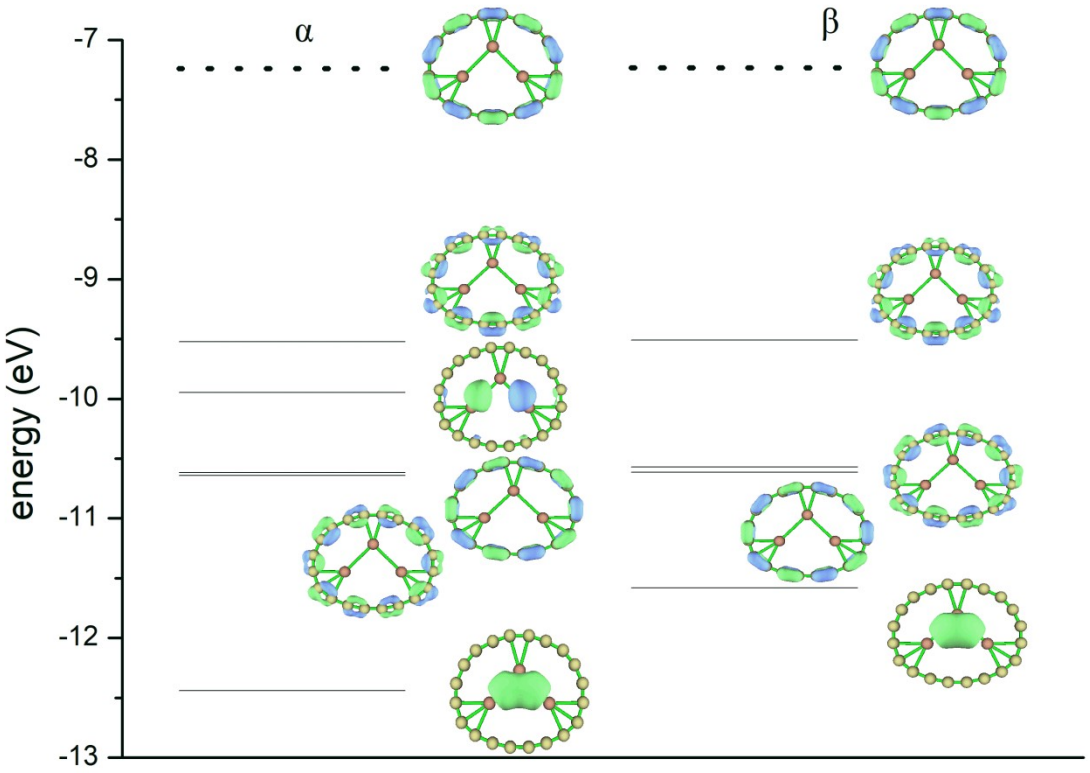


Table S4 Hyperfine coupling parameters of Mg and carbon atoms in$[Mg_3@C_{20}]^+$ (MHz). Hyperfine interaction of the isotropic Fermi contact term (A^{FC}), the traceless spin-dipolar term (A^{SD}) for Mg atoms are listed.

atoms		A_{xx}	A_{yy}	A_{zz}	A_{iso}
Mg1		2.7148	3.0328	5.7676	0.0067
	A^{FC}	-0.0067	-0.0067	-0.0067	
	A^{SD}	2.7215	3.0395	-5.7609	
Mg2		-122.3191	-122.4276	-127.320	-124.0223
	A^{FC}	-124.0223	-124.0223	-124.0223	
	A^{SD}	1.7031	1.5946	-3.2978	
Mg3		-124.1876	-124.2987	-129.1782	-125.8882
	A^{FC}	-125.8882	-125.8882	-125.8882	
	A^{SD}	1.7005	1.5894	-3.2900	
C		0.0002	-0.2235	0.8067	0.1944
C		1.0727	1.2340	2.8935	1.7334
C		1.3282	1.4478	2.4968	1.7576
C		1.1295	1.2196	2.2048	1.5180
C		1.9893	2.1641	3.9364	2.6966
C		2.5894	2.7726	5.7950	3.7190
C		3.5667	3.8142	5.4551	4.2787
C		2.0720	2.2749	4.0008	2.7826
C		2.2234	2.4641	4.1564	2.9480
C		-0.0783	-0.3301	1.0497	0.2138
C		-0.1082	-0.3482	1.1325	0.2254
C		2.2604	2.4981	4.0824	2.9469
C		2.1510	2.3470	3.9789	2.8257
C		3.4096	3.6342	5.3847	4.1428
C		1.9156	2.0918	4.6651	2.8908
C		2.2127	2.3628	3.9540	2.8431
C		1.0731	1.1625	2.1051	1.4469
C		1.2834	1.4207	2.5636	1.7559
C		0.9976	1.1853	3.0321	1.7383
C		-0.1038	0.3280	1.0078	0.1920