Supporting Information

Theoretical probing of twenty-coordinate actinide-centered boron molecular drums

Juan Wang,[a,b] Nai-Xin Zhang,[a] Cong-Zhi Wang,[a] Qun-Yan Wu,[a] Jian-Hui Lan,[a] Zhi-Fang Chai,[a,c] Chang-Ming Nie,[b] and Wei-Qun Shi*[a]*

[a]Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

[b]School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

[c]Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Materials Technolog y and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

*Email: shiwq@ihep.ac.cn; wangcongzhi@ihep.ac.cn

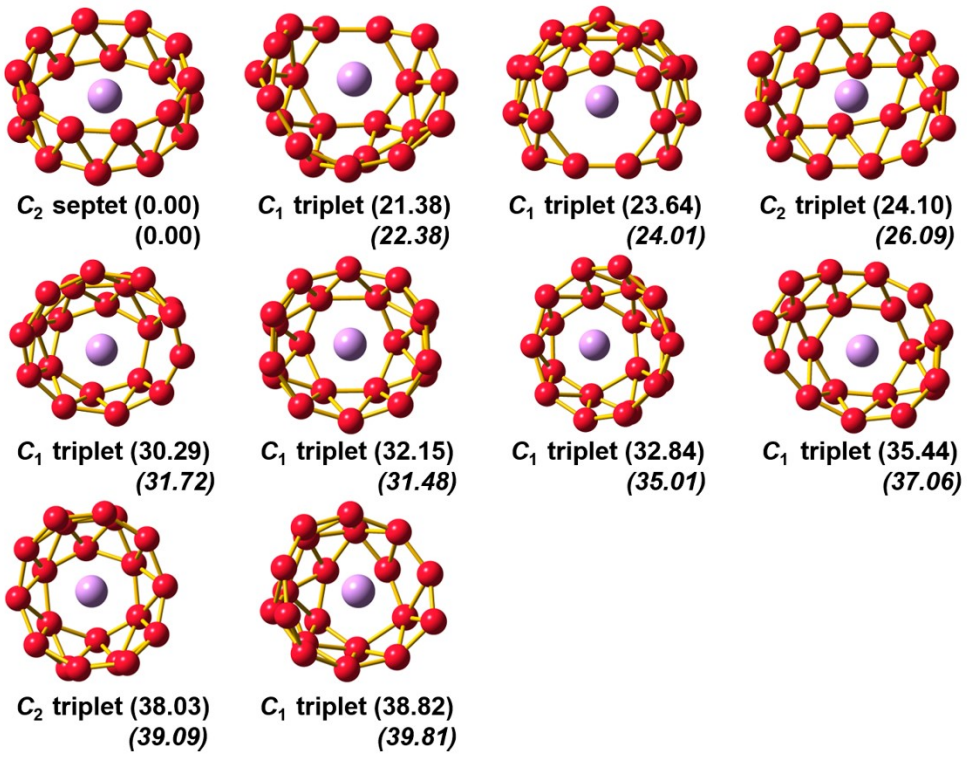

Fig. S1 Low-lying isomers of U@B_{20} with the relative energies (kcal/mol) at the DFT/PBE0/6-311+G*/RECP in the first row and DFT/TPSSh/6-311+G*/RECP levels in the second rows (*in italic*). Red and pink spheres represent B and U, respectively. All the energies have been corrected for zero-point energies.

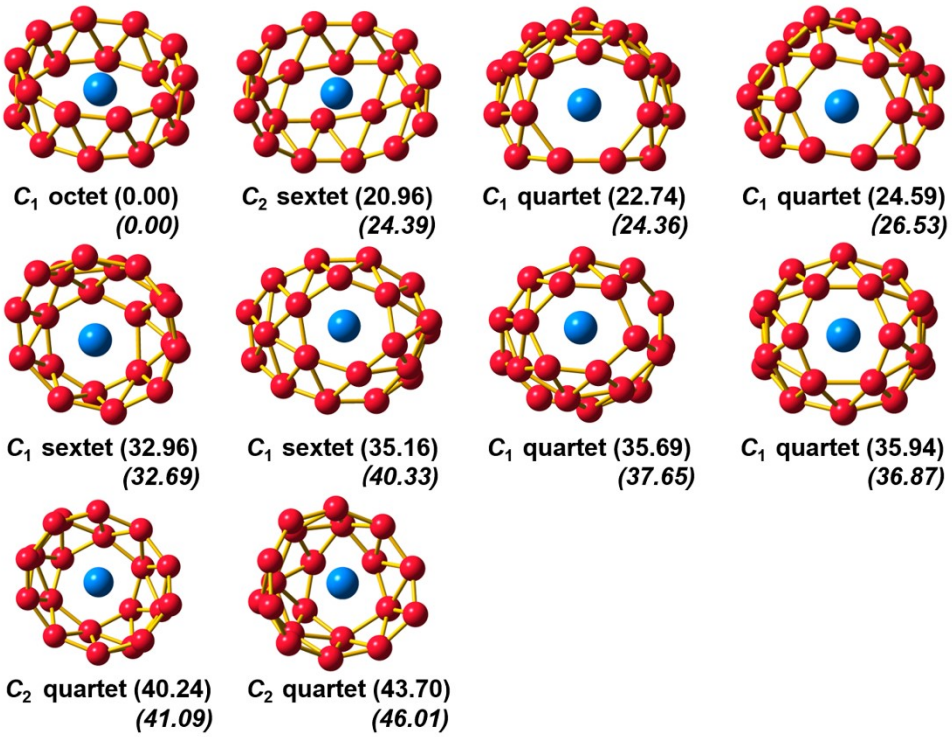

Fig. S2 Low-lying isomers of Np@B_{20} with the relative energies (kcal/mol) at the DFT/PBE0/6-311+G*/RECP in the first row and DFT/TPSSh/6-311+G*/RECP levels in the second rows (*in italic*). Red and blue spheres represent B and Np, respectively. All the energies have been corrected for zero-point energies.

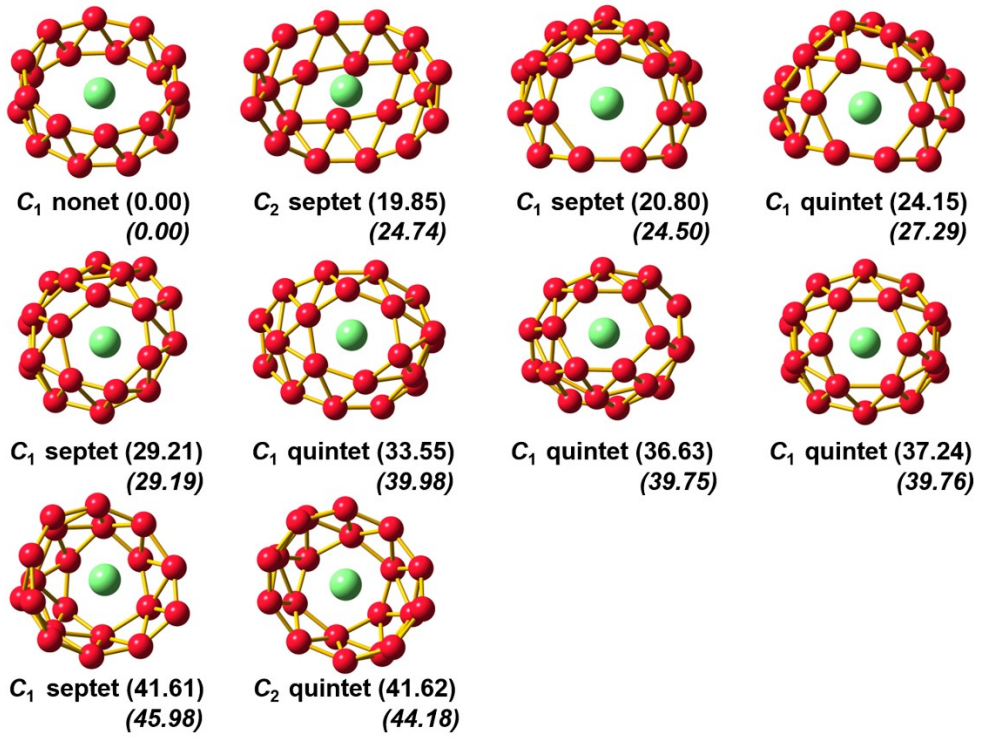

Fig. S3 Low-lying isomers of $Pu@B_{20}$ with the relative energies (kcal/mol) at the DFT/PBE0/6-311+G*/RECP in the first row and DFT/TPSSh/6-311+G*/RECP levels in the second rows (*in italic*). Red and green spheres represent B and Pu, respectively. All the energies have been corrected for zero-point energies.

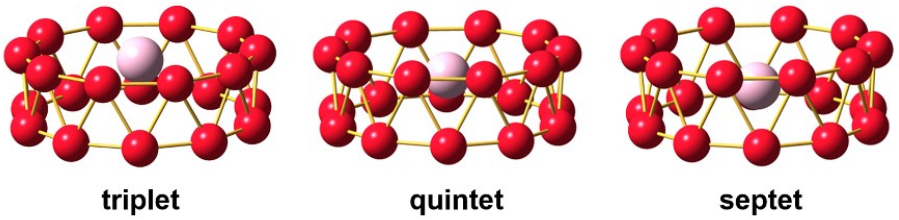

Fig. S4 Optimized geometries of $U@B_{20}$ with triplet, quintet, and septet spin states at the DFT/PBE0/6-311+G*/RECP level of theory.

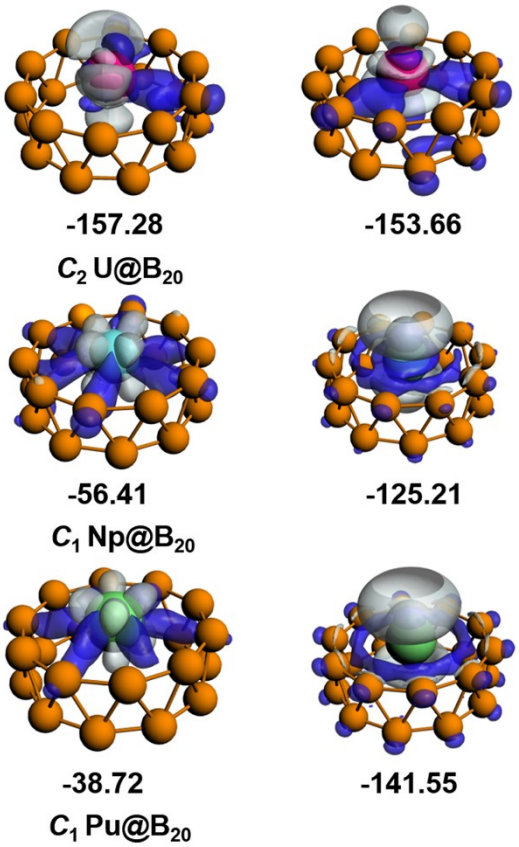

Fig. S5 Contours of representative deformation densities (isovalue = 0.001) between the interacting fragments of An and B_{20} via the ETS-NOCV analysis at the DFT/PBE/TZP/ZORA level of theory, describing the density in inflow (blue) and outflow (white).

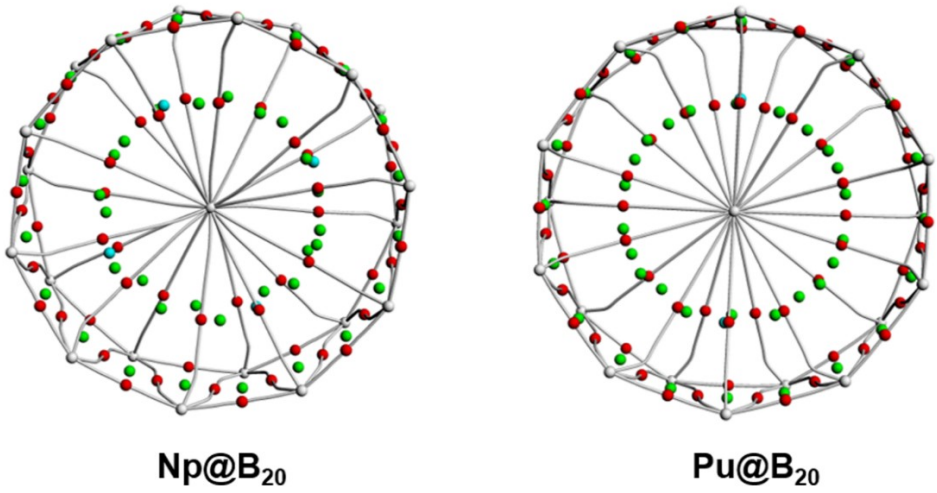

Fig. S6 Density analysis of $Np@B_{20}$ and $Pu@B_{20}$. Red points represent bond critical points, and gray lines represent bond paths. Green points represent ring critical points, and blue points represent cage critical points.

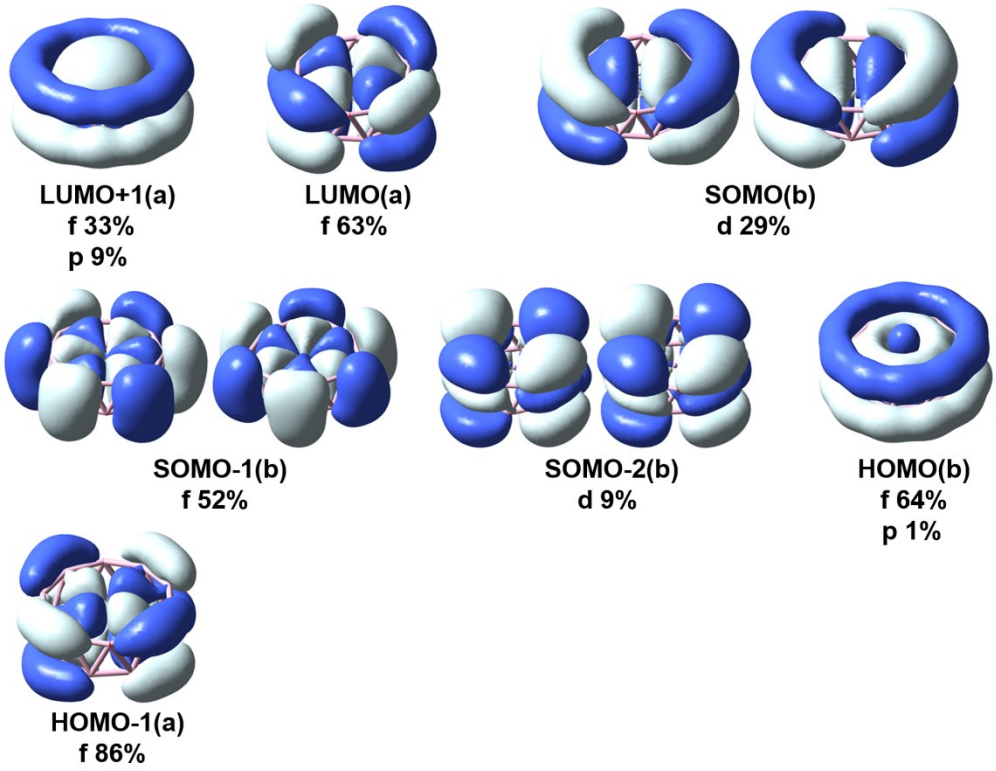

Fig. S7 The frontier molecular orbitals of U@B_{20} at the DFT/PBE0/6-311+G*/RECP level of theory.

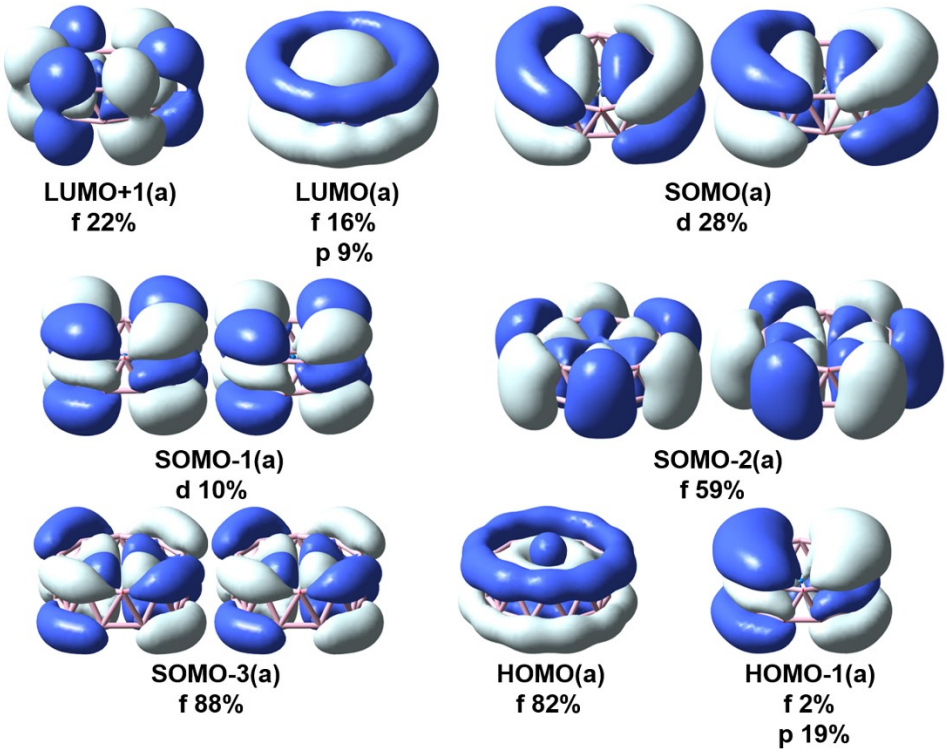

Fig. S8 The frontier molecular orbitals of $Np@B_{20}$ at the DFT/PBE0/6-311+G*/RECP level of theory.

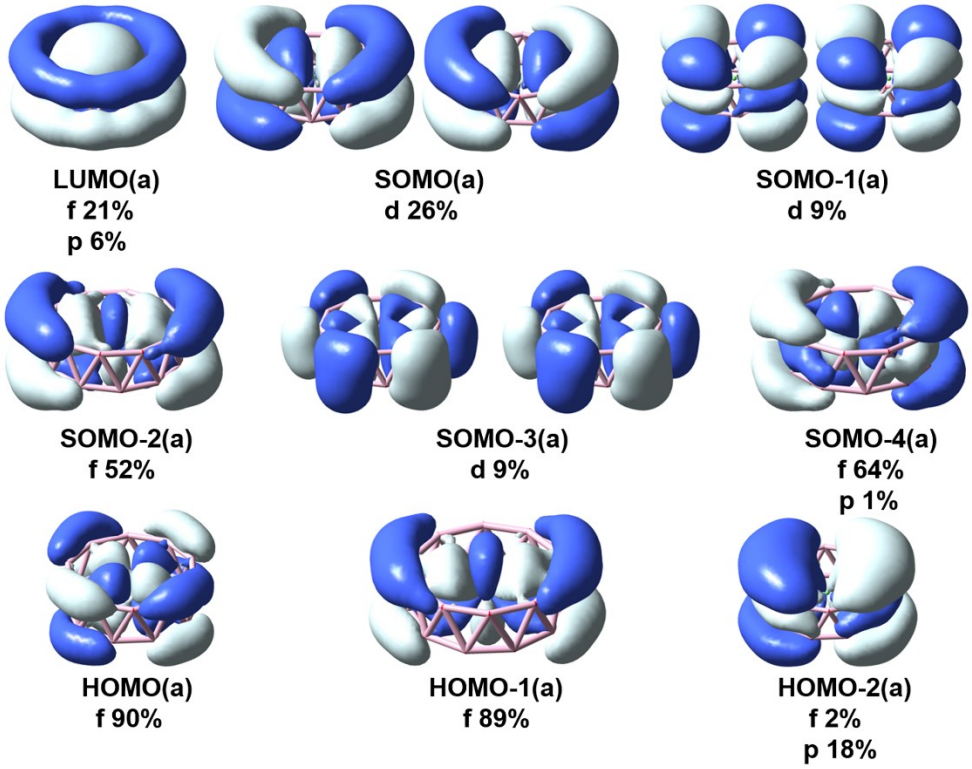

Fig. S9 The frontier molecular orbitals of $Pu@B_{20}$ at the DFT/PBE0/6-311+G*/RECP level of theory.

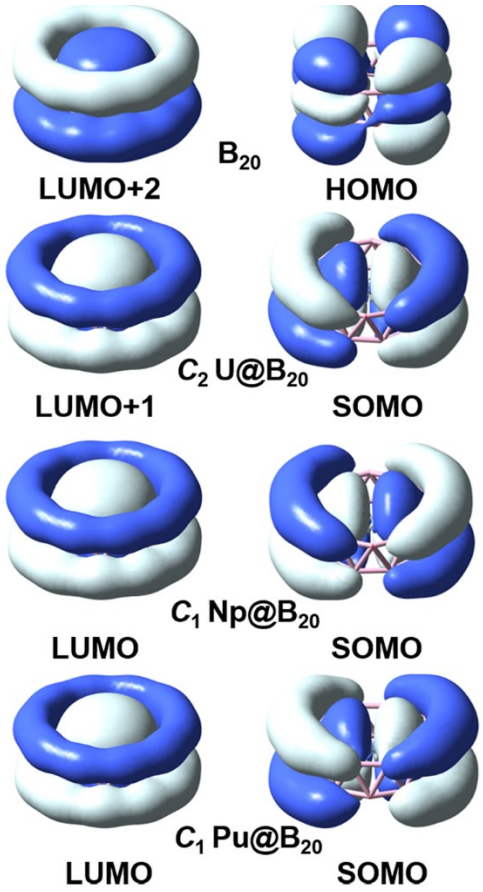

Fig. S10 Some molecular orbitals in B_{20}, $U@B_{20}$, $Np@B_{20}$ and $Pu@B_{20}$.

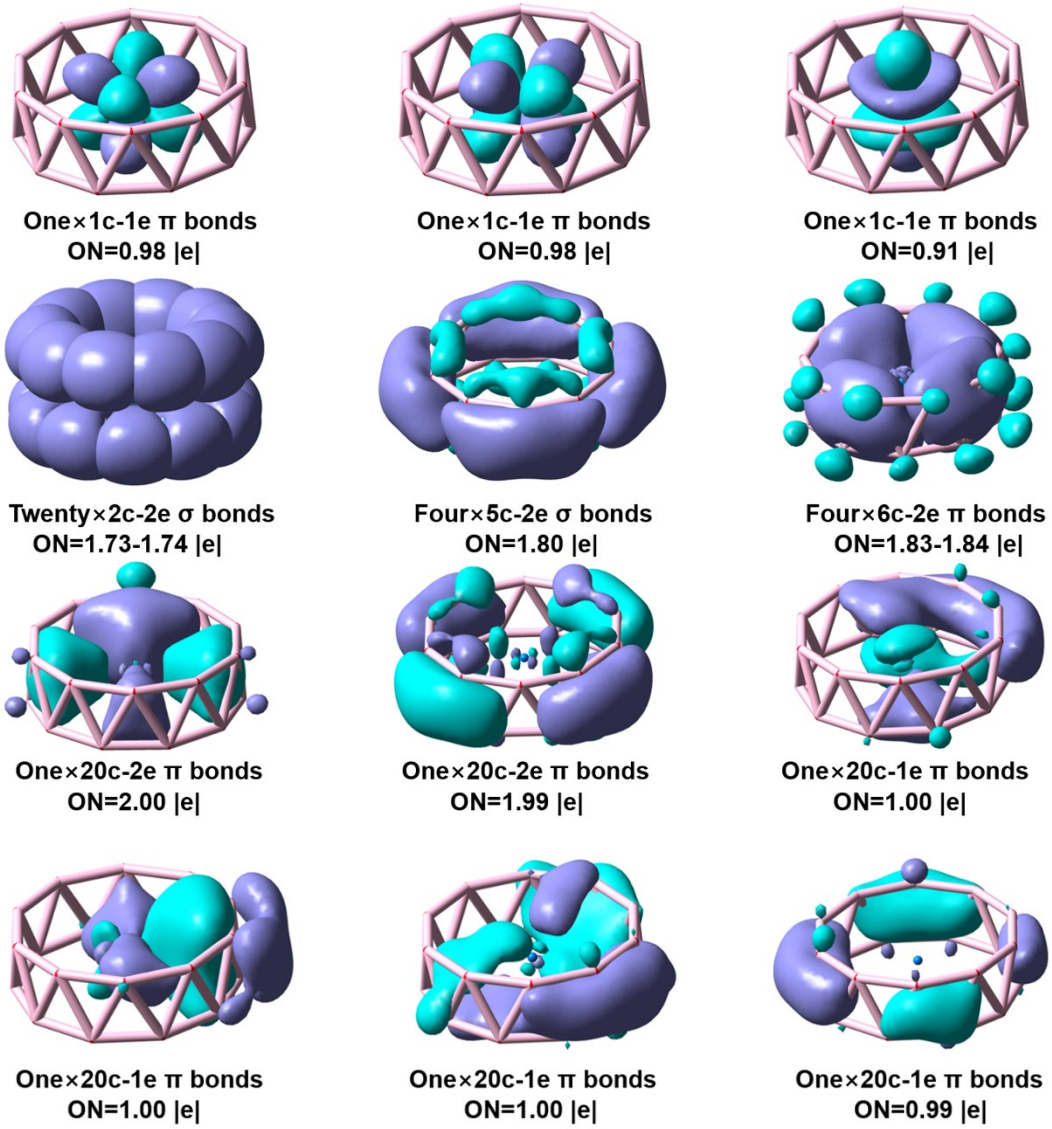

Fig. S11 Bonding pattern of C_1 Np@B_{20} from AdNDP analysis with the occupation number (ON) indicated.

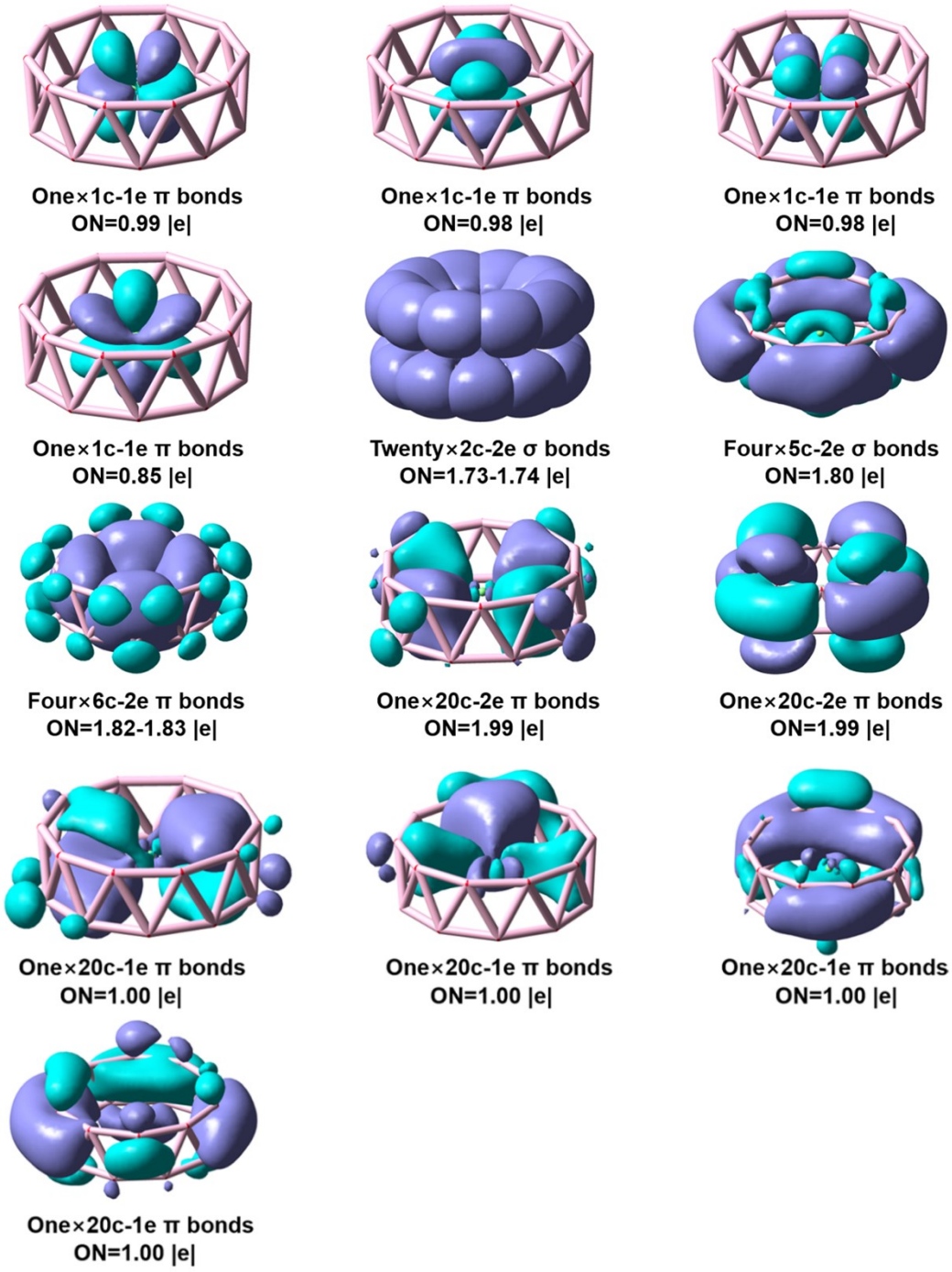

Fig. S12 Bonding pattern of C_1 Pu@B_{20} from AdNDP analysis with the occupation number (ON) indicated.

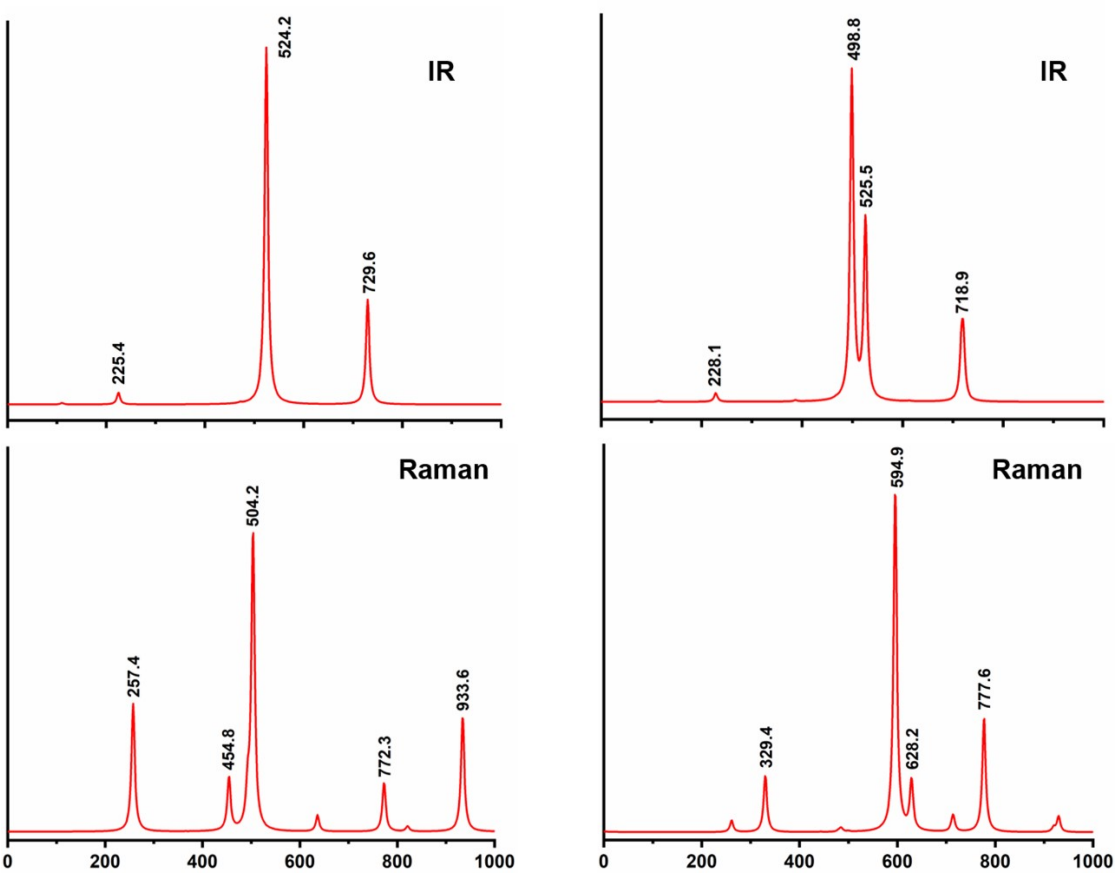

Fig. S13 The simulated IR and Raman of Np@B_{20} (left) and Pu@B_{20} (right) at the DFT/PBE0/6-311+G*/RECP level of theory.

Table S1. The spin states, the relative energies (ΔE, kcal/mol) compared with the most stable isomers of $U@B_{20}$ at the DFT/PBE0/6-311+G*/RECP and DFT/TPSSh/6-311+G*/RECP theoretical level (*in italic*). The numbers 1-10 represent the ten low-lying isomers.

Species	Singlet	Triplet	Quintet	Septet
	C_2	C_1	C_2	C_2
1	24.15	6.77	6.77	0.00
	20.10	*3.47*	*7.23*	*0.00*
	C_1	C_1	C_1	C_1
2	41.45	21.38	27.13	50.20
	36.78	*22.38*	*28.11*	*49.46*
	C_1	C_1	C_1	C_1
3	46.80	23.64	26.53	50.88
	42.14	*24.01*	*27.56*	*50.83*
	C_2	C_2	C_2	C_1
4	36.66	24.10	27.14	56.64
	32.98	*29.28*	*26.09*	*56.79*
	C_1	C_1	C_1	C_1
5	47.82	30.29	41.95	65.81
	45.65	*31.72*	*43.76*	*66.42*
	C_1/C_2	C_1	C_1	C_1
6	42.91	32.15	35.24	53.32
	38.51	*31.48*	*35.17*	*53.73*
	C_1	C_1	C_1	C_1
7	49.01	32.84	44.68	81.13
	47.40	*35.01*	*45.90*	*81.62*
	C_1	C_1	C_1	C_1
8	49.23	35.44	37.50	62.66
	43.48	*37.06*	*41.68*	*63.13*
	C_2	C_2	C_2	C_2
9	50.43	38.03	48.26	84.68
	49.46	*39.09*	*49.56*	*84.12*
	C_1	C_1	C_1	C_1
10	52.92	38.82	43.96	69.81
	49.59	*39.81*	*46.19*	*69.31*

Table S2. The spin states, the relative energies (ΔE, kcal/mol) compared with the most stable isomers of $Np@B_{20}$ at the DFT/PBE0/6-311+G*/RECP, DFT/TPSSh/6-311+G*/RECP (*in italic*), and DFT/PBE0/TZ2P/ZORA (in parentheses) theoretical levels. The numbers 1-10 represent the ten low-lying isomers.

Species	Doublet	Quartet	Sextet	Octet
1	C_1 20.44 *28.46*	C_1 9.46 *11.49* (5.10)	C_1 7.01 *7.11* (5.49)	C_1 0.00 *0.00* (0.00)
2	C_2 38.61 *36.27*	C_2 22.76 *25.09*	C_2 20.96 *24.39*	C_1 52.45 *53.83*
3	C_1 39.53 *37.05*	C_1 22.74 *24.36*	C_1 23.97 *26.25*	C_1 47.20 *48.02*
4	C_1 42.37 *39.78*	C_1 24.59 *26.53*	C_1 25.94 *28.76*	C_1 46.85 *47.41*
5	C_1/ C_2 47.01 *44.58*	C_1 35.09 *34.70*	C_1 32.96 *32.69*	C_1 50.08 *51.08*
6	C_1 49.92 *49.62*	C_1 35.55 *39.78*	C_1 35.16 *40.33*	C_1 58.50 *62.67*
7	C_1 52.13 *49.34*	C_1 35.69 *37.65*	C_1 39.38 *42.05*	C_1 61.87 *66.13*
8	C_1 52.05 *50.90*	C_1 35.94 *36.87*	C_1 44.09 *53.52*	C_1 78.45 *80.63*
9	C_2 69.30 *55.14*	C_2 40.24 *41.09*	C_2 48.13 *50.61*	C_2 83.08 *83.86*
10	C_1 58.93 *56.63*	C_1 43.70 *46.01*	C_1 44.14 *46.94*	C_1 68.31 *68.49*

Table S3. The spin states, the relative energies (ΔE, kcal/mol) compared with the most stable isomers of $Pu@B_{20}$ at the DFT/PBE0/6-311+G*/RECP and DFT/TPSSh/6-311+G*/RECP theoretical levels (*in italic*). The numbers 1-10 represent the ten low-lying isomers.

Species	Singlet	Triplet	Quintet	Septet	Nonet
	C_1	C_{5V}/ C_1	C_1	C_1	C_1
1	69.72	64.08	5.10	6.76	0.00
	57.02	*19.91*	*7.53*	*4.72*	*0.00*
	C_2	C_2	C_2	C_2	C_1
2	88.16	44.79	21.42	19.85	47.22
	75.24	*45.43*	*26.30*	*24.74*	*49.86*
	C_1	C_1	C_1	C_1	C_1
3	98.44	46.73	23.68	20.80	43.51
	82.68	*45.12*	*27.26*	*24.50*	*45.98*
	C_1	C_1	C_1	C_1	C_1
4	102.40	47.63	24.15	24.71	45.32
	88.95	*47.60*	*27.29*	*28.35*	*46.64*
	C_1	C_1	C_1	C_1	C_1
5	94.02	51.52	31.93	29.21	44.30
	78.03	*52.04*	*33.16*	*29.19*	*46.59*
	C_1	C_1	C_1	C_1	C_1
6	108.75	53.09	34.72	33.55	52.48
	94.14	*54.50*	*39.98*	*39.98*	*58.58*
	C_1	C_1	C_1	C_1	C_1
7	103.56	64.87	36.63	36.95	56.46
	90.60	*61.86*	*39.75*	*41.14*	*62.41*
	C_1	C_1	C_1	C_1	C_1
8	103.64	62.75	37.24	42.77	70.87
	91.63	*65.89*	*39.76*	*45.28*	*78.87*
	C_1	C_1	C_1	C_1	C_1
9	106.30	63.01	45.83	41.61	64.05
	93.39	*65.69*	*49.52*	*45.98*	*64.55*
	C_1	C_2	C_2	C_2	C_2
10	106.52	72.92	41.62	47.15	81.61
	94.19	*69.51*	*44.18*	*50.32*	*85.45*

Table S4. The EDA results (kcal/mol) of $An@B_{20}$ with An and B_{20} as interacting fragments at the DFT/PBE/TZP/ZORA level of theory.

Species	ΔE_{Pauli}	ΔE_{elstat} [a]	ΔE_{steric}	ΔE_{orb} [b]	ΔE_{int}
$U@B_{20}$	925.2	-501.0 (44.2%)	424.2	-632.0 (55.8%)	-207.9
$Np@B_{20}$	841.4	-470.6 (45.2%)	370.8	-570.0 (54.8%)	-199.2
$Pu@B_{20}$	762.1	-428.6 (46.3%)	333.5	-497.1 (53.7%)	-163.6

[a] The values in brackets represent ΔE_{elstat} /(ΔE_{orb}+ΔE_{elstat})

[b] The values in brackets represent ΔE_{orb}/(ΔE_{elstat}+ΔE_{elstat})

Table S5. Density analysis (average value, a.u.) of $An@B_{20}$ at the DFT/PBE0/6-311+G*/RECP theoretical level.

Species	ρ	$\nabla^2\rho$	H(r)
C_2 U@B_{20}	0.047	0.094	-0.00867
C_1 Np@B_{20}	0.045	0.095	-0.00808
C_1 Pu@B_{20}	0.044	0.097	-0.00759

Table S6. Density analysis (average value, a.u.) of $U@B_{20}$ at the DFT/PBE/TZP/ZORA theoretical level with ADF software.

Species	ρ	$\nabla^2\rho$
C_2 $U@B_{20}$	0.046	0.095
C_1 $Np@B_{20}$	0.045	0.096
C_1 $Pu@B_{20}$	0.043	0.098

Table S7. Calculated compositions (%) of the frontier molecular orbitals of $U@B_{20}$.

MOs	U		
	5f	6d	7p
LUMO	63.18		
SOMO		28.93	
SOMO		28.92	
SOMO-1	51.53		
SOMO-1	51.59		
SOMO-2		8.75	
SOMO-2		9.10	
HOMO	64.31		1.27
HOMO-1	85.9		

Table S8. Calculated compositions (%) of the frontier molecular orbitals of $Np@B_{20}$.

MOs	Np		
	5f	6d	7p
LUMO+1	22.22		
LUMO	15.97		8.03
SOMO		27.84	
SOMO		27.82	
SOMO-1		9.69	
SOMO-1		9.68	
SOMO-2	58.72		
SOMO-2	59.04		
SOMO-3	88.12		
HOMO	88.13		
HOMO-1	82.21		

Table S9. Calculated compositions (%) of the frontier molecular orbitals of $Pu@B_{20}$.

MOs	Pu		
	5f	6d	7p
LUMO	21.36		5.91
SOMO		26.22	
SOMO		26.34	
SOMO-1		9.02	
SOMO-1		9.02	
SOMO-2	76.97		0.69
SOMO-3	72.49		
SOMO-3	72.12		
SOMO-4	85.87		3.84
HOMO	89.99		
HOMO-1	89.19		
HOMO-2	1.70		18.15