Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Binding for endohedral-metallofullerene superatoms induced by magnetic coupling

Weiyu Xie [1, 2], Wanrun Jiang [1, 2], Yang Gao [1, 2], Jia Wang [1, 2] and Zhigang Wang [, 1, 2]*

a. Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

b. Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy, Jilin University, Changchun 130012, China

*Corresponding author. E-mail: wangzg@jlu.edu.cn (Z. W.)

Part 1. Computational result details.

In this work, the relativistic DFT calculations are adopted, which successfully predicted the magnetic coupling phenomenon in the actinide-contained systems in previous reports. [1-3] The magnetic coupling can be described by:

$$J = 2(E_{BS}-E_{HS})/S^2_{max}$$

using Heisenberg-Dirac-van Vleck (HDVV) spin Hamiltonian (SH) and spin-projection technique. [4, 5] Here, J is the exchange coupling constant, E_{BS} and E_{HS} are the energies of broken-symmetry state and highest spin state respectively. S_{max} is the value of the maximum spin. Thus, we could analyses the magnetic coupling from the relative energies of different spin states. In terms of the realistic effect, M06-2X functional [6] were adopted, which is proved to have an advantage in the calculation of intermolecular interaction [7], small-core relativistic effective core potentials (RECP) covering 60 core electrons with the (14s13p10d8f6g)/ [10s9p5d4f3g] valence basis set [8] is used for U, while the valence double-zeta with d-polarization basis set 6-31G* [9] is for C. Basis sets superposition error (BSSE) is defined as:

$$E_{stable} = E_{corrected} - 2E_{M0}$$

$$E_{corrected} = E_{total} + E_{BSSE}$$

$$E_{BSSE} = E_{M1} - E\ (M1\_M2_{ghost}) + E_{M2} - E\ (M1_{ghost}\_M2)$$

E_{M0} and E_{total} are the total optimized energy of two monomers and complex, respectively. E_{M1} *and* E_{M2} are single-point energies for the monomer 1 and 2 with their geometries abstracted form the $(U@C_{28})_2$ and using only the monomeric basis sets. $E\ (M1\_M2_{ghost})$ and $E\ (M1_{ghost}\_M2)$ are single-point energies with the same geometry but under the dimeric basis sets, implemented by adding ghost atoms at nuclear positions of the other monomer. The stability of the wavefunctions of all the electronic states involved in this system are calculated using specialized method [10] in Gaussian 09 [11] software. The calculations showed that all these wavefunctions are stable under the perturbations considered. In ADF 2012 [12], the density functional theory with the third generation empirical dispersion correction (DFT-D3 [13]) at PBE level are used to reproduce the structure and energy of $(U@C_{28})_2$. TZ2P Slater basis sets (relativistic valence triplet-zeta with polarization function) are adopted with a 1s-4d frozen core. For verification, scalar relativistic and spin-orbit calculations

using zero-order regular approximations at PBE-D3 level have been performed to optimize the two adsorptions and it was found that the relative energies between the two optimized adsorption structures are almost the same among these functionals as shown in Table S5.

Table S1. Total and relative energies of $U@C_{28}$ at M06-2x/RECP levels in Gaussian 09.

	El. State	Total Energy (Hartree)	Relative Energy (eV)
$U@C_{28}$	Closed-shell	-1542.95976	0.05
	Triplet	-1542.96144	0.0
	Quintet	-1542.23700	19.7

Table S2. Total and relative energies (including ZPE corrections) of $(U@C_{28})_2$ at M06-2x/RECP levels in Gaussian 09.

	El. State	Total Energy (Hartree)	Relative Energies (eV)
Chemical adsorption	BS	-3085.68227	0
	Triplet	-3085.68226	0.0003
Physical adsorption	BS	-3085.59532	2.3660
	Quintet	-3085.59464	2.3845

Table S3. Bond and relative energies of $(U@C_{28})_2$ using Scalar-ZORA-PBE-D3 functional in ADF 2012.

	El. State	Bond Energy (Hartree)	Relative Energies (eV)
Chemical adsorption	BS	-18.26702	0
	Triplet	-18.26693	0.0002
Physical adsorption	BS	-18.19155	2.0536
	Quintet	-18.18956	2.1126

Table S4. Bond and relative energies of $(U@C_{28})_2$ using SOC-ZORA-PBE-D3 functional.

	Bond Energy (Hartree)	Relative Energies (eV)
Chemical adsorption	-18.94594	0
Physical adsorption	-18.87121	2.0334

Table S5. The relative energies of $(U@C_{28})_2$ using different functionals.

		Relative Energies (eV)
M06-2X/RECP	Chemical adsorption	0
	Physical adsorption	2.3660
Scalar-ZORA-PBE-D3	Chemical adsorption	0
	Physical adsorption	2.0536
SOC-ZORA-PBE-D3	Chemical adsorption	0
	Physical adsorption	2.0334

Table S6. Coordinates of the optimized structures.

Structure	Number	Atom	x (Å)	y (Å)	z (Å)
BSc	1	U	-0.000475	3.537512	0.009525
	2	C	-0.745900	5.552117	-1.180528
	3	C	2.454124	3.497534	0.218350
	4	C	-1.025905	3.407889	2.246243
	5	C	-0.728364	1.471181	-1.329490
	6	C	1.160755	2.691107	1.965208
	7	C	-1.802150	3.520696	-1.609185
	8	C	-0.521306	3.553467	-2.355839
	9	C	1.150992	4.181516	2.014355
	10	C	-0.816964	1.431950	1.015849
	11	C	1.451727	4.821776	-1.423125
	12	C	1.336263	5.521036	-0.125060
	13	C	-1.972761	2.186668	0.515418
	14	C	1.356945	1.488201	-0.250352
	15	C	-0.852124	5.464724	1.150069
	16	C	-2.010709	4.732933	0.594609
	17	C	1.461449	2.274708	-1.485709
	18	C	2.107178	3.534502	-1.184937
	19	C	-2.076747	3.427078	1.253298

20	C	-0.018828	0.764171	-0.144422
21	C	-0.050229	5.958210	0.031399
22	C	1.944527	2.273402	0.813087
23	C	0.139032	2.278291	-2.141726
24	C	-0.226739	4.623010	2.184226
25	C	-1.928703	4.772811	-0.866815
26	C	-0.210831	2.217779	2.068995
27	C	1.959977	4.679374	0.909936
28	C	-1.892448	2.226242	-0.957912
29	C	0.139004	4.825871	-2.072020
30	U	0.000475	-3.537512	0.009525
31	C	0.745900	-5.552117	-1.180528
32	C	1.025905	-3.407889	2.246243
33	C	0.728364	-1.471181	-1.329490
34	C	-2.454124	-3.497534	0.218350
35	C	0.816964	-1.431950	1.015849
36	C	-1.451727	-4.821776	-1.423125
37	C	-1.336263	-5.521036	-0.125060
38	C	1.972761	-2.186668	0.515418
39	C	-1.356945	-1.488201	-0.250352
40	C	0.852124	-5.464724	1.150069
41	C	2.010709	-4.732933	0.594609
42	C	-1.461449	-2.274708	-1.485709
43	C	-1.160755	-2.691107	1.965208
44	C	1.802150	-3.520696	-1.609185
45	C	0.521306	-3.553467	-2.355839
46	C	-1.150992	-4.181516	2.014355
47	C	-1.944527	-2.273402	0.813087
48	C	-0.139032	-2.278291	-2.141726
49	C	0.226739	-4.623010	2.184226
50	C	1.928703	-4.772811	-0.866815
51	C	0.210831	-2.217779	2.068995
52	C	-1.959977	-4.679374	0.909936
53	C	1.892448	-2.226242	-0.957912
54	C	-0.139004	-4.825871	-2.072020
55	C	0.050229	-5.958210	0.031399
56	C	2.076747	-3.427078	1.253298
57	C	-2.107178	-3.534502	-1.184937
58	C	0.018828	-0.764171	-0.144422

Structure	Number	Atom	x (Å)	y (Å)	z (Å)
Triplet	1	U	-0.000512	3.537571	0.009527
	2	C	-0.745038	5.552335	-1.180818
	3	C	2.453934	3.497505	0.220094
	4	C	-1.027530	3.407715	2.245513
	5	C	-0.727534	1.471367	-1.330229
	6	C	1.159308	2.690918	1.965933
	7	C	-1.801040	3.520991	-1.610451
	8	C	-0.519667	3.553811	-2.356186
	9	C	1.149549	4.181317	2.015246
	10	C	-0.817769	1.431908	1.015034
	11	C	1.452733	4.821961	-1.421933
	12	C	1.336384	5.521091	-0.123879
	13	C	-1.973186	2.186723	0.513866
	14	C	1.357051	1.488213	-0.249598
	15	C	-0.852915	5.464673	1.149692
	16	C	-2.011125	4.732977	0.593328
	17	C	1.462433	2.274888	-1.484803
	18	C	2.107983	3.534637	-1.183432
	19	C	-2.077663	3.427049	1.251822
	20	C	-0.018824	0.764196	-0.144726
	21	C	-0.050213	5.958262	0.031649
	22	C	1.943874	2.273335	0.814325
	23	C	0.140478	2.278600	-2.141725
	24	C	-0.228289	4.622827	2.184205
	25	C	-1.928098	4.773026	-0.868034
	26	C	-0.212363	2.217604	2.068699
	27	C	1.959345	4.679283	0.911473
	28	C	-1.891831	2.226482	-0.959395
	29	C	0.140478	4.826168	-2.071750
	30	U	0.000512	-3.537571	0.009527
	31	C	0.745038	-5.552335	-1.180818
	32	C	1.027530	-3.407715	2.245513
	33	C	0.727534	-1.471367	-1.330229
	34	C	-2.453934	-3.497505	0.220094
	35	C	0.817769	-1.431908	1.015034
	36	C	-1.452733	-4.821961	-1.421933
	37	C	-1.336384	-5.521091	-0.123879

	38	C	1.973186	-2.186723	0.513866
	39	C	-1.357051	-1.488213	-0.249598
	40	C	0.852915	-5.464673	1.149692
	41	C	2.011125	-4.732977	0.593328
	42	C	-1.462433	-2.274888	-1.484803
	43	C	-1.159308	-2.690918	1.965933
	44	C	1.801040	-3.520991	-1.610451
	45	C	0.519667	-3.553811	-2.356186
	46	C	-1.149549	-4.181317	2.015246
	47	C	-1.943874	-2.273335	0.814325
	48	C	-0.140478	-2.278600	-2.141725
	49	C	0.228289	-4.622827	2.184205
	50	C	1.928098	-4.773026	-0.868034
	51	C	0.212363	-2.217604	2.068699
	52	C	-1.959345	-4.679283	0.911473
	53	C	1.891831	-2.226482	-0.959395
	54	C	-0.140478	-4.826168	-2.071750
	55	C	0.050213	-5.958262	0.031649
	56	C	2.077663	-3.427049	1.251822
	57	C	-2.107983	-3.534637	-1.183432
	58	C	0.018824	-0.764196	-0.144726

Structure	Number	Atom	x (Å)	y (Å)	z (Å)
BSp	1	U	-3.626108	0.010846	-0.081289
	2	C	-2.722241	1.141145	-2.093035
	3	C	-2.862408	1.211486	1.947940
	4	C	-6.097834	0.016413	-0.167035
	5	C	-2.802366	-2.325282	-0.011942
	6	C	-5.022637	0.352398	1.867225
	7	C	-2.824837	-1.180107	-2.034354
	8	C	-1.646231	-0.744156	-1.262874
	9	C	-4.993577	1.617143	1.108045
	10	C	-4.985121	-1.857982	0.642509
	11	C	-1.683582	1.464405	-0.039092
	12	C	-2.884336	2.318680	-0.095523
	13	C	-4.933934	-1.883827	-0.831791
	14	C	-2.963438	-1.110522	1.963124
	15	C	-4.905825	1.573156	-1.417368
	16	C	-4.883881	0.282778	-2.132483

17	C	-1.733475	-0.700315	1.260351
18	C	-3.640040	-2.126204	1.155184
19	C	-5.626672	-0.697887	-1.338779
20	C	-1.671766	0.762983	1.246546
21	C	-3.542256	2.105665	-1.385454
22	C	-3.677737	0.094923	2.385843
23	C	-1.633974	-1.462370	0.013555
24	C	-5.662530	1.400496	-0.176052
25	C	-3.506607	0.009062	-2.547275
26	C	-5.710029	-0.656104	1.058703
27	C	-3.630330	2.149752	1.152136
28	C	-3.556819	-2.167975	-1.240325
29	C	-1.583587	0.718798	-1.295902
30	U	3.626081	-0.011398	0.081194
31	C	2.732914	1.232942	2.029236
32	C	2.878102	1.089185	-2.009525
33	C	6.097501	-0.029047	0.170610
34	C	2.776266	-2.338883	0.133491
35	C	5.028421	0.211354	-1.880247
36	C	2.809597	-1.089144	2.092880
37	C	1.636724	-0.681404	1.297720
38	C	5.012717	1.514547	-1.188588
39	C	4.964841	-1.931126	-0.541053
40	C	1.699969	1.459323	-0.040494
41	C	2.910387	2.301858	-0.026986
42	C	4.911865	-1.878661	0.932493
43	C	2.953093	-1.231417	-1.902502
44	C	4.921985	1.604490	1.335641
45	C	4.884693	0.353761	2.117307
46	C	1.727026	-0.771116	-1.224407
47	C	3.617349	-2.210857	-1.041091
48	C	5.617321	-0.675467	1.377518
49	C	1.681757	0.691487	-1.287476
50	C	3.564445	2.149750	1.273438
51	C	3.681302	-0.057920	-2.386806
52	C	1.617767	-1.465504	0.060687
53	C	5.677683	1.358276	0.106163
54	C	3.504027	0.117684	2.543852
55	C	5.703452	-0.760780	-1.018626

	56	C	3.655624	2.059406	-1.262989
	57	C	3.531209	-2.125545	1.353224
	58	C	1.590480	0.781820	1.253597

Structure	Number	Atom	x (Å)	y (Å)	z (Å)
Quintet	1	U	0.000000	0.000000	3.673995
	2	C	-2.022141	-1.167484	2.847420
	3	C	0.000000	2.334967	2.847420
	4	C	0.000000	0.000000	6.149711
	5	C	2.022141	-1.167484	2.847420
	6	C	0.737595	1.884883	5.005936
	7	C	0.000000	-2.310955	2.942493
	8	C	0.000000	-1.459421	1.737624
	9	C	-0.737595	1.884883	5.005936
	10	C	2.001154	-0.303665	5.005936
	11	C	-1.263895	0.729710	1.737624
	12	C	-2.001346	1.155478	2.942493
	13	C	1.263559	-1.581217	5.005936
	14	C	2.001346	1.155478	2.942493
	15	C	-2.001154	-0.303665	5.005936
	16	C	-1.263559	-1.581217	5.005936
	17	C	1.263895	0.729710	1.737624
	18	C	2.470585	-0.040787	3.644166
	19	C	0.000000	-1.385363	5.718909
	20	C	0.000000	1.467181	1.684997
	21	C	-2.470585	-0.040787	3.644166
	22	C	1.199970	2.159982	3.644166
	23	C	1.270616	-0.733591	1.684997
	24	C	-1.199759	0.692681	5.718909
	25	C	-1.270615	-2.119195	3.644166
	26	C	1.199759	0.692681	5.718909
	27	C	-1.199970	2.159982	3.644166
	28	C	1.270615	-2.119195	3.644166
	29	C	-1.270616	-0.733591	1.684997
	30	U	0.000000	0.000000	-3.673995
	31	C	0.000000	2.334967	-2.847420
	32	C	-2.022141	-1.167484	-2.847420
	33	C	0.000000	0.000000	-6.149711
	34	C	2.022141	-1.167484	-2.847420

35	C	-1.263559	-1.581217	-5.005936
36	C	2.001346	1.155478	-2.942493
37	C	1.263895	0.729710	-1.737624
38	C	-2.001154	-0.303665	-5.005936
39	C	1.263559	-1.581217	-5.005936
40	C	-1.263895	0.729710	-1.737624
41	C	-2.001346	1.155478	-2.942493
42	C	2.001154	-0.303665	-5.005936
43	C	0.000000	-2.310955	-2.942493
44	C	-0.737595	1.884883	-5.005936
45	C	0.737595	1.884883	-5.005936
46	C	0.000000	-1.459421	-1.737624
47	C	1.270615	-2.119195	-3.644166
48	C	1.199759	0.692681	-5.718909
49	C	-1.270616	-0.733591	-1.684997
50	C	-1.199970	2.159982	-3.644166
51	C	-1.270615	-2.119195	-3.644166
52	C	1.270616	-0.733591	-1.684997
53	C	-1.199759	0.692681	-5.718909
54	C	1.199970	2.159982	-3.644166
55	C	0.000000	-1.385363	-5.718909
56	C	-2.470585	-0.040787	-3.644166
57	C	2.470585	-0.040787	-3.644166
58	C	0.000000	1.467181	-1.684997

Part 2. Potential energy surface scanning.

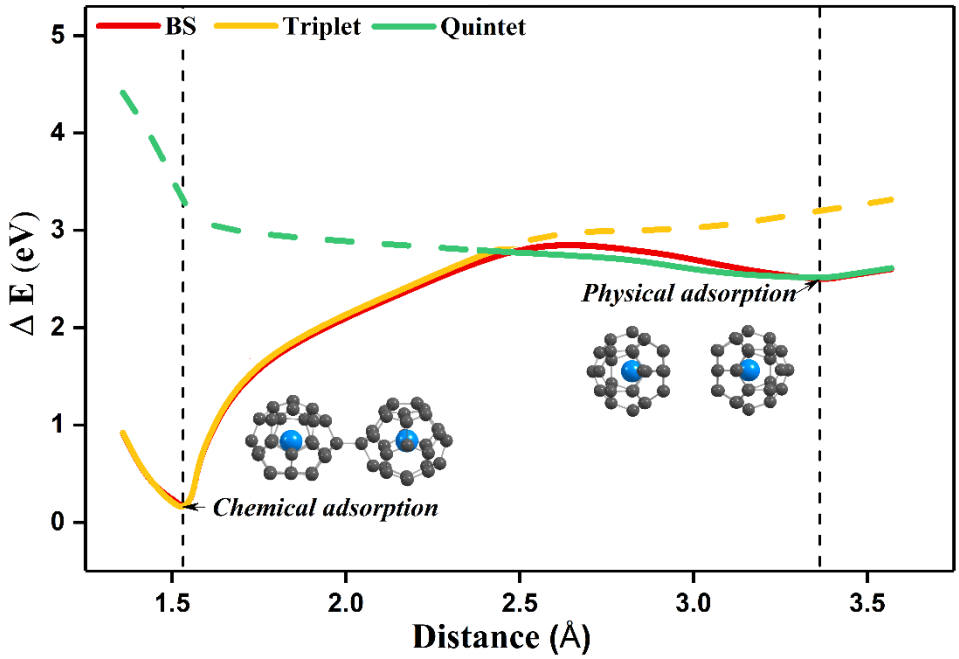


Figure S1. The potential energy surface scanning of the involved electronic states in this system. The distance is according to the length of nearest C atoms between superatoms. Two dash lines are equilibrium positions of chemical adsorption (left) and physical adsorption (right), respectively. It should be noticed that the PES scanning is reliable with regard to the triplet solid curve and the quintet solid curve. However, the reliability of the triplet and quintet dash curves is not supported by the HDVV SH. The presence of these dash curves are just for the completeness of the results and a qualitative demonstration of corresponding PESs with smooth profiles.

Actually, the two adsorption structures have different spin states respectively, because of the electron rearrangement of two superatoms during the combining. To prove it, we scan the potential energy surface for different electronic states. The potential energy curves of triplet state are monotone decreasing and the quintet state is monotone increasing. On the contrary, the BS state has a global-minimum point and a local-minimum point on the potential energy curve. And the BS state is the ground state both in chemical and physical adsorptions. These results show that there is only one stable adsorption structure in triplet and quintet states, but two stable adsorption structures in BS state.

Part 3. Structures, spin properties of both adsorptions.

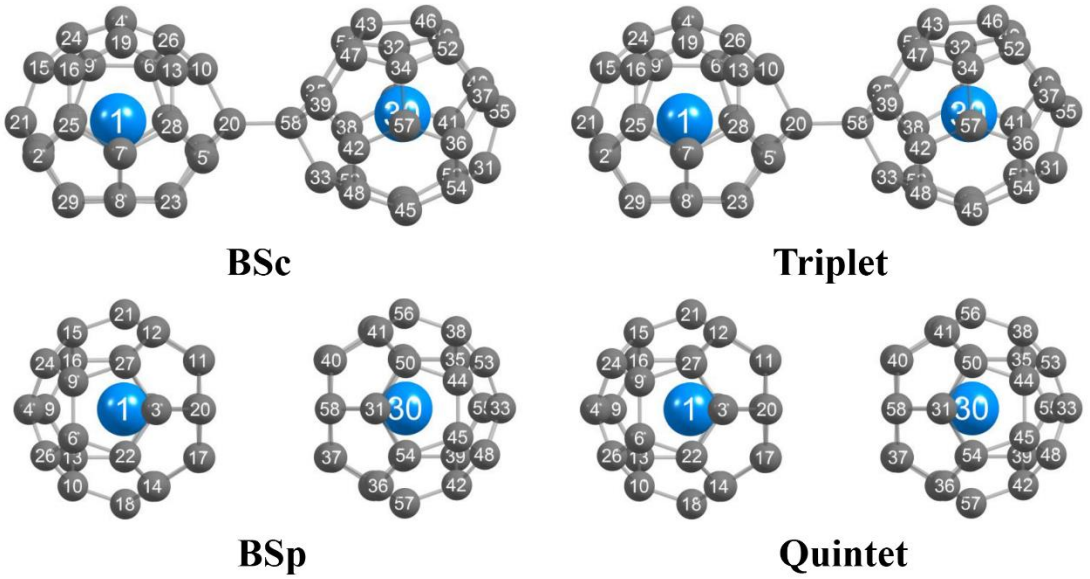


Figure S2. Structures with atom labels of involved states in both adsorptions.

Table S7. Spin population of involved states in both adsorptions.

	Chemical adsorption		**Physical adsorption**	
	BSc	Triplet	BSp	Quintet
1U	-0.188577	-0.188005	-0.381058	-0.374765
2C	-0.020693	-0.020635	-0.037012	-0.038102
3C	-0.012649	-0.012686	-0.035779	-0.036627
4C	-0.012681	-0.012698	-0.035909	-0.036917
5C	-0.027595	-0.027464	-0.038791	-0.035736
6C	-0.013622	-0.013664	0.025541	0.025840
7C	-0.019134	-0.019187	0.024627	0.024449
8C	-0.019203	-0.019169	0.021856	0.028213
9C	-0.023851	-0.023860	0.025316	0.025572
10C	0.021280	0.020975	0.025611	0.025558
11C	0.023280	0.023252	0.028144	0.021782
12C	0.024669	0.024775	0.022658	0.027870
13C	0.055866	0.055875	0.024997	0.025720
14C	0.020768	0.020942	0.026103	0.024739
15C	0.024874	0.024884	0.025033	0.025920
16C	0.023214	0.023190	0.026109	0.025123
17C	0.056205	0.056227	0.021378	0.025829
18C	-0.002203	-0.002220	0.181738	0.181120

19C	-0.002179	-0.002188	0.180390	0.182965
20C	-0.002359	-0.003227	0.183376	0.190499
21C	0.003623	0.003581	0.181422	0.181099
22C	0.096262	0.096516	0.177322	0.183200
23C	0.160781	0.160863	0.200748	0.181069
24C	0.142782	0.142840	0.179463	0.184159
25C	0.144682	0.144756	0.177356	0.184358
26C	0.096863	0.096926	0.181283	0.183649
27C	0.142933	0.143031	0.182248	0.181287
28C	0.160929	0.161181	0.184642	0.180731
29C	0.145212	0.145188	0.188667	0.201337
SUM	**≈1.00**	**≈1.00**	**≈2.00**	**≈2.00**
30U	0.188577	-0.188005	0.381373	-0.374894
31C	0.020693	-0.020635	0.036839	-0.036839
32C	0.012681	-0.012698	0.035844	-0.035754
33C	0.027595	-0.027464	0.035850	-0.036845
34C	0.012649	-0.012686	0.039075	-0.038009
35C	-0.021280	0.020975	-0.025400	0.025810
36C	-0.023280	0.023252	-0.023970	0.027961
37C	-0.024669	0.024775	-0.022570	0.022098
38C	-0.055866	0.055875	-0.025435	0.025484
39C	-0.020768	0.020942	-0.025381	0.025006
40C	-0.024874	0.024884	-0.026640	0.025218
41C	-0.023214	0.023190	-0.023502	0.025053
42C	-0.056205	0.056227	-0.025300	0.026144
43C	0.013622	-0.013664	-0.025802	0.024204
44C	0.019134	-0.019187	-0.025476	0.025917
45C	0.019203	-0.019169	-0.025860	0.025538
46C	0.023851	-0.023860	-0.021929	0.028367
47C	-0.096262	0.096516	-0.181866	0.184768
48C	-0.160781	0.160863	-0.179883	0.184092
49C	-0.142782	0.142840	-0.184384	0.181344
50C	-0.144682	0.144756	-0.180766	0.183544
51C	-0.096863	0.096926	-0.177831	0.180964
52C	-0.142933	0.143031	-0.200177	0.198640
53C	-0.160929	0.161181	-0.179772	0.183542
54C	-0.145212	0.145188	-0.178590	0.182025
55C	-0.003623	0.003581	-0.181579	0.182869
56C	0.002179	-0.002188	-0.182187	0.181170

57C	0.002203	-0.002220	-0.184169	0.180880
58C	0.002359	-0.003227	-0.187990	0.191763
Sum	**≈-1.00**	**≈1.00**	**≈-2.00**	**≈2.00**
Total Sum	**≈ 0.00**	**≈2.00**	**≈ 0.00**	**≈4.00**

Part 4. Frontier MOs diagrams for involved states.

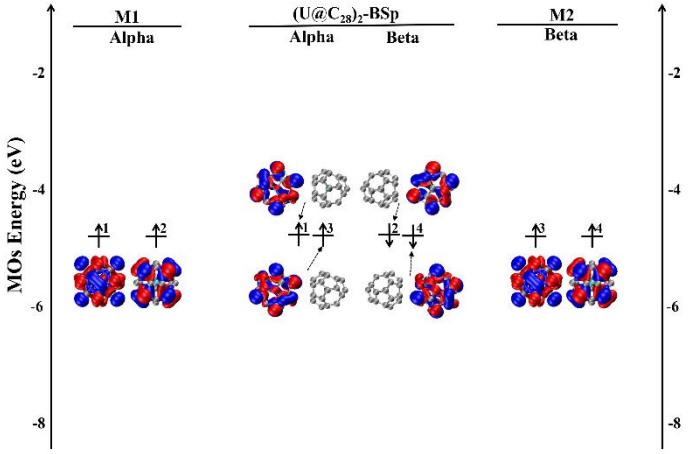


Figure S3. The $(U@C_{28})_2$-BSp frontier MOs diagram between two $U@C_{28}$ superatoms. M1 and M2 are the two $U@C_{28}$ monomers. The same number represents the composition of $U@C_{28}$ monomers' orbitals in $(U@C_{28})_2$-BSp orbitals. Isosurface=0.02

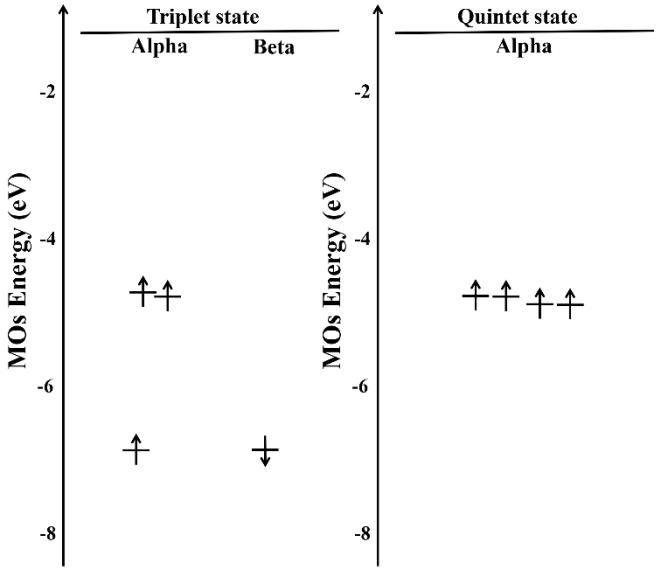


Figure S4. The high-spin state frontier MOs diagrams in both adsorptions between two $U@C_{28}$ superatoms.

Part 5. Orbital compositions of $(U@C_{28})_2$-BSc by different methods.

We analyzed the orbital components of U valence shells by different methods. As shown in Table S7 and S8, the U-5f contribution area has 28 MOs which is from HOMO-1 to HOMO-14 in alpha and beta spin state. The compositions of these MOs are from 26.75% to 17.64% in Mulliken method, which is proved by Hirshfeld method (22.51% to 15.13%). The U-6d, 7p contributions area is from HOMO-27 to HOMO-42, the composition of these MOs are from 13.19% to 5.05% (in Mulliken method) and from 11.10% to 5.35% (in Hirshfeld method). The U-7s contributions area is HOMO-65 and HOMO-66, the composition of these MOs are 6.14% and 6.93% (in Mulliken method), 6.31% and 7.06% (in Hirshfeld method). Overall, the composition data obtained by different methods have the same direction. These date indicate that all the valence shells of U should be fully closed upon hybridization with the cage, similar to the $U@C_{28}$ report [14].

Table S8. The orbital compositions of $(U@C_{28})_2$-BSc by Mulliken method.

$(U@C_{28})_2$-BSc	**U composition**				**Occ**
Alpha, beta	5f	6d	7p	7s	—
HOMO	0.5%				2
HOMO-1	19.97 %				2
HOMO-2	26.75 %				2
HOMO-3	19.41 %				2
HOMO-4	18.81 %				2
HOMO-5	22.44 %				2
HOMO-6	22.31 %				2
HOMO-7	21.49 %				2
HOMO-8	20.69%				2
HOMO-9	20.43%				2
HOMO-10	20.43%				2
HOMO-11	18.95%				2
HOMO-12	18.98%				2
HOMO-13	18.17%				2
HOMO-14	17.64%				2
Total					28
HOMO-27		5.89%	5.51%		2
HOMO-28		4.40%	4.94%		2

HOMO-29	5.27%	7.92%		2
HOMO-30	5.48%	7.16%		2
HOMO-31	4.24%	7.71%		2
HOMO-32	2.84%	8.23%		2
HOMO-33	4.43%	7.47%		2
HOMO-34	3.49%	7.16%		2
HOMO-35	3.53%	7.22%		2
HOMO-36	3.58%	6.68%		2
HOMO-37	9.32%	0.61%		2
HOMO-38	8.32%	1.99%		2
HOMO-39	6.19%	1.50%		2
HOMO-40	7.17%	0.87%		2
HOMO-41	9.70%	0.34%		2
HOMO-42	4.78%	0.27%		2
Total				32
HOMO-65			6.14%	2
HOMO-66			6.93%	2
Total				4
Total all				64

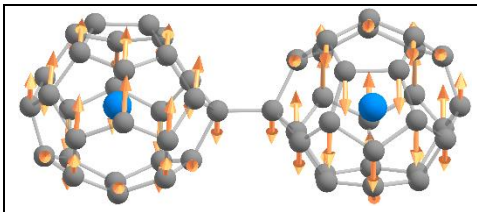
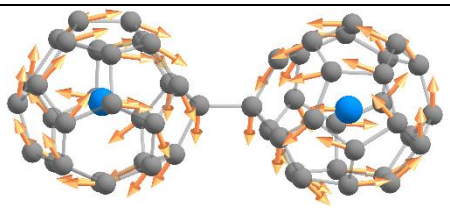
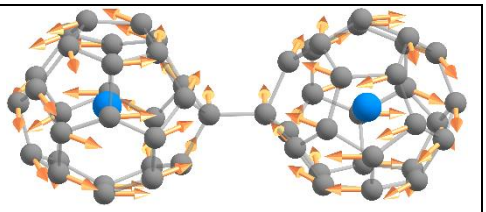
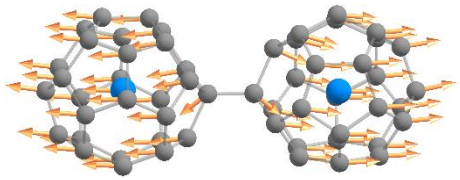
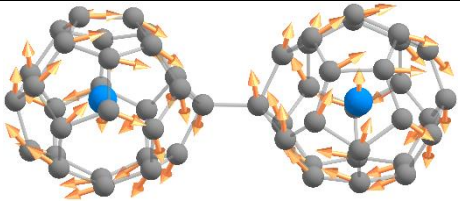
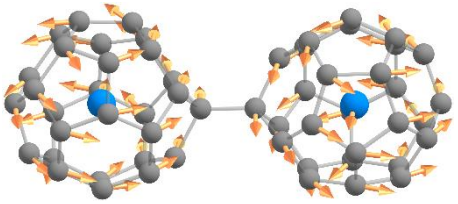
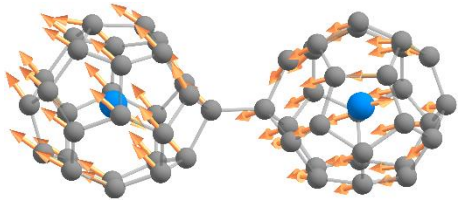
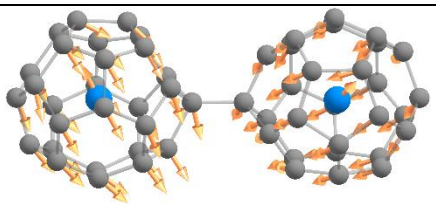
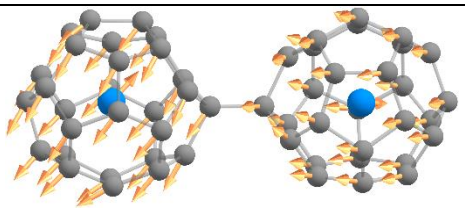
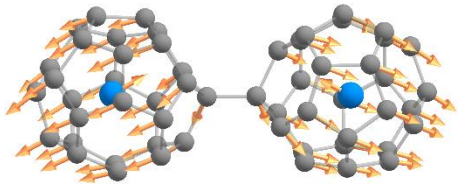
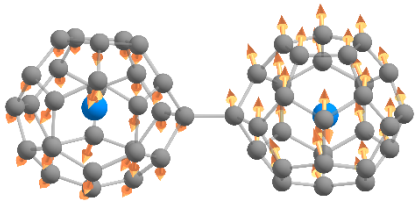
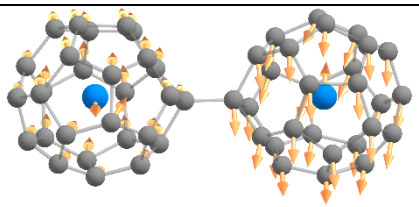
Table S9. The orbital compositions of $(U@C_{28})_2$-BSc by Hirshfeld method

$(U@C_{28})_2$-BSc Alpha, beta	**U**	**Occ**
HOMO	2.00%	2
HOMO-1	18.38%	2
HOMO-2	22.51%	2
HOMO-3	17.77%	2
HOMO-4	16.76%	2
HOMO-5	19.58%	2
HOMO-6	19.19%	2
HOMO-7	18.59%	2
HOMO-8	18.24%	2
HOMO-9	19.14%	2
HOMO-10	17.39%	2
HOMO-11	17.96%	2
HOMO-12	17.64%	2

HOMO-13	15.84%	2
HOMO-14	15.13%	2
HOMO-27	9.92%	2
HOMO-28	8.32%	2
HOMO-29	11.10%	2
HOMO-30	10.87%	2
HOMO-31	10.04%	2
HOMO-32	9.39%	2
HOMO-33	10.20%	2
HOMO-34	9.03%	2
HOMO-35	9.29%	2
HOMO-36	8.90%	2
HOMO-37	9.11%	2
HOMO-38	9.09%	2
HOMO-39	7.12%	2
HOMO-40	7.61%	2
HOMO-41	9.24%	2
HOMO-42	5.35%	2
HOMO-65	6.31%	2
HOMO-66	7.06%	2

Part 6. Schemes for all the involved vibration mode.

Table S10. The twelve vibration mode diagrams from 0 to 400 cm^{-1} in $(U@C_{28})_2$-BSc.

 21 cm^{-1} mode 1	 33 cm^{-1} mode 2	 36 cm^{-1} mode 3
 99 cm^{-1} mode 4	 156 cm^{-1} mode 5	 163 cm^{-1} mode 6
 261 cm^{-1} mode 7	 265 cm^{-1} mode 8	 289 cm^{-1} mode 9
 293 cm^{-1} mode 10	 300 cm^{-1} mode 11	 305 cm^{-1} mode 12

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