Supplementary Information

Synthesis and Characterization of Carbene Derivatives of Th@C_{3v}(8)-C_{82} and U@C_{2v}(9)-C_{82} : Exceptional Chemical Properties Induced by Strong Actinide-Carbon Cage Interaction

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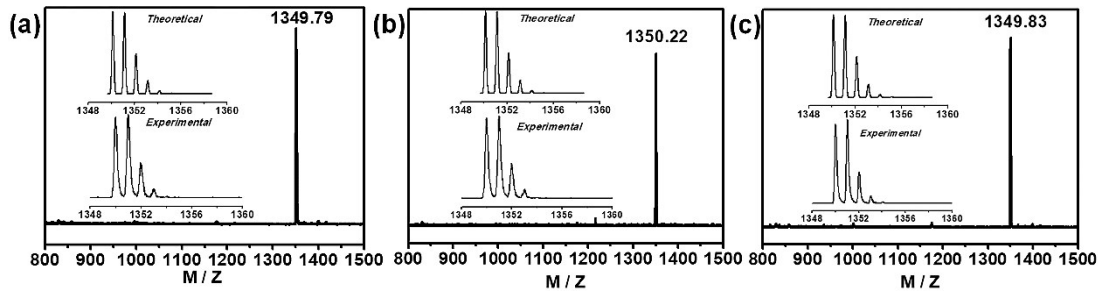

Fig. S1. Positive-ion mode MALDI-TOF mass spectra of the purified (a) Th@C_{3v}(8)-C_{82}Ad(I), (b) Th@C_{3v}(8)-C_{82}Ad(II) and (c) Th@C_{3v}(8)-C_{82}Ad(III). Using Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix.

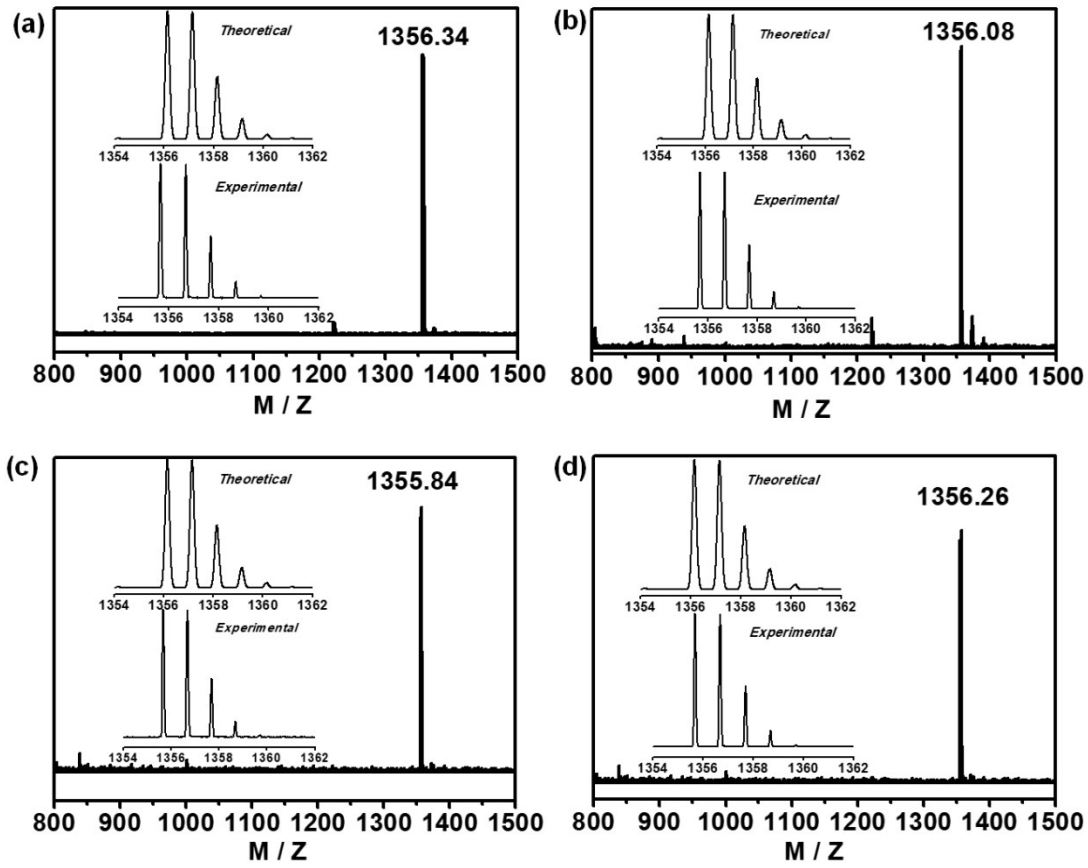

Fig. S2. Positive-ion mode MALDI-TOF mass spectra of the purified (a) U@C_{2v}(9)-C_{82}(I), (b) U@C_{2v}(9)-C_{82}(II), (c) U@C_{2v}(9)-C_{82}(III), and (d) U@C_{2v}(9)-C_{82}(IV). Using Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix.

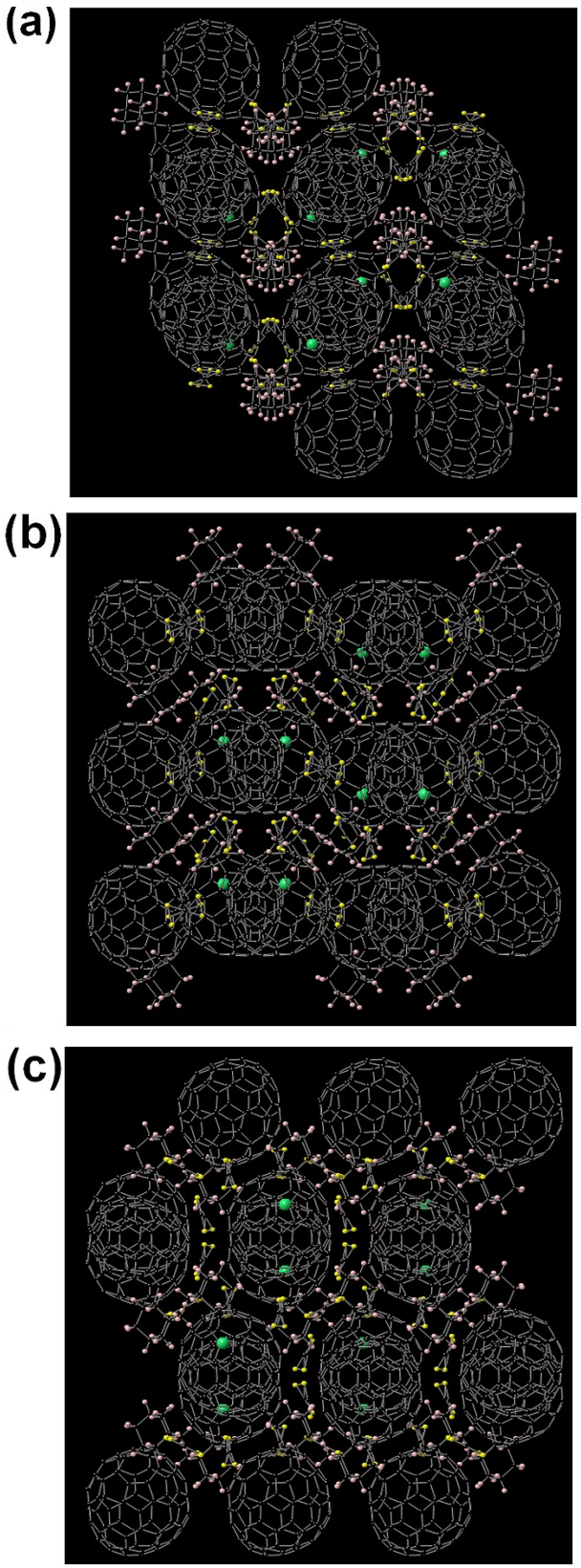

Fig. S3. Packing diagrams in the crystal of Th@C_{3v}(8)-C_{82}Ad(I) viewed along the (a) a-axis, (b) b-axis, and (c) c-axis.

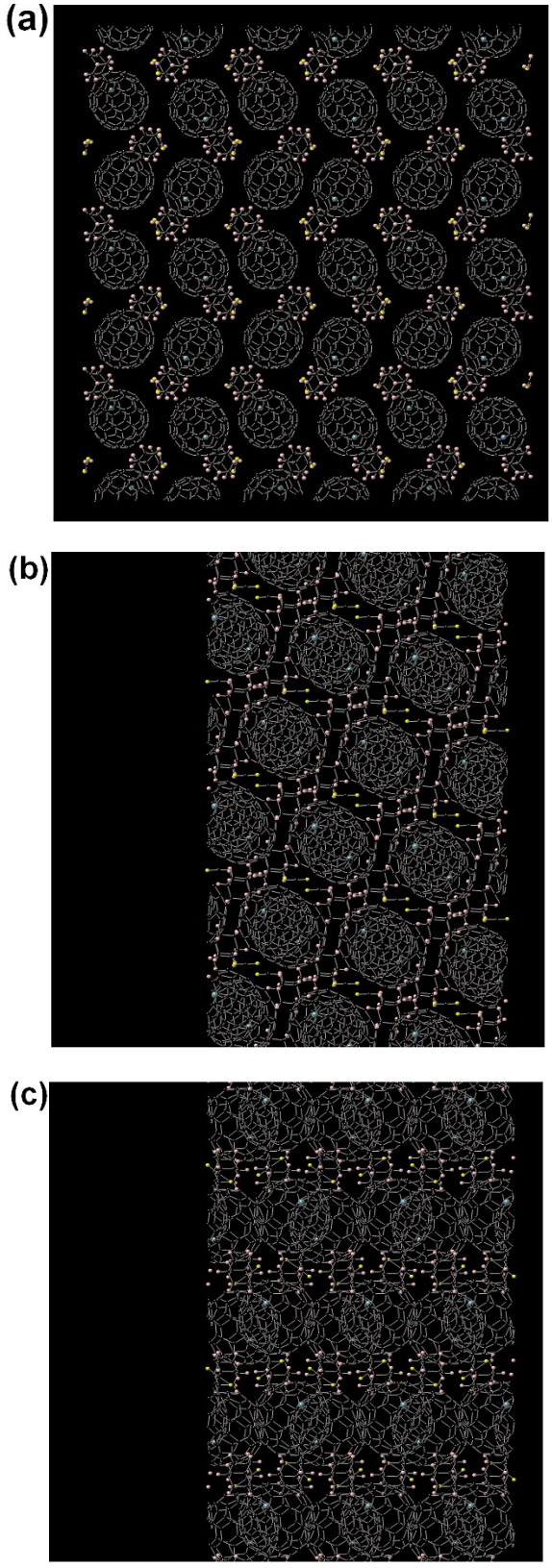

Fig. S4. Packing diagrams in the crystal of U@C_{2v}(9)-C_{82}Ad(I) viewed along the (a) a-axis, (b) b-axis, and (c) c-axis.

Table S1. Charge densities (e) and POAV (in degree) values of all the nonequivalent carbon atoms in Th@C_{3v}(8)-C_{82}.

Carbon number	Charge density value	POAV value
1	**-0.159**	**14.137**
2	**-0.127**	10.954
3	**-0.087**	10.209
4	**-0.108**	9.339
5	-0.066	10.152
6	-0.062	8.784
7	-0.078	9.288
8	-0.072	10.464
9	-0.044	10.740
10	-0.014	10.097
11	-0.043	7.702
12	-0.012	11.010
13	-0.017	7.483
14	-0.008	10.582
15	-0.017	10.841
16	0.011	10.725
17	-0.012	11.524

Table S2. Relative energies (Δ*E*, kcal/mol) of different Th@C_{3v}(8)-C_{82}Ad isomers.

C-C bond	Δ*E*	C-C bond	Δ*E*
1-2 (I)	**0.00**	3-6	17.14
3-4 (II)	**1.08**	6-7	18.48
2-3 (III)	**6.69**	9-12	18.97
13-13’	10.04	14-15	19.42
17-17’	11.26	15-16	19.77
4-5	11.55	6-6’	20.83
13-16	12.23	7-8	21.23
17-17’’	12.30	5-8	21.75
11-12	13.73	16-17	23.25
7-9	14.48	12-14	25.13
9-9’	15.81	10-11	26.01
8-10	16.47	10-10’	30.05
11-13	17.12		

Table S3. Comparison between experimental and calculated interatomic distances (Å) of Th@C_{3v}(8)-C_{82}Ad(I) and U@C_{2v}(9)-C_{82}Ad(I).

compound	bond	experiment	calculation
Th@C_{3v}(8)-C_{82}Ad(I)	C1-C2	2.136	2.165
	Th-C1	2.565	2.604
	Th-C2	2.568	2.615
U@C_{2v}(9)-C_{82}Ad(I)	C1-C2	2.071	2.232
	U-C1	2.557	2.523
	U-C2	2.544	2.590

Table S4. Charge densities (e) and POAV (in degree) values of all the nonequivalent carbon atoms in U@C_{2v}(9)-C_{82}.

Carbon number	Charge density value	POAV value
1	**-0.209**	11.331
2	**-0.144**	**11.623**
3	**-0.122**	8.722
4	**-0.096**	9.312
5	-0.022	10.203
6	-0.071	9.081
7	-0.014	8.836
8	-0.001	9.868
9	-0.011	10.564
10	-0.043	9.046
11	-0.039	7.983
12	-0.004	10.807
13	-0.016	10.525
14	-0.026	7.622
15	-0.012	10.707
16	0.001	10.954
17	0.006	10.834
18	-0.005	10.797
19	-0.032	8.503
20	-0.004	10.681
21	0.004	10.367
22	-0.024	8.645
23	0.007	10.610
24	-0.024	8.587

Table S5. Relative energies (Δ*E*, kcal/mol) of different U@C_{2v}(9)-C_{82}Ad isomers.

C-C bond	Δ*E*	C-C bond	Δ*E*
1-2(I)	**0.00**	4-7	14.89
2-2′(II)	**3.97**	9-12	15.43
2-4(III)	**7.62**	4-6	15.73
1-3(IV)	**10.50**	18-21	16.19
24-24′	10.91	10-13	16.47
14-17	11.34	11-12	17.19
20-20′	11.45	17-18	17.62
6-9	11.95	20-23	17.73
15-18	12.23	7-10	18.14
16-19	12.36	15-16	19.83
13-16	12.86	5-6	20.21
11-14	13.03	17-20	21.52
21-22	13.06	3-5	21.64
23-24	13.49	8-8′	21.65
9-13	13.59	12-15	21.67
5-8	14.10	8-11	35.19
21-23	14.29	14-14′	36.09
19-22	14.43		

Table S6. The calculated nearest metal-cage distances in Th@C_{3v}(8)-C_{82} and M@C_{2v}(9)-C_{82}(M = U, Sc, La).

Compound	ion radius/Å	bond	distance/Å
Th@C_{3v}(8)-C_{82}	Th^{4+}	Th-C1	2.365
	0.940	Th-C2	2.459
U@C_{2v}(9)-C_{82}	U^{3+}	U-C1	2.428
	1.025	U-C2	2.436
Sc@C_{2v}(9)-C_{82}	Sc^{3+}	Sc-C1	2.265
	0.745	Sc-C2	2.272
La@C_{2v}(9)-C_{82}	La^{3+}	La-C1	2.550
	1.061	La-C2	2.557