Supplementary Materials

$C_{64}H_4$: Production, Isolation and Structural Characterizations of a Stable Unconventional Fulleride

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1. HPLC separation of $C_{64}H_4$

In Buckyprep column, the retention time of $C_{64}H_4$ is between that of C_{60} and C_{70}, as indicated in Figure S1. The sample can be enriched by repeatedly collecting the $C_{64}H_4$-containing fraction, and finally isolated and purified by recycling HPLC method with the Buckyprep and Buckyclutcher columns. The purity of $C_{64}H_4$ was confirmed by both HPLC and TOF mass spectrometry as a single peak. For example, Figure S2 shows a recycling HPLC profile of the purified sample with buckyprep column. A single peak was observed to maintain after 18 cycles, indicating no impurities in the sample at all.

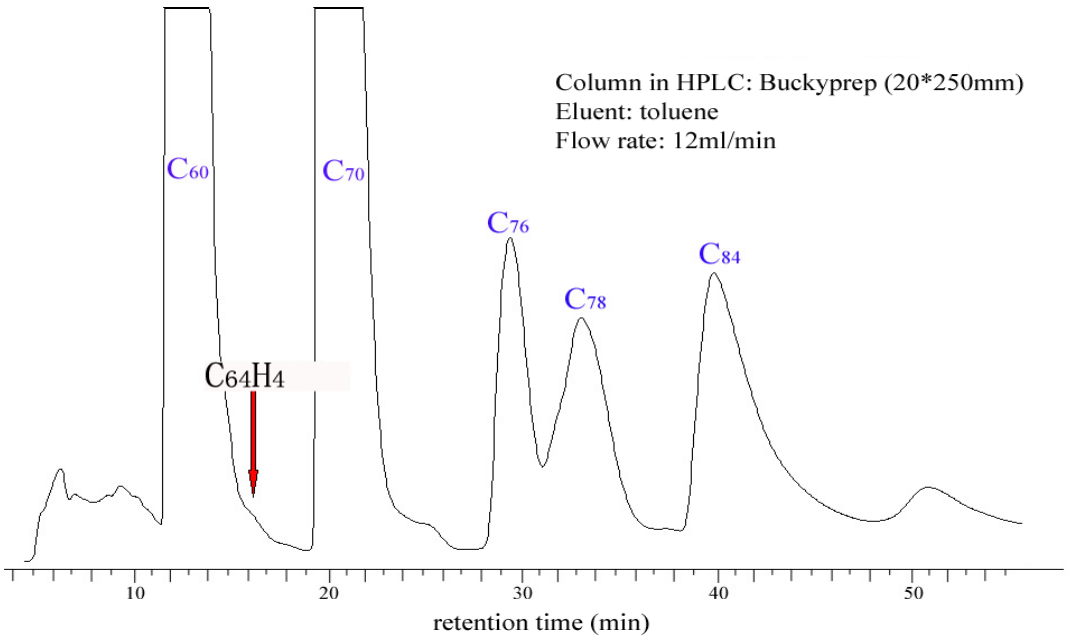

Figure S1. HPLC profile for the first stage separation of $C_{64}H_4$ in Buckyprep column.

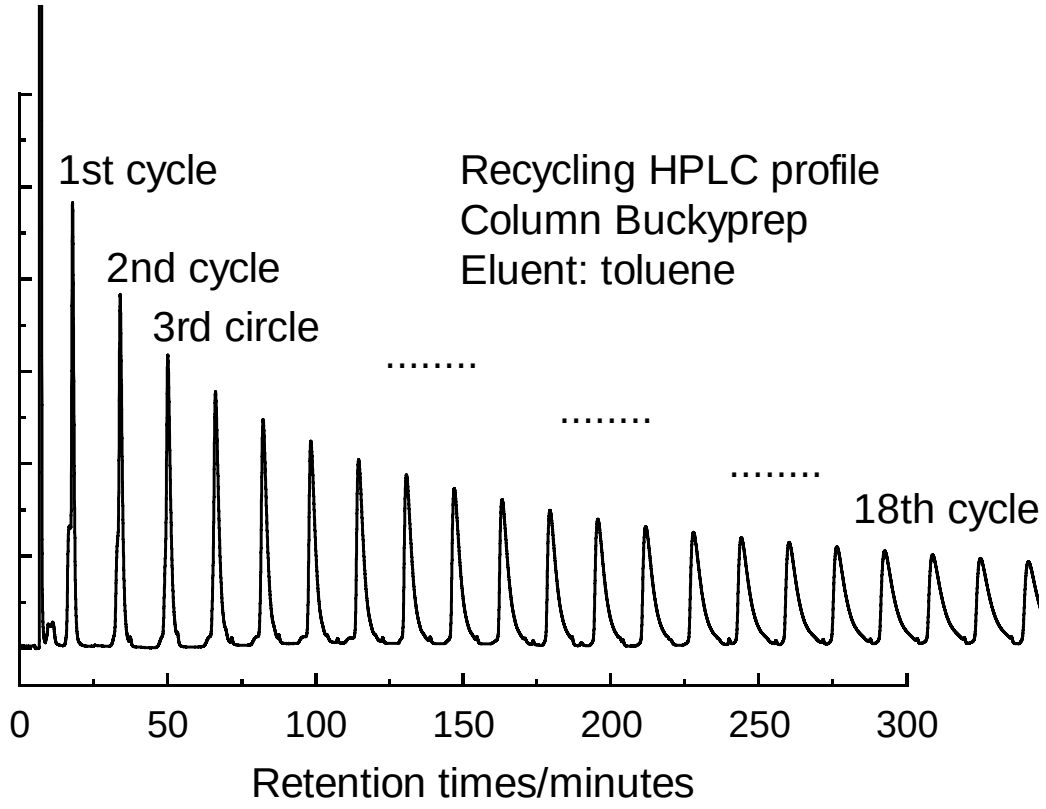

Figure S2. Recycling HPLC profile for the purified $C_{64}H_4$ in Buckyprep column to show the high purity of this sample.

2. 2D-HMQC NMR

2D NMR measurement is a powerful tool to pair the hydrogen atoms and relative carbon atoms within a molecule. As shown in Figure S3, it is obviously that the 4 sp^3 hybridized carbon atoms connect with the 4 hydrogen atoms respectively, which strongly support the endohedral structure of $C_{64}H_4$.

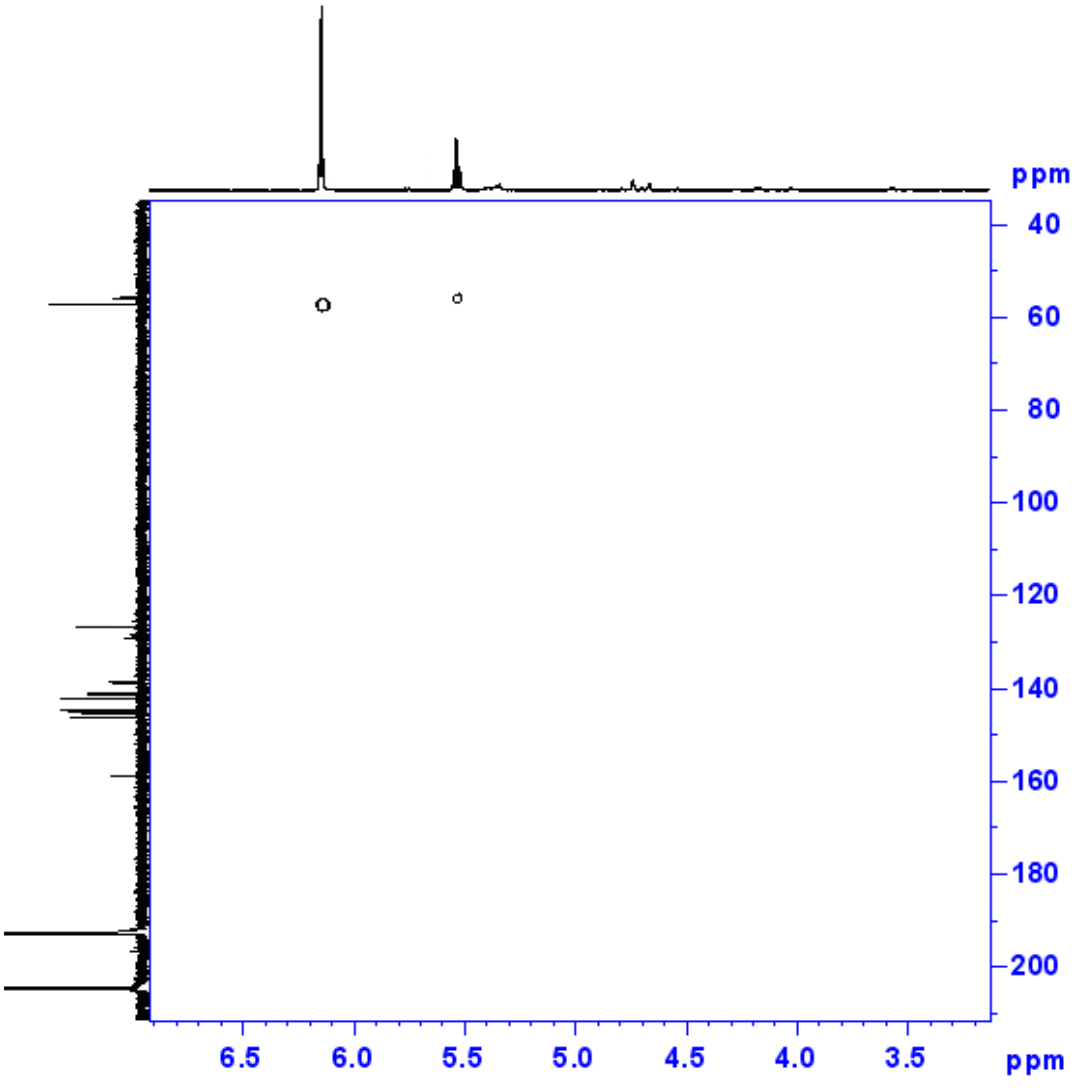

Figure S3. 2D-HMQC ^{1}H-^{13}C NMR spectrum.

3. Theoretical simulations of ^{13}C NMR and IR specta of $C_{64}H_4$

The calculation was performed using the Gaussian 03W program. ^{13}C nuclear magnetic shielding tensors of the C_{3v}-$C_{64}H_4$ molecule were calculated at the GIAO-B3LYP/6-31G* level of theory with the geometry optimised at same level. Based on the predicted ^{13}C nuclear magnetic shielding tensors, the ^{13}C chemical shifts were computed relative to C_{60} and converted to the tetramethylsilane scale using the experimental value for C_{60} (δ = 142.5 ppm). The numbering of carbon atoms were shown in Figure S4

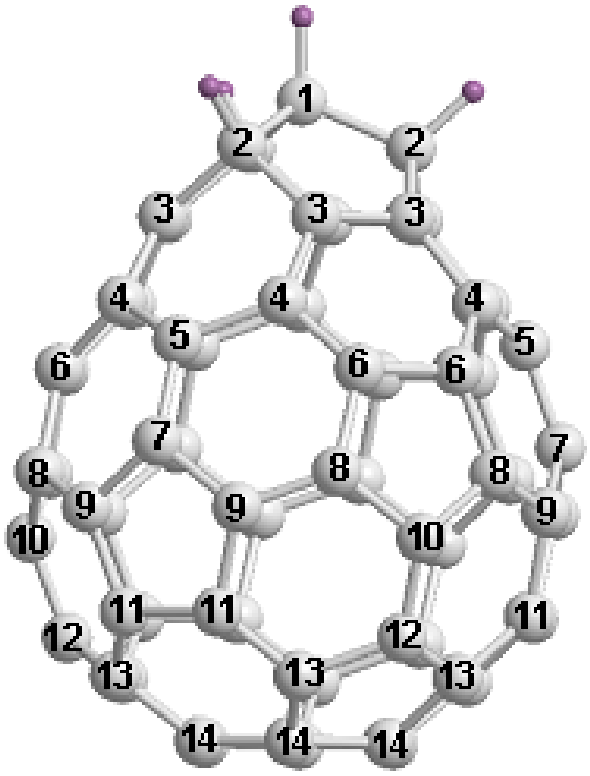

Figure S4 The numbering of carbon atoms in $C_{64}H_4$

The simulated IR spectrum(Fig. 5) is based on the theoretical vibrational frequencies predicted at the B3LYP/6-31G* level using the Gaussian 03W program. The theoretical vibrational frequencies (unscaled and scaled values) are given in Table S1, along with predicted IR intensities and Raman activities for each mode.

4. The mass spectrometry study of raw soot.

After arc-discharging graphite in the helium/methane atmosphere, the raw soot contains a large range of fullerenes beginning from C_{48}. However, most of the fullerenes in soot can't be dissolved in toluene so are removed by the Soxhlet-extraction process with toluene solvent. Figure S5 is a typical mass spectrum of the raw soot.

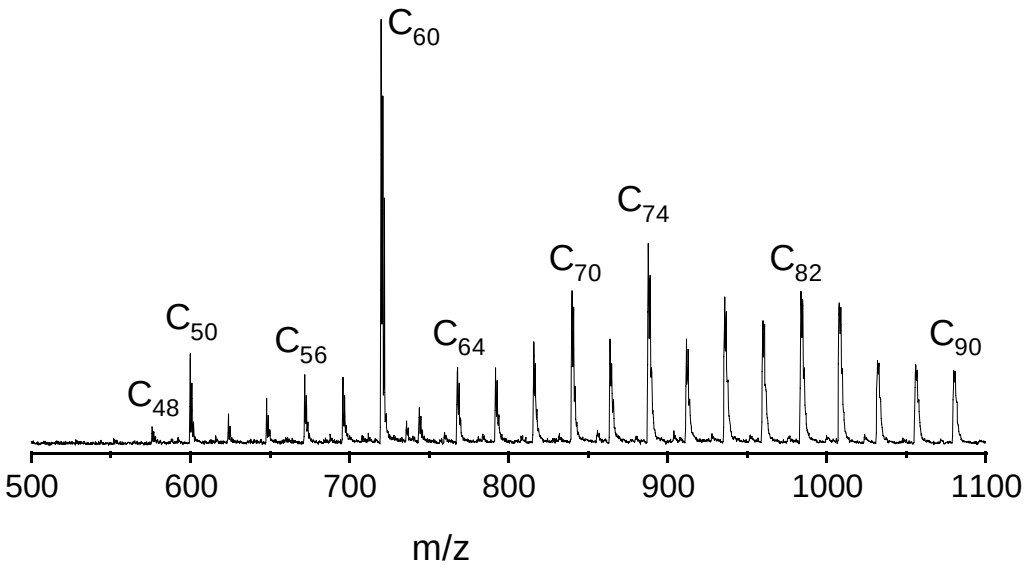

Figure S5. TOF mass spectrum of the raw soot.

Table S1 Vibrational frequencies[a] (cm^{-1}), IR intensities (KM/Mole) and Raman activities (A^4/amu) of $C_{64}H_4$ predicted at the B3LYP/.6-31G* level of theory.

Sym.	Freq. (cm^{-1}) Unscaled	Scaled[b]	IR Int.	Raman Act.	Sym.	Freq. (cm^{-1}) Unscaled	Scaled[b]	IR Int.	Raman Act.	Sym.	Freq. (cm^{-1}) Unscaled	Scaled[b]	IR Int.	Raman Act.
E	218	213	0.024	17.6	E	727	712	0.372	2.7	E	1262	1237	1.534	11.0
E	265	259	0.028	18.3	E	736	721	0.187	0.38	A_2	1265	1240	0.000	0.0
A_1	266	260	0.387	24.1	E	741	726	0.123	0.10	E	1273	1248	6.233	25.6
A_1	320	313	0.030	0.07	A_2	745	730	0.000	0.0	A_1	1279	1253	0.387	12.7
E	322	315	0.013	3.6	A_2	746	731	0.000	0.0	E	1292	1266	0.248	12.2
A_2	324	317	0.000	0.0	E	746	731	0.767	2.4	E	1296	1270	0.751	5.4
E	338	331	0.057	0.87	A_1	752	737	0.009	0.33	E	1311	1285	1.287	2.3
E	347	340	0.444	0.74	E	753	738	0.094	0.19	A_1	1314	1288	0.154	62.8
A_1	364	356	0.982	0.42	A_2	761	746	0.000	0.0	A_2	1320	1294	0.000	0.0
A_2	370	362	0.000	0.0	E	763	748	0.195	0.78	E	1322	1296	1.867	1.0
E	396	388	0.009	0.34	A_1	766	751	1.949	3.7	A_2	1333	1306	0.000	0.0
E	415	406	0.004	0.36	A_1	771	756	0.376	0.89	A_1	1337	1310	0.001	4.2
A_2	425	416	0.000	0.0	A_1	773	758	0.658	3.87	E	1338	1311	0.482	1.5
E	435	426	0.065	0.33	E	779	763	0.080	2.4	A_2	1341	1314	0.000	0.0
A_1	436	427	0.423	2.8	E	784	768	0.111	1.9	E	1365	1338	0.222	1.5
A_1	455	445	0.695	54.3	A_2	790	774	0.000	0.0	E	1368	1341	0.713	9.6
E	456	446	0.888	0.02	E	807	791	0.153	1.9	E	1378	1350	0.133	0.04
A_1	479	469	1.189	58.9	A_2	814	798	0.000	0.0	A_2	1380	1352	0.000	0.0
A_2	492	482	0.000	0.0	E	840	823	0.569	0.28	A_1	1386	1358	1.765	10.0
E	497	487	5.171	0.37	E	846	829	0.531	0.12	A_2	1397	1369	0.000	0.0
E	513	502	2.787	0.01	A_1	875	858	0.614	6.5	E	1403	1375	2.206	1.9
A_1	520	509	11.542	1.9	A_1	899	881	0.600	0.55	A_1	1408	1380	4.369	128
E	522	511	3.200	0.14	E	919	901	0.347	4.1	E	1433	1404	0.003	17.2
E	535	524	0.018	0.04	A_2	944	925	0.000	0.0	E	1454	1425	4.798	6.4
A_2	537	526	0.000	0.0	E	953	934	1.574	0.24	E	1462	1433	0.052	2.7
A_1	544	533	12.515	1.1	A_1	977	957	0.560	2.2	A_1	1463	1434	5.034	37.8
A_2	557	545	0.000	0.0	A_2	983	963	0.000	0.0	E	1472	1443	6.584	5.5
E	565	553	20.922	0.05	A_1	1005	985	1.025	0.97	A_1	1478	1448	0.584	27.9
A_2	573	561	0.000	0.0	E	1010	990	0.0002	0.93	A_2	1493	1463	0.000	0.0
A_1	575	563	5.025	8.0	E	1060	1039	0.053	1.1	A_1	1496	1466	6.449	350
E	576	564	4.275	0.57	A_2	1082	1060	0.000	0.0	A_2	1533	1502	0.000	0.0
E	583	571	1.766	0.10	E	1087	1065	0.082	3.5	E	1546	1515	1.356	3.8
A_1	617	604	0.259	2.3	A_1	1101	1079	4.692	5.9	A_1	1561	1530	0.301	22.2
E	632	619	4.291	0.66	E	1114	1092	0.660	5.1	E	1562	1531	0.0004	0.5
E	642	629	0.328	0.39	A_1	1132	1109	0.993	1.6	E	1597	1565	0.034	4.8
A_2	658	644	0.000	0.0	A_2	1133	1110	0.000	0.0	A_2	1608	1576	0.000	0.0
A_2	675	661	0.000	0.0	E	1156	1133	1.092	6.8	A_1	1608	1576	5.906	5.3
E	680	666	0.655	0.20	E	1193	1169	0.027	0.5	E	1611	1579	0.778	38.6
E	685	671	0.072	0.92	A_1	1199	1175	11.244	4.6	E	1615	1583	0.149	31.4

A_2	685	671	0.000	0.0	E	1200	1176	0.002	4.9	E	1618	1586	0.004	28.3
E	700	686	0.040	1.8	E	1219	1195	0.017	4.1	A_1	1630	1597	0.437	95.2
A_1	719	704	0.073	0.54	A_2	1241	1216	0.000	0.0	E	3049	2988	17.251	260
E	721	706	0.001	0.21	A_1	1243	1218	0.048	1.2	A_1	3050	2989	65.123	727
A_1	726	711	0.552	1.3	E	1256	1231	1.299	3.3	A_1	3136	3073	55.674	399

[a] 198 normal modes = 132 unique vibrational modes = 37 A_1 + 66 E + 29 A_2

[b] Scaled by 0.98.