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Supporting Information

Capturing Nonclassical C_{70} with Double Heptagons in Low-Pressure Combustion

Fang-Fang Xie, Zuo-Chang Chen, Min Zhang, Xiao-Ming Xie, Ling-Fang Chen, Han-Rui Tian, Shun-Liu Deng, Su-Yuan Xie and Lan-Sun Zheng

State Key Lab for Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Contents

1. Synthesis of dihept-$C_{70}H_6$

The carbon soot containing dihept-$C_{70}H_6$ was synthesized by our homemade setup in low-pressure benzene-acetylene-oxygen diffusion flame combustion.[1] The specific combustion conditions are given as follows: gas flow rate, vapoured benzene, 1.0 L/min; C_2H_2, 0.50 L/min; O_2, 1.10 L/min; chamber pressure, around 25 Torr. Approximately 2.5 g of carbon soot was produced per hour inside the combustion chamber and filter. Repeating the aforementioned synthetic experiments until 1kg carbon soot was accumulated for subsequent multi-stage HPLC separation of dihept-$C_{70}H_6$.

2. Separation and purification of dihept-$C_{70}H_6$ via HPLC

The synthesized carbon soot was extracted with toluene by ultrasonic method followed by filtration and concentration at room temperature. All the separation and purification were conducted at room temperature using toluene as the mobile phase at a 4 mL/min flow rate on a Shimadzu LC-6AD HPLC instrument. The chromatogram was monitored at 330 nm. Three HPLC columns (Cosmosil 5PBB, Cosmosil Buckyprep, and Cosmosil 5NPE, i.d. 10 × 250 mm) suitable for fullerene isolation were used here alternately. The upper right corner of each chromatogram as follows manifests the elution conditions in each isolation step of dihept-$C_{70}H_6$.

The procedure includes four stages of HPLC run for the isolation of dihept-$C_{70}H_6$, among which the last two were carried out in a recycling mode (Figure S1). First, the crude toluene extracts of carbon soot were separated into several components using a Cosmosil 5PBB column (i.d. 10 × 250 mm), and the component containing dihept-$C_{70}H_6$ with retention time in the range of 22.5~24.5 min was enriched for the next HPLC stage (Figure S1a). Second, the primarily collected samples were further isolated by a Cosmosil 5NPE column (i.d. 10 × 250 mm) eluted with toluene, and then the component with retention time ranging from 12.1 to 13.0 min was collected (Figure S1b). Finally, the subsequent recycling separation and purification were conducted under the same HPLC conditions (5PBB and Buckyprep column, i.d. 10 × 250 mm, respectively), and after several cycles of isolation, the purified dihept-$C_{70}H_6$ was obtained eventually (Figure S1c, S1d)

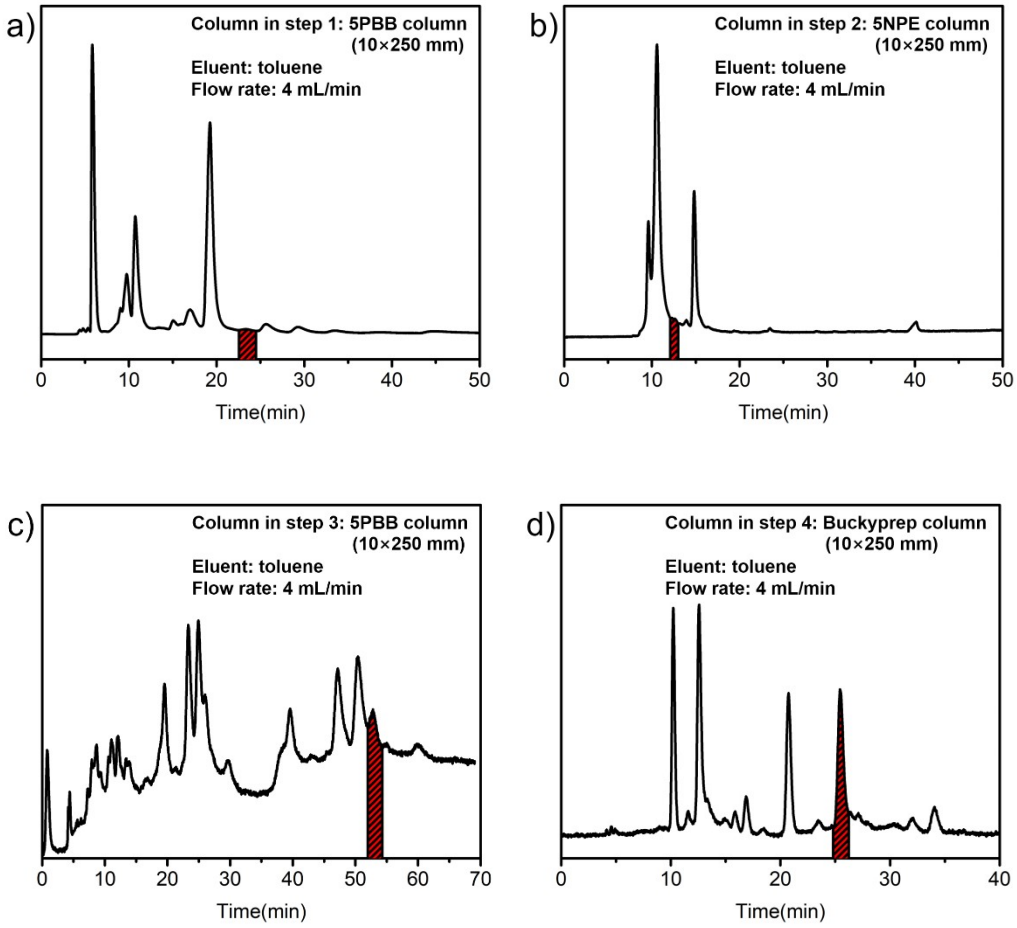

Figure S1. HPLC chromatograms for the separation of dihept-$C_{70}H_6$.
(The areas highlighted in red shadow correspond to the collected components containing dihept-$C_{70}H_6$.)

3. Multistage mass spectrometry

The multistage mass (MS/MS) data were obtained by the Bruker HCT ion trap instrument. In the experiment, only one ion with a particular m/z value of all is captured at a time by appropriately setting the parameters of the ion trap. The MS signal of m/z 846.0 was selected and subjected to collision-induced dissociation with Argon for obtaining the MS/MS spectrum of dihept-$C_{70}H_6$.

4. Crystallographic information

The purified dihept-$C_{70}H_6$ was dissolved in toluene and concentrated to form a saturated solution. Slow evaporation from a mixed solution of decapyrrylcorannulene (abbreviated as DPC)[2] and dihept-$C_{70}H_6$ (2:1 in volume) in toluene at low temperatures provided black block co-crystals of 2DPC{dihept-$C_{70}H_6$} suitable for single-crystal X-ray diffraction analysis. X-ray diffraction data were collected on an XtaLAB Synergy R diffractometer with Cu Kα (λ = 1.54184 Å) Rigaku

X-ray source. The data were processed using CrysAlis^{Pro3}.[3] The structure was solved by the intrinsic phasing method and refined using full-matrix least-squares based on F^2 with the programs SHELXT and SHELXL-2015[4] within OLEX2,[5] respectively. All the non-hydrogen atoms were refined anisotropically, while the positions of all the hydrogen atoms were generated and refined using a riding model. Olex2 was used to determine the void volume and estimate the number of electrons in this void, which was found to match 1 molecule of toluene per formula unit. The contribution of this disordered solvent molecule has been removed from the intensity data. The crystallographic data for dihept-$C_{70}H_6$ reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under the deposition number CCDC 2166694, which can be obtained free of charge from www.ccdc.cam.ac.uk/data request/cif.

The unit with DPC molecules and dihept-$C_{70}H_6$ molecules is shown in Figure S2. The toluene molecules in the unit are omitted for clarity. Crystallographic data and other details of 2DPC{dihept-$C_{70}H_6$} are listed in Table S1.

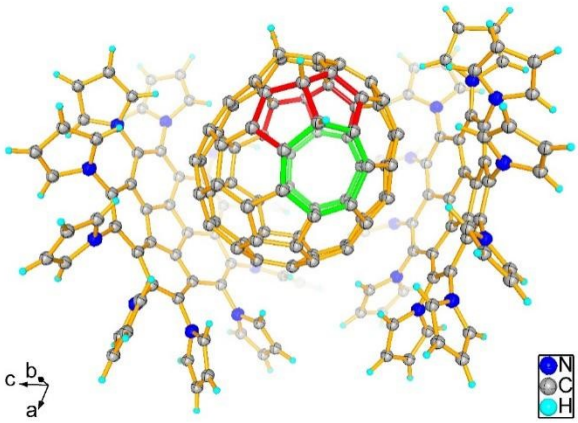

Figure S2. Dihept-$C_{70}H_6$ molecule and two co-crystallized DPC molecules in the unit. (C grey, H cyan, N navy blue). The fused pentagons are highlighted in red, and the heptagons are highlighted in green.

Table S1. Crystallographic data for dihept-$C_{70}H_6$.

	dihept-$C_{70}H_6$
Empirical formula	$C_{218}H_{118}N_{20}$
formula weight	3017.32
Temperature/K	100K
crystal system	triclinic
space group	P-1
***a*/Å**	14.8934(4)
***b*/Å**	17.2624(5)
***c*/Å**	30.2493(9)
***α*/deg**	78.553(3)
***β*/deg**	77.136(2)
***γ*/deg**	70.866(3)
Volume/Å^3	7096.1(4)
Z	2
ρ_{calc}/g·cm^{-3}	1.412
μ/mm^{-1}	0.652
***F* (000)**	3132
Crystal size/mm^3	0.2×0.1×0.1
Radiation	Cu Kα (λ = 1.54184)
***2ϑ* range/°**	5.47 to 122.338
parameters	2231
Index ranges	-16 ≤ h ≤ 14 -19 ≤ k ≤ 19 -34 ≤ l ≤ 34
Reflections collected	75997
Independent reflections	21720
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0809, wR_2 = 0.2139
Final R indexes [all data]	R_1 = 0.1265, wR_2 = 0.2474
$R1 = \Sigma\| \|Fo\|-\|Fc\| \|/ \Sigma\|Fo\|$, $wR2 = [\Sigma w(Fo^2-Fc^2)^2]/ \Sigma w(Fo^2)^2]^{1/2}$	

5. UV-Vis spectrum of dihept-$C_{70}H_6$

UV-Vis spectrum was recorded on a Cary 5000 UV-Vis-NIR spectrometer in toluene. As shown in Figure S3, the UV-Vis absorption spectrum of dihept-$C_{70}H_6$ was enlarged by 5 times and 10 times respectively, making the positions of the absorption peaks clear.

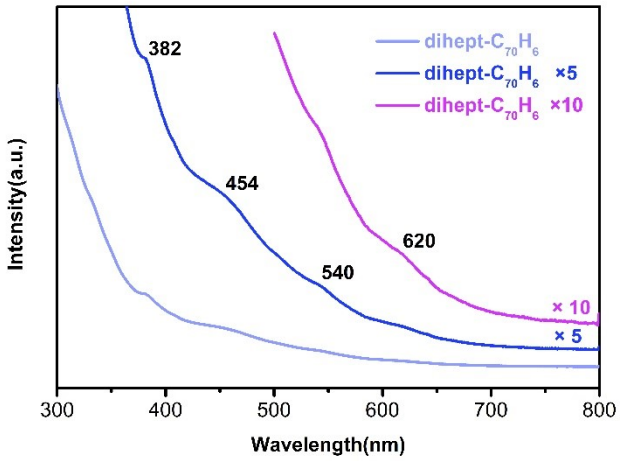

Figure S3. UV−Vis spectrum of the dihept-$C_{70}H_6$ in toluene.

6. Theoretical calculations

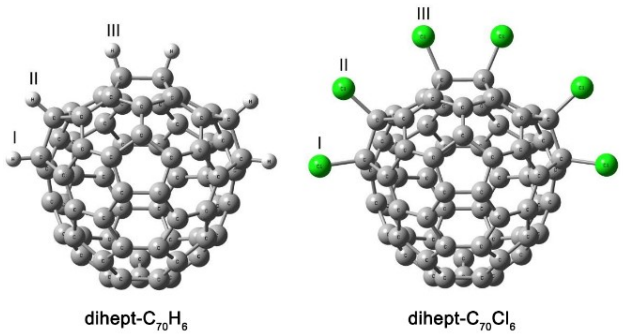

Figure S4. Three kinds of H/Cl groups in dihept-$C_{70}H_6$(left) and dihept-$C_{70}Cl_6$(right) optimized at B3LYP/6-31G(d,p) level on Gaussian 16 program[6].

Table S2. The orbital composition analysis results of both dihept-$C_{70}H_6$ and dihept-$C_{70}Cl_6$ are calculated by Hirshfeld method using build-in sphericalized atomic densities in free-states on Multiwfn program[7].

Dihept-$C_{70}H_6$	Fragment C_{70} (%)	Fragment 6H (%)	Dihept-$C_{70}Cl_6$	Fragment C_{70} (%)	Fragment 6Cl (%)
LUMO+1	99.006	0.994	LUMO+1	97.068	2.932
LUMO	99.556	0.444	LUMO	95.216	4.784
HOMO	98.794	1.206	HOMO	97.009	2.991
HOMO-1	98.166	1.834	HOMO-1	96.262	3.738

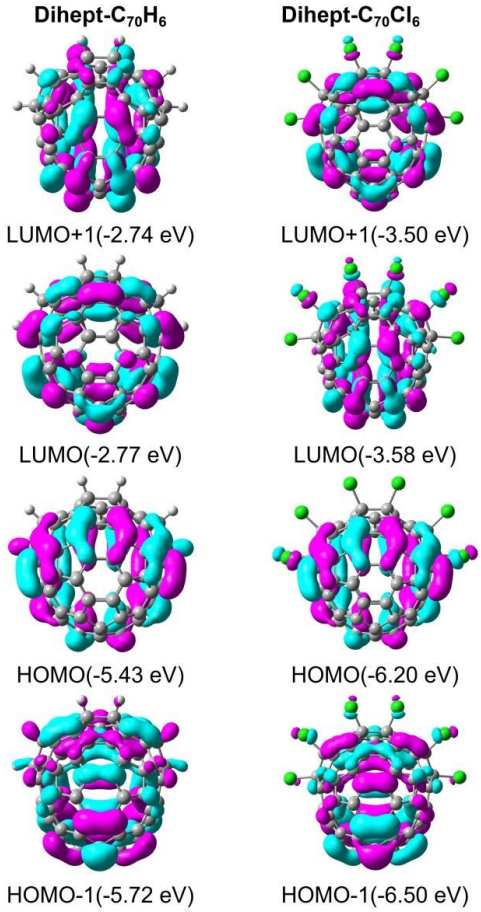

Figure S5. The molecular orbitals of dihept-$C_{70}H_6$ and dihept-$C_{70}Cl_6$ calculated at B3LYP/6-31G(d,p) level.

Table S3. Cartesian coordinates of optimized species at the B3LYP/6-31G(d,p) level.

Dihept-$C_{70}H_6$

C	3.5737640	1.1727740	-1.3084460	C	-3.9842280	-1.1741400	-0.0951080
C	2.8338430	0.7263130	2.6877980	C	-0.8231100	1.3951060	-3.2711910
C	3.9493500	0.0000010	-0.5915000	C	-1.0006530	2.5973650	-2.5077250
C	-2.3433620	-2.9637790	-0.5250260	C	-0.6164940	-1.4266050	3.4111240
C	3.2386010	-2.3086650	-0.6104660	C	0.5989330	-0.7012590	3.6660490
C	-2.2793570	2.5816030	-1.8669720	C	2.3493730	-3.3589040	-1.1936350
C	3.5737690	-1.1727620	-1.3084670	C	1.8884190	2.9807490	1.1938830
C	3.5527480	1.1584180	1.5298070	C	2.8338440	-0.7263530	2.6877890
C	3.0864090	-2.2660650	0.8152400	C	0.0139570	3.6168610	-0.4857950
C	-2.0873920	-0.6907700	-3.2080560	C	-1.1660110	-3.4104680	0.2144060
C	0.4344230	-0.7379100	-3.2891840	C	1.3889380	2.6810000	-2.1487640
C	-2.6318740	2.2596670	1.6769530	C	0.0814550	-3.1499390	-1.8498990
C	-2.3433630	2.9637820	-0.5249860	C	1.6859100	-1.4190980	3.0631170
C	1.5866960	-1.4638310	-2.7920060	C	3.5527470	-1.1584400	1.5297910
C	1.5866950	1.4638680	-2.7919920	C	3.2385980	2.3086700	-0.6104320

C	4.0092980	-0.0000050	0.8118850	C	-2.9934220	-1.4174300	-2.3352480
C	-3.8404130	0.7236860	-1.4682200	C	-3.5754920	-0.0000140	2.0241220
C	1.1525090	-2.5323460	2.2884330	C	0.0814610	3.1499680	-1.8498620
C	-1.8194000	0.7288610	3.3876710	C	-4.1200580	-0.0000060	0.7464700
C	3.0864090	2.2660550	0.8152740	C	1.3889370	-2.6809610	-2.1487980
C	1.1525100	2.5323130	2.2884690	C	-3.2331850	-2.2647360	0.3633110
C	-0.3269210	-2.5342280	2.5009790	C	0.4344300	0.7379590	-3.2891730
C	0.5989330	0.7012060	3.6660580	C	-2.8691270	1.1700950	2.5205830
C	-1.3352370	-2.9369190	1.6187110	C	0.0139560	-3.6168530	-0.4858470
C	-3.2331830	2.2647320	0.3633420	C	-1.3352340	2.9368950	1.6187520
C	-2.9934220	1.4174670	-2.3352290	C	1.8884190	-2.9807620	1.1938410
C	1.6859110	1.4190540	3.0631380	C	-2.6318770	-2.2596910	1.6769210
C	2.3493770	3.3589110	-1.1935980	C	1.4382980	-3.8545060	0.0156690
C	2.9668130	-0.7975280	-2.6715020	C	-3.8404120	-0.7236630	-1.4682310
C	2.9668110	0.7975670	-2.6714880	C	1.4382920	3.8545040	0.0157310
C	-2.0873930	0.6908190	-3.2080490	C	-2.2793540	-2.5815750	-1.8670080
C	-2.8691280	-1.1701280	2.5205650	H	1.5995460	-4.9169190	0.2365220
C	-1.0006570	-2.5973340	-2.5077600	H	2.8933210	-4.1872830	-1.6639690
C	-1.8194000	-0.7289090	3.3876610	H	3.5923390	-1.1420610	-3.5052100
C	-0.6164930	1.4265570	3.4111460	H	3.5923470	1.1421110	-3.5051860
C	-1.1660050	3.4104630	0.2144540	H	2.8933270	4.1873120	-1.6638900
C	-0.3269190	2.5341930	2.5010160	H	1.5995530	4.9169160	0.2365810
C	-3.9842270	1.1741420	-0.0950930				
C	-0.8231080	-1.3950540	-3.2712130				

Dihept-$C_{70}Cl_6$

Cl	-1.5373750	4.8275050	-1.4527930	C	-2.9620380	-2.4102560	-1.6061900
Cl	-5.6062980	0.5074540	1.2638710	C	1.4573540	2.1230350	-1.5892640
Cl	1.5363420	4.8277320	-1.4528500	C	-1.4577900	2.1227670	-1.5893080
Cl	-4.6642130	3.2170420	-0.0954750	C	1.1744040	-4.0440020	-2.0611120
Cl	4.6634840	3.2180820	-0.0955970	C	-1.3952980	0.2867630	-3.2142450
Cl	5.6062020	0.5084770	1.2639780	C	-2.5965090	-0.2508600	-2.6430460
C	-1.1704880	3.1007540	0.6788000	C	1.4263500	-2.8950280	2.6654190
C	-0.7261340	0.4550880	3.7609550	C	0.7011780	-1.9711180	3.4945970
C	-0.0003100	3.0701680	1.4848180	C	3.3483080	1.9899490	0.1650150
C	2.9625670	-2.4096500	-1.6061710	C	-2.9739360	0.3840640	1.9949070
C	2.3065950	2.4600390	1.1168480	C	0.7260410	0.4552400	3.7609660
C	-2.5796980	-1.6783660	-2.7317620	C	-3.6132540	-0.3935950	-0.3865770
C	1.1698640	3.1010060	0.6788130	C	3.4033630	-1.7649170	-0.3720760
C	-1.1578850	1.6581270	3.1200160	C	-2.6758210	1.6257810	-1.1316470
C	2.2656560	1.6142310	2.2696720	C	3.1510130	0.3536260	-1.5317630
C	0.6909110	-0.8373790	-3.7960000	C	1.4173660	-0.7268790	3.5132420
C	0.7365540	1.3838340	-2.6016950	C	1.1575470	1.6583690	3.1200300
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C	-0.0002510	2.4121330	2.7274680	C	-3.4029900	-1.7656040	-0.3720900
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C	2.5267550	-0.8030700	2.5716690	C	-1.1735480	-4.0442380	-2.0611220
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C	2.5325790	-2.1868830	2.0210270	C	-3.1510680	0.3529940	-1.5317850
C	-0.7007760	-1.9712630	3.4945920	C	0.0004820	-4.5847570	-1.4021710
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C	0.8154260	3.2700370	-0.7993480	C	-2.9343320	-2.6164370	0.7518030
C	-0.8160770	3.2698010	-0.7993290	C	2.9738450	0.3846750	1.9949140
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C	2.5965980	-0.2503320	-2.6430360	C	0.7238330	-3.2273910	-3.1747570
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C	-1.4257590	-2.8953210	2.6654150	C	2.5800710	-1.6778300	-2.7317450

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