Supporting Information for

Very Large, Soluble Endohedral Fullerenes in the Series La_2C_{90} to La_2C_{138}: Isolation and Crystallographic Characterization of a $La_2@D_5(450)$-C_{100}

Christine M. Beavers,[a] Hongxiao Jin,[b] Hua Yang,[b] Zhimin Wang,[b] Xinqing Wang,[b] Hongliang Ge,[b] Ziyang Liu,[b]* Brandon Q. Mercado,[c] Marilyn M. Olmstead,[c]* Alan L. Balch[c]*

[a] *Advanced Light Source, Lawrence Berkeley National Lab, One Cyclotron Rd, Berkeley, CA 94720. U.S.A. E-mail: cmbeavers@lbl.gov*

[b] *College of Materials Science and Engineering, China Jiliang University, Hangzhou 310027, China. E-mail: zyliu@cjlu.edu.cn*

[c] *Department of Chemistry, University of California, One Shields Avenue, Davis, CA, 95616. U. S. A. E-mail: mmolmstead@ucdavis.edu; albalch@ucdavis.edu; Fax +1 (530) 752 2820; Tel +1 (530) 752 0941*

Synthesis of the $La_2@C_{100}$. A 8 × 150 mm graphite rod filled with La_2O_3 and graphite powder (La:C atomic ratio 1:50) was vaporized as the anode in a DC arc discharge under optimized conditions. The raw soot was sonicated in *o*-dichlorobenzene for eight hours and then filtered with aid of vacuum. After removing the solvent with a rotary evaporator, chlorobenzene was added to re-dissolve the dry extract. The resulting solution was subjected to a four-stage HPLC isolation process without recycling. The first stage was carried out using a Buckyprep-M column with chlorobenzene mobile phase. The eluent in the range from 13.3 to 14.4 minutes, which is labeled as F in Figure SI-1, was collected. Fraction F was then subjected to the second stage of chromatography on a Buckyprep column with also chlorobenzene as the eluent, and the fraction S1 was collected, as shown in Figure SI-2. The fraction S1 was reinjected into the Buckyprep-M column for the third stage separation using toluene as the eluent. The main peak marked with shaded area, shown in Figure SI-3, was collected, and $La_2@C_{100}$ was finally obtained. The purity of the isolated $La_2@C_{100}$ isomer was also examined using LDI-TOF-MS. The Buckyprep and Buckyprep-M columns are 10mm in diameter and 250mm in length from Nacalai Tesque Inc.

Computations of hexa-anions of C_{100}.

The number of the IPR cages of C_{100} is 450, according to the spiral algorithm.[1] All geometries of the 450 cages were fully optimized using semiempirical molecular orbital method (AM1),[22] and density functional theory with the B3LYP density functional[3] together with 6-31G(d) basis set for carbon atoms. All calculations were carried out using the Gaussian 03 program package.[4] The inverse pentagon separation index (IPSI) for the tetra-anions were calculated based on the optimized geometries. In addition, the numbers of pyracyclenes of the above cages were enumerated using a small program written by ourselves. The results are drawn in the Figure SI-4 and SI-5, respectively.

1. Fowler, P. W.; Manolopoulous, D. E. *An Atlas of Fullerenes*, Clarendon, Oxford, 1995.
2. Dewar, M.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4499 .
3. (a) Becke, A. D. *Phys. Rev. A* 1988, 38, 3098; (b) Becke, A. D. *J. Chem. Phys.* 1993, 98, 5648;. (c) Lee, C., Yang, W., Parr, R. G., *Phys. Rev. B* 1988, 37, 785.
4. Complete citation for this software:
   Gaussian 03, Revision C.02. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

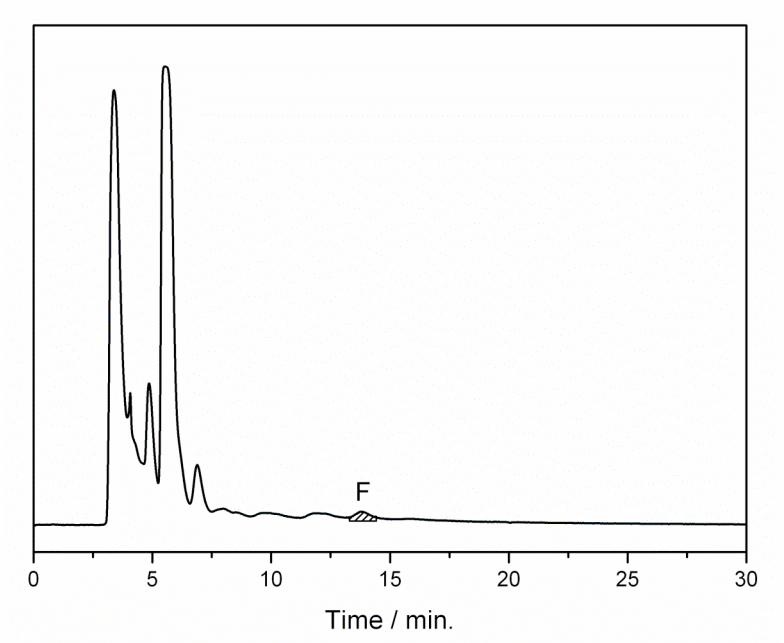

Figure SI-1. Chromatogram of the first stage using Buckprep-M column with chlorobenzene as eluent. The HPLC conditions were: flow rate 4.0 mL/min, detection wavelength of 450 nm.

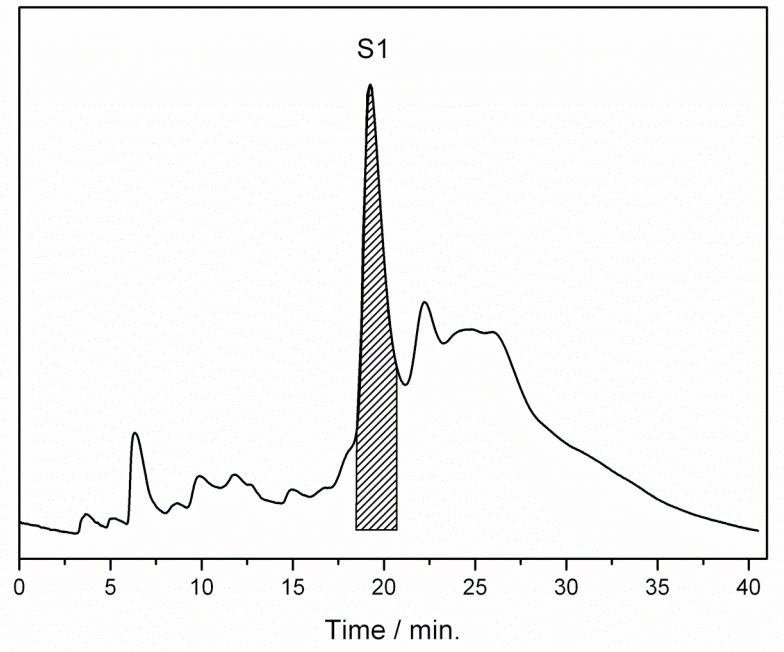

Figure SI-2. The second chromatogram of the F on a Buckyprep column with chlorobenzene as eluent. The HPLC conditions were: flow rate 4.0 mL/min, detection wavelength of 450nm.

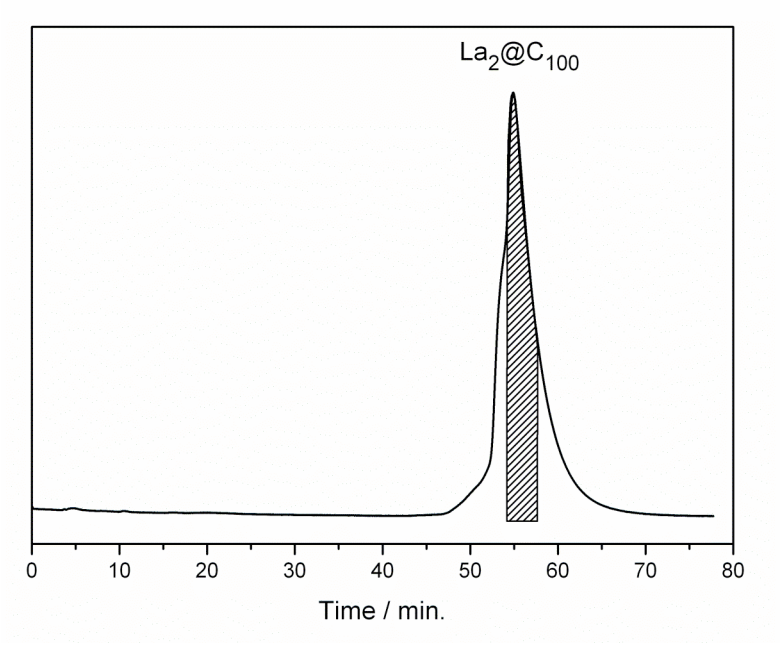

Figure SI-3 The third and fourth stage chromatogram of the $La_2@C_{100}$ isolation on a Buckyprep-M column. The HPLC conditions were: flow rate of toluene eluent 4.5 mL/min, detection wavelength of 450nm.

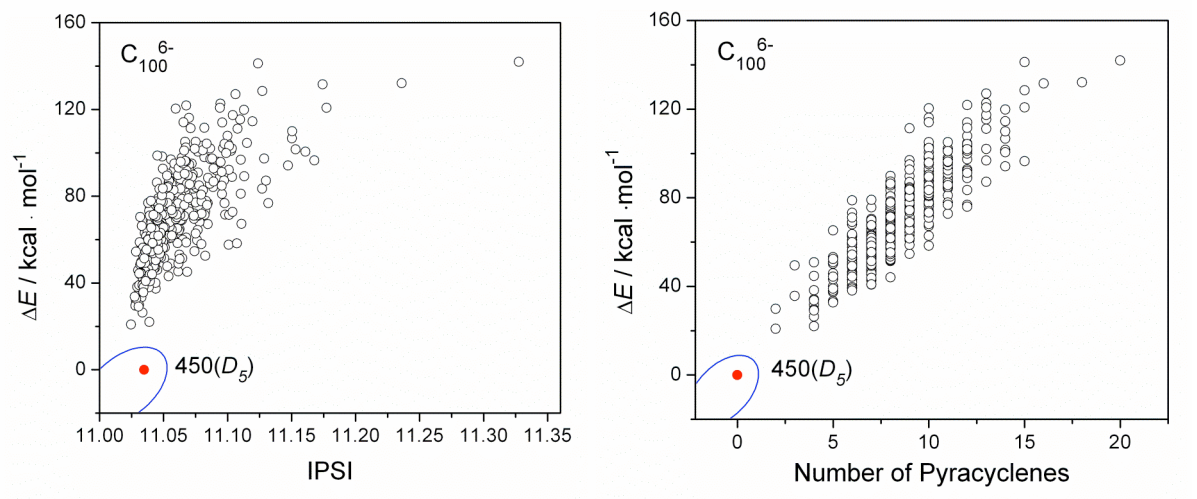

Figure SI-4 Correlations between relative stability of the fullerene hexa-anions and the IPSI, as well as the number of pyracyclene units in the IPR cages of C_{100}. The calculations were carried out at B3lyp/3-21g level. The isomer with a red mark was experimentally identified in this work. For more information on the IPSI see: Rodriguez-Fortea, A.; Alegret, N.; Balch, A. L.; Poblet, J. M. *Nature Chem.*, **2010**, *2*, 955-961.

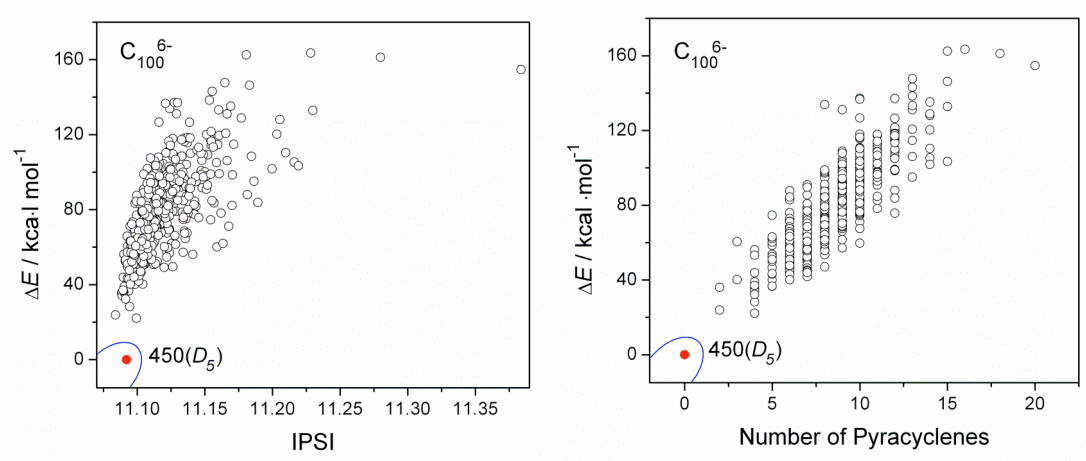

Figure SI-5 Correlations between relative stability of the fullerene hexa-anions and the IPSI, as well as the number of pyracyclene units in the IPR cages of C_{100}. The calculations were carried out at AM1 level. The isomer with a red mark was experimentally identified in this work.

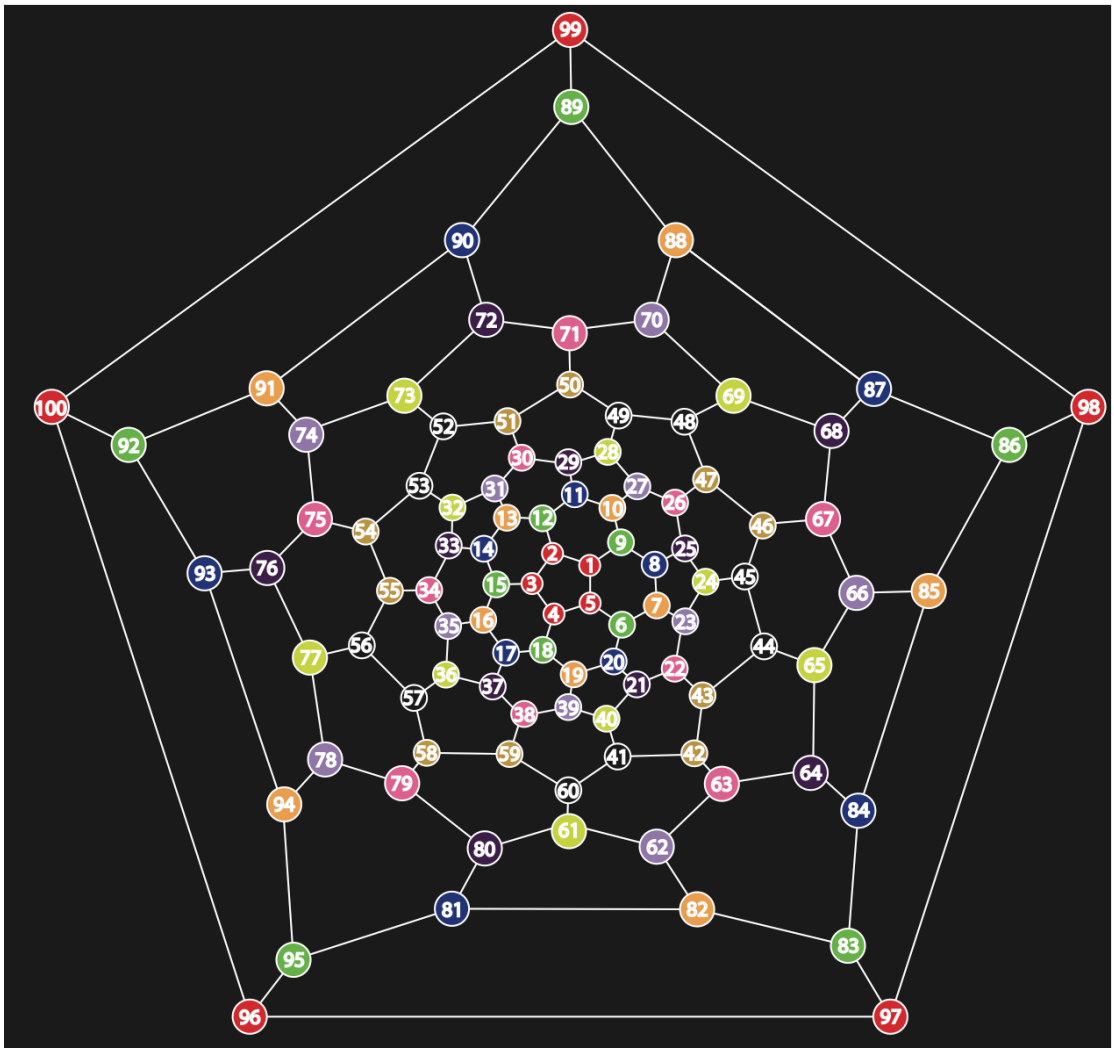

Figure SI-6 Schlegel diagram for D_5(450)-C_{100}.

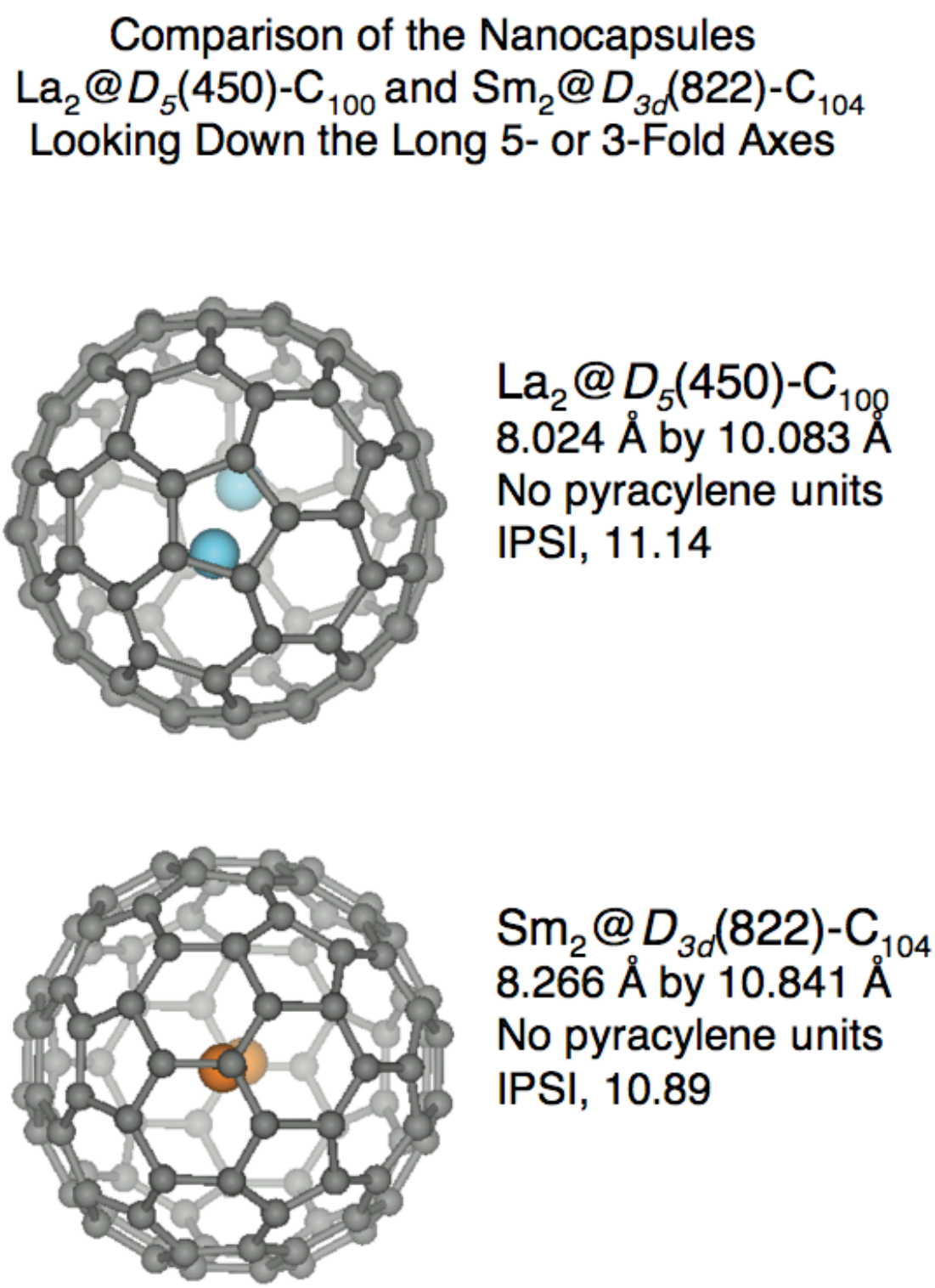

Figure SI-7 Comparison of the nanocapsules $La_2@D_5(450)$-C_{100} and $Sm_2@D_{3d}(822)$-C_{104} looking down the long 5- or 3-fold axes.