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Is the Isolated Pentagon Rule Always Satisfied for Metallic Carbide Endohedral Fullerenes?

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Supporting Information

ABSTRACT: Quantum-chemical calculations reveal that metallic carbide endohedral fullerene $Y_2C_2@C_{84}$ possesses a novel fullerene cage, C_1(51383)-C_{84}, with one pair of pentagon adjacencies. One of the encapsulated yttrium atoms is located on the adjacent pentagons, while the other stays on a hexagonal ring in the fullerene cage. As one of numerous metallic carbide endohedral fullerenes, $Y_2C_2@C_1$(51383)-C_{84} is the first example that violates the well-known isolated pentagon rule (IPR). More interestingly, compared with the fact that $Sc_2C_2@C_{84}$ has a conventional IPR-satisfying cage, D_{2d}(51591)-C_{84}, $Y_2C_2@C_{84}$ utilizes the novel fullerene cage C_1(51383)-C_{84} with one pair of pentagon adjacencies.

With an even number of sp^2-hybridized carbon atoms, fullerenes are spherical carbon cages that consist of exactly 12 pentagonal rings and a certain number of hexagonal rings.[1,2] The isolated pentagon rule (IPR),[3] which requires that each pentagonal ring in a fullerene cage is isolated only by five hexagonal rings, is successfully used to predict and investigate the structures of numerous empty fullerene cages.[4−6] Except a few novel fullerenes like C_{72},[7] the pristine non-IPR fullerenes with abutting pentagons are usually unstable and synthetically unattainable in experiments.[3] Fortunately, with encapsulating metal atoms or clusters inside, several non-IPR fullerene cages can be synthesized and extracted,[8,9] like $La@C_{72}$,[10] $Sc_2@C_{66}$,[11] and $Sc_3N@C_{68}$.[12] These fullerene derivates with metal atoms or clusters inside are commonly called endohedral metallofullerenes (EMFs).[13]

As one special type of EMFs, metallic carbide EMFs encapsulate a carbide moiety and several metal atoms, such as $Sc_2C_2@C_{84}$,[14] $Sc_3C_2@C_{80}$,[15] and $Sc_4C_2@C_{80}$.[16] Interestingly, even though numerous metallic carbide EMFs have been isolated and characterized, to the best of our knowledge, all of them obey the IPR.[14−17] The previously reported exception, $Sc_2C_2@C_{2v}$(6073)-C_{68}, is still disputable because the ^{13}C NMR chemical shifts of $Sc_2C_2@C_{2v}$(6073)-C_{68} do not match the experimental ones.[18] Furthermore, recent theoretical calculations revealed that dimetallofullerene $Sc_2@C_{70}$ is much more stable than $Sc_2C_2@C_{68}$, indicating that the isolated Sc_2C_{70} should be a conventional dimetallofullerene $Sc_2@C_{70}$ rather than the non-IPR metallic carbide EMF $Sc_2C_2@C_{68}$.[19] Consequently, an opening question is, can metallic carbide be encaged inside an unconventional fullerene cage violating the IPR? Herein we report the first IPR-violating metallic carbide endohedral fullerene through quantum-chemical calculations on $Y_2C_2@C_{84}$.

$Y_2C_2@C_{84}$ has been isolated very recently.[20] Although the ^{13}C NMR spectrum of $Y_2C_2@C_{84}$ has been provided, the cage structure has not be assigned because of the poor signal-to-noise ratio in the aromatic region.[20] There are totally 51592 classical C_{84} cage isomers, including 24 IPR-satisfying ones.[2] We have taken both IPR and non-IPR isomers with the number of fused pentagons less than three into consideration. Extensive semiempirical calculations on the tetraanions of these isomers were performed at the AM1[21] level because metallic carbide transfers four electrons to fullerene cages formally.[17,22] $Y_2C_2@C_{84}$ were optimized at the B3LYP[23] level of theory with the 6-31G(d) basis set for carbon atoms and the Lanl2dz[24] basis set with the corresponding effective core potential for yttrium atoms. With employing the gauge-independent atomic orbital method, ^{13}C NMR chemical shifts were evaluated at the B3LYP/6-311G(d)−Lanl2dz level.[25] Theoretical chemical shift values have been calibrated to the observed C_{60} line (142.5 ppm).[26] All quantum-chemical calculations were carried out using the *Gaussian 03* program.[27]

Even though an IPR structure, $Y_2C_2@D_{2d}$(51591)-C_{84}, has the lowest energy among all of the $Y_2C_2@C_{84}$ isomers, we successfully find a stable non-IPR structure, $Y_2C_2@C_1$(51383)-C_{84} which is only 4.9 kcal/mol in energy higher than the lowest energy structure. $Y_2C_2@D_{2d}$(51591)-C_{84} and $Y_2C_2@C_1$(51383)-C_{84} are shown in Figures 1 and 2, respectively. $Y_2C_2@C_1$(51383)-C_{84} has one pair of pentagon adjacencies. In $Y_2C_2@C_1$(51383)-C_{84}, one metal atom is located upon the pentagon adjacencies, which is frequently seen in non-IPR endohedral fullerenes. The other metal atom stays on a hexagonal ring. It is worth noting that $Sc_2C_2@C_{84}$, which is the first metallic carbide endohedral fullerene found in the experiment, also utilizes the D_{2d}(51591)-C_{84} cage.[14]

Because endohedral fullerene formation always occurs in a high-temperature region from 500 to 3000 K, the thermodynamic stabilities of endohedral fullerene isomers rather than their relative energies is the key factor in determining which isomer can be obtained in experiments.[28] Thus, relative concentrations, which reflect the thermodynamic stabilities of $Y_2C_2@C_{84}$ isomers, have been evaluated. As shown in Figure 3, even though $Y_2C_2@D_{2d}$(51591)-C_{84} is overwhelming at low

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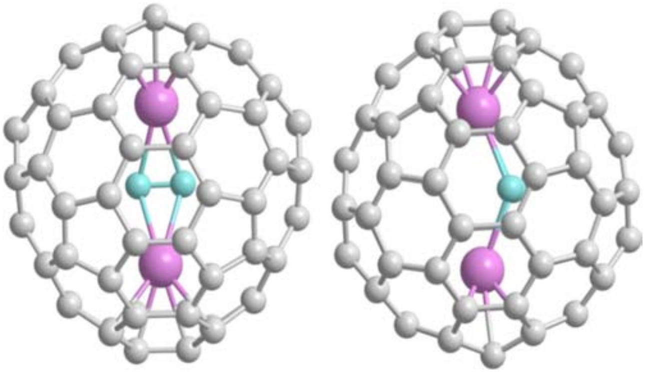

Figure 1. Top (left) and side (right) views of $Y_2C_2@D_{2d}(51591)\text{-}C_{84}$.

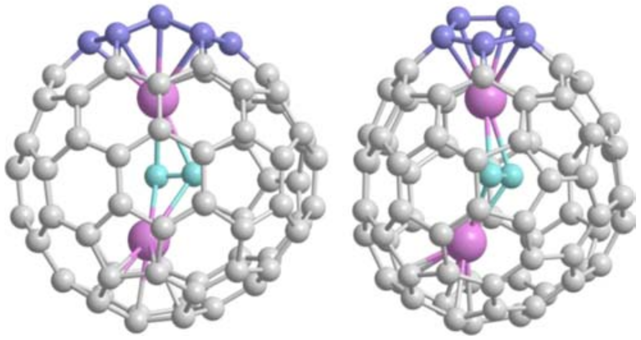

Figure 2. Top (left) and side (right) views of $Y_2C_2@C_1(51383)\text{-}C_{84}$.

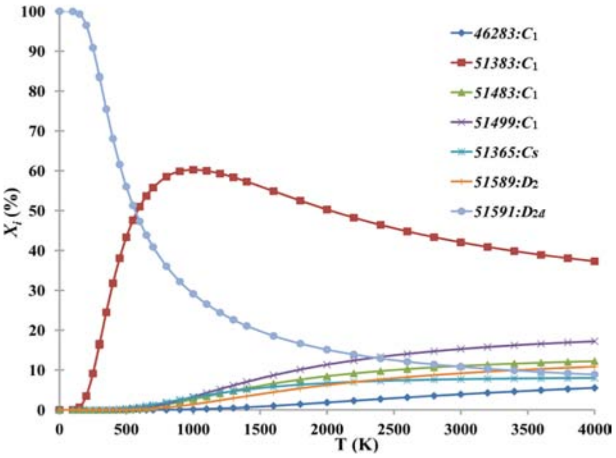

Figure 3. Relative concentrations of $Y_2C_2@C_{84}$ isomers.

temperatures, the relative concentration of $Y_2C_2@C_1(51383)\text{-}C_{84}$ increases rapidly as the temperature rises. Interestingly, the relative concentration of $Y_2C_2@C_1(51383)\text{-}C_{84}$ surpasses $Y_2C_2@D_{2d}(51591)\text{-}C_{84}$ at 570 K and reaches its maximum with 60.5% at 1050 K. Even when the temperature increases up to 4000 K, $Y_2C_2@C_1(51383)\text{-}C_{84}$ still has the highest relative concentration. Therefore, $Y_2C_2@C_1(51383)\text{-}C_{84}$ should be the isomer obtained in Dorn's experiment. This is the first metallic carbide endohedral fullerene that violates the IPR.

Compared with other C_{84}-based EMFs, $Y_2C_2@C_1(51383)\text{-}C_{84}$ is special and interesting. The major isomers of divalent mono-EMFs $M@C_{84}$ (M = Ca, Sm, and Yb) all possess the IPR-obeying cages $C_2(51581)$, $C_1(51580)$, and $C_2(51579)$,[29] even though there are 51592 total classical C_{84} cage isomers. Likewise, the non-IPR $C_s(51365)\text{-}C_{84}$ cage is adopted by all trimetallic nitride EMFs $Gd_3N@C_{84}$, $Tb_3N@C_{84}$, and $Tm_3N@C_{84}$.[30] Fascinatingly, the situation of metallic carbide EMFs is obviously different. $Sc_2C_2@C_{84}$ bears a conventional IPR cage, $D_{2d}(51591)$,[14] which is also the most abundant isomer of pristine C_{84}. In contrast, when scandium is changed to yttrium, the novel IPR-violating $C_1(51383)\text{-}C_{84}$ becomes the best host for the metallic carbide Y_2C_2. The high thermodynamic stability of $Y_2C_2@C_1(51383)\text{-}C_{84}$ seems to be a key factor in determining the successful isolation of this special endohedral fullerene.

The main frontier molecular orbital diagram of $Y_2C_2@C_1(51383)\text{-}C_{84}$ has been presented in Figure 4. It is revealed that the metallic carbide cluster transfers four electrons to the fullerene cage, leading to a formal valence structure of $[M_2]^{6+}[C_2]^{2-}@[C_{2n}]^{4-}$, in agreement with previous theoretical studies.[17,22] The highest occupied molecular orbital (HOMO) is fully occupied by the orbital from the C_{84}^{4-} cage. In contrast, the lowest unoccupied molecular orbital (LUMO) is derived mainly from the cage orbital with minor contribution from the encaged metal cluster. Because the frontier molecular orbitals (HOMO−1, HOMO, LUMO, and LUMO+1) are mainly contributed by the cage orbitals, the electrochemical redox reactions will mainly take place on the fullerene cage. More importantly, the large HOMO−LUMO gap (1.70 eV) suggests that $Y_2C_2@C_1(51383)\text{-}C_{84}$ has high kinetic stability.

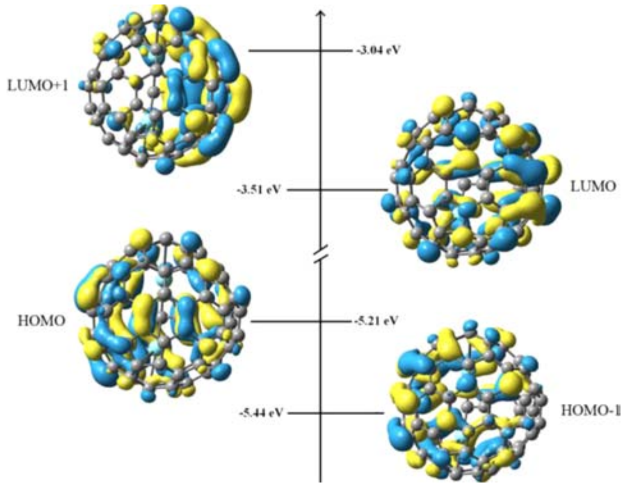

Figure 4. Main frontier molecular orbitals of $Y_2C_2@C_{84}$.

Because the [5,5]-carbon atoms of pentagon adjacencies are highly pyramidalized, they will display highly deshielded ^{13}C NMR resonances.[20] Our theoretical calculations at B3LYP/6-311G(d)−Lanl2dz level of theory predicted that two [5,5]-carbon atoms in $Y_2C_2@C_1(51383)\text{-}C_{84}$ exhibit two signals at 160.2 and 161.6 ppm, respectively, in very good conformity with the experimental values of 160.6 and 161.7 ppm.[20] On the contrary, according to its C_s symmetry, there are only 44 signals (42 full-intensity lines and 2 half-intensity lines) in the ^{13}C NMR spectrum of $Y_2C_2@D_{2d}(51591)\text{-}C_{84}$. Since more than 70 separate spectral lines were detected in the experimental ^{13}C NMR spectrum, $Y_2C_2@C_1(51383)\text{-}C_{84}$ is the more reasonable candidate in the experiment than $Y_2C_2@D_{2d}(51591)\text{-}C_{84}$. The simulated UV−vis−near-IR (NIR) spectrum of $Y_2C_2@C_1(51383)\text{-}C_{84}$ is rather featureless with two weak absorption bands (500−600 and 630−750 nm), in agreement with the experimental UV−vis spectrum of $Y_2C_2@C_{84}$. All of the calculated ^{13}C NMR chemical shifts and the UV−vis−NIR spectrum can be obtained in the Supporting Information.

In summary, the first violation of the IPR in metallic carbide endohedral fullerenes, $Y_2C_2@C_1(51383)$-C_{84}, has been disclosed with quantum-chemical calculations. Compared with $Sc_2C_2@C_{84}$ having the conventional IPR-satisfying cage $D_{2d}(51591)$-C_{84}, $Y_2C_2@C_{84}$ utilizes the novel fullerene cage $C_1(51383)$-C_{84}, which has one pair of pentagon adjacencies.

■ ASSOCIATED CONTENT

Supporting Information

Relative energies of tetraanions and $Y_2C_2@C_{84}$, Cartesian coordinates, ^{13}C NMR chemical shifts and UV−vis−NIR spectrum of $Y_2C_2@C_{84}$, and the full reference of ref 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kroto, H. W.; Heath, J. R.; Obrien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Fowler, P. W.; Manoloupoulos, D. E. *An Atlas of Fullerenes*; Oxford University Press: Oxford, U.K., 1995.

(3) Kroto, H. W. *Nature* **1987**, *329*, 529.

(4) Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. *Nature* **1991**, *353*, 149.

(5) Diederich, F.; Whetten, R. L.; Thilgen, C.; Errl, R.; Chao, I.; Alvarez, M. M. *Science* **1991**, *254*, 1768.

(6) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142.

(7) Kobayashi, K.; Nagase, S.; Yoshida, M.; Osawa, E. *J. Am. Chem. Soc.* **1997**, *119*, 12693.

(8) Popov, A. A.; Dunsch, L. *J. Am. Chem. Soc.* **2007**, *129*, 11835.

(9) Rodíguez-Fortea, A.; Alegret, N.; Balch, A. L.; Poblet, J. M. *Nat. Chem.* **2010**, *2*, 955.

(10) Wakahara, T.; Nikawa, H.; Kikuchi, T.; Nakahodo, T.; Rahman, G. M. A.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Yamamoto, K.; Mizorogi, N.; Slanina, Z.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 14228.

(11) Wang, C.-R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Nature* **2000**, *408*, 426.

(12) Stevenson, S.; Fowler, P. W.; Heine, T. J.; Duchamp, C.; Rice, G.; Glass, T.; Harich, K.; Hajdu, E.; Bible, R.; Dorn, H. C. *Nature* **2000**, *408*, 428.

(13) (a) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843. (b) Akasaka, T.; Nagase, S. *Endofullerenes: A New Family of Carbon Clusters*; Kluwer: Dordrecht, The Netherlands, 2002; (c) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514. (d) Akasaka, T.; Wudl, F.; Nagase, S. *Chemistry of Nanocarbons*; Wiley-Blackwell: London, 2010. (e) Rodíguez-Fortea, A.; Balch, A. L.; Poblet, J. M. *Chem. Soc. Rev.* **2011**, *40*, 3551.

(14) Wang, C.-R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 397.

(15) Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; Liu, M. T. H.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 12500.

(16) Wang, T.-S.; Chen, N.; Xiang, J.-F.; Li, B.; Wu, J.-Y.; Xu, W.; Jiang, L.; Tan, K.; Shu, C.-Y.; Lu, X.; Wang, C.-R. *J. Am. Chem. Soc.* **2009**, *131*, 16646.

(17) (a) Inoue, T.; Tomiyama, T.; Sugai, T.; Okasaki, T.; Suematsu, T.; Fujii, N.; Utsumi, H.; Nojima, K.; Shinohara, H. *J. Phys. Chem. B* **2004**, *108*, 7573. (b) Tan, K.; Lu, X. *Chem. Commun.* **2005**, 4444. (c) Iiduka, Y.; Wakahara, T.; Nakajima, K.; Tsuchiya, T.; Nakahodo, T.; Maeda, Y.; Akasaka, T.; Mizorogi, N.; Nagase, S. *Chem. Commun.* **2006**, 2057. (d) Iiduka, Y.; Wakahara, T.; Nakajima, K.; Nakahodo, T.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Liu, M. T. H.; Mizorogi, N.; Nagase, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5562. (e) Yang, H.; Lu, C.; Liu, Z.; Jin, H.; Che, Y.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 17296. (f) Lu, X.; Nakajima, K.; Iiduka, Y.; Nikawa, H.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *J. Am. Chem. Soc.* **2011**, *133*, 19553. (g) Kurihara, H.; Lu, X.; Iiduka, Y.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Akasaka, T.; Nagase, S. *J. Am. Chem. Soc.* **2011**, *133*, 2382. (h) Lu, X.; Nakajima, K.; Iiduka, Y.; Nikawa, H.; Tsuchiya, T.; Mizorogi, N.; Slanina, Z.; Nagase, S.; Akasaka, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 5889.

(18) Shi, Z.-Q.; Wu, X.; Wang, C.-R.; Lu, X.; Shinohara, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 2107.

(19) Zheng, H.; Zhao, X.; Wang, W. W.; Yang, T.; Nagase, S. *J. Chem. Phys.* **2012**, *137*, 014308.

(20) Zhang, J.; Fuhrer, T.; Fu, W.; Ge, J.; Bearden, D. W.; Dallas, J.; Duchamp, J.; Walker, K.; Champion, H.; Azurmendi, H.; Harich, K.; Dorn, H. C. *J. Am. Chem. Soc.* **2012**, *134*, 8487.

(21) Dewar, M. J. S.; Zoebisch, E.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(22) Valencia, R.; Rodríguez-Fortea, A.; Poblet, J. M. *J. Phys. Chem. A* **2008**, *112*, 4550.

(23) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **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.

(24) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(25) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(26) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

(27) Frisch, M. J.; et al. *Gaussian 03*, revision E.01. See the Supporting Information for the full reference.

(28) (a) Yang, T.; Zhao, X.; Xu, Q.; Zhou, C.; He, L.; Nagase, S. *J. Mater. Chem.* **2011**, *21*, 12206. (b) Zhao, X.; Gao, W.-Y.; Yang, T.; Zheng, J.-J.; Li, L.-S.; He, L.; Cao, R.-J.; Nagase, S. *Inorg. Chem.* **2012**, *51*, 2039. (c) Yang, T.; Zhao, X.; Nagase, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5034.

(29) (a) Xu, Z. D.; Nakane, T.; Shinohara, H. *J. Am. Chem. Soc.* **1996**, *118*, 11309. (b) Lu, X.; Slanina, Z.; Akasaka, T.; Tsuchiya, T.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2010**, *132*, 5896. (c) Yang, H.; Yu, M.; Jin, H.; Liu, Z.; Yao, M.; Liu, B.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2012**, *134*, 5331.

(30) (a) Beavers, C. M.; Zuo, T.; Duchamp, J. C.; Harich, K.; Dorn, H. C.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 11352. (b) Zuo, T.; Walker, K.; Olmstead, M. M.; Melin, F.; Holloway, B. C.; Echegoyen, L.; Dorn, H. C.; Chaur, M. N.; Chancellor, C. J.; Beavers, C. M.; Balch, A. L.; Athans, A. J. *Chem. Commun.* **2008**, 1067.