Electronic Supplementary Information

Crystallographic Evidence and Spin Activation for the Russian-Doll-Type Metallofullerene $Sc_4C_2@C_{80}$

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Experimental methods

Synthesis and characterization. $Sc_4C_2@C_{80}$ metallofullerenes were synthesized and purified as-reported method.¹

Single-crystal X-ray Diffraction. Black block cocrystals of $Sc_4C_2(a)I_h(7)$ - $C_{80}{\cdot}Ni^{II}(OEP){\cdot}CS_2$ were obtained by slow diffusion of a toluene solution of $Ni^{II}(OEP)$ (1 mg/mL, 2 mL) into a CS₂ solution of Sc₄C₂@C₈₀ (1 mg/mL, 1 mL). X-ray diffraction data were collected at 100 K using a diffractometer (Rigaku Saturn724+) equipped with a CCD collector. Multi-scan method was used for absorption correction. The structure was resolved using direct methods (SIR2004)² and refined on F^2 anisotropically by full-matrix least-squares using SHELXL2014³ within the WinGX package.⁴ To construct the I_h-C₈₀ fullerene cage, FLAT and SADI DFIX commands were used for regulating the five-member rings, as suggested by previous publications.^{5, 6} In addition, the (5,6) and (6,6) bond lengths were defined by DFIX commands according to the previously established bond lengths.^{7, 8} The cage carbons were anisotropic with SIMU or EADP command. The disordered endohedral C sites (i.e., C101 and C102 sites) were freely refined in the beginning. In the final refinement, they were assigned to the major and minor cages, respectively, according to their comparable occupancies. All Sc sites (i.e., Sc1-17) were freely refined including their occupancies and anisotropic with SIMU command. There are still some unresolved electron densities inside the fullerene cage due to the highly disordered Sc atoms. So, the sum of the occupancies of all Sc sites is less than 4, which is comparable to the previous reports where the endohedral atoms are highly disordered.^{9, 10} Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. In addition, there are

highly disordered solvent molecules, which are removed from the formula unit by the SQUEEZE in Platon package. The SQUEEZE results including the data for all voids in the unit cell are attached in the end of cif file, which include a mixture of toluene (50 electrons) and CS_2 (38 electrons). As the obtained cocrystal is slightly twinned, the TwinRotMat in Platon was used to generate HKLF5 file, which was further refined. CCDC 2012882 contains the supplementary crystallographic data.

Crystallographic data and structure refinement parameters for "Sc4C2 C80, Ni N₄ C₃₆ H₄₄, CS₂": Mr =1832.28, 0.06×0.10×0.15 mm³, triclinic, P-1, a = 14.5681(4), b = 14.6511(5), c = 19.9842(6), $a = 83.154(3)^{\circ}$, $\beta = 84.459(2)^{\circ}$, $\gamma = 61.176(3)^{\circ}$, $V = 3706.6(2)^{\circ}$ Å³, Z = 2, $\rho_{calcd} = 1.642$ g cm⁻³, μ (MoK_a) = 0.720 mm⁻¹, $\theta = 1.858\sim27.498$, T = 100(2) K, $R_1 = 0.1300$, $wR_2 = 0.3366$ for all data; $R_1 = 0.1158$, $wR_1 = 0.3217$ for 16934 reflections (I> 2.0 σ (I)) with 1574 parameters. Goodness of fit indicator 1.041.



Figure S1. X-ray structure of $Sc_4C_2@I_h(7)-C_{80} \cdot Ni^{II}(OEP)$, with major cage orientation, major C_2 moiety and all disordered Sc sites. Solvent molecules are omitted for clarity. Note: Among all disordered Sc sites, Sc1-8 sites with major occupancies ranging from 0.487(3) to 0.3013(3) are in first priority, which have been considered in the manuscript for building X-ray model. As other Sc sites (Sc9-17) have much lower occupancies of 0.212(4)-0.060(3), they shall be considered with less priority and not discussed in the text. Nevertheless, the presence of multiple Sc sites with small occupancies indicates almost free rotation of the Sc₄C₂ cluster inside the I_h -C₈₀ cage.



Figure S2. (a) X-ray structure of $Sc_4C_2@I_h(7)-C_{80}$ ·Ni^{II}(OEP), with only minor cage orientation and minor Sc_4C_2 . Solvent molecules are omitted for clarity. (b) An orthogonal view of the minor Sc_4C_2 cluster with C-C and Sc-C distances. Green for Sc and pink for endohedral C₂ moiety.



Figure S3. Orthogonal views of (a) major cage containing major Sc_4C_2 cluster and (b) minor cage containing minor Sc_4C_2 cluster, showing comparable cluster position relative to the I_h - C_{80} cage. Green for Sc and pink for endohedral C_2 moiety.



Figure S4. An orthogonal view of the (a) major and (b) minor Sc_4C_2 cluster with C-C and Sc-C distances. Green for Sc and pink for endohedral C_2 moiety.



Figure S5. The positive-ion MALDI-TOF mass spectrum of $Sc_4C_2@C_{80}$.



Figure S6. CV spectrum of Ferrocene (Fc) in *o*-DCB solution (as internal standard). The electrolyte was 0.1 M TBAPF₆, scan rate was 100 mV s⁻¹.

1. T.-S. Wang, N. Chen, J.-F. Xiang, B. Li, J.-Y. Wu, W. Xu, L. Jiang, K. Tan, C.-Y. Shu, X. Lu and C.-R.

Wang, J. Am. Chem. Soc., 2009, 131, 16646-16647.

- M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, 38, 381-388.
- 3. G. M. Sheldrick, Acta Crystallogr. C Struct. Chem., 2015, 71, 3-8.
- 4. L. J. Farrugia, J. Appl. Crystallogr., 2012, 45, 849-854.
- B. Q. Mercado, M. M. Olmstead, C. M. Beavers, M. L. Easterling, S. Stevenson, M. A. Mackey, C. E. Coumbe, J. D. Phillips, J. P. Phillips, J. M. Poblet and A. L. Balch, *Chem. Commun.*, 2010, 46, 279-281.
- Y. Zhang, K. B. Ghiassi, Q. Deng, N. A. Samoylova, M. M. Olmstead, A. L. Balch and A. A. Popov, Angew. Chem. Int. Ed., 2015, 54, 495-499.
- S. Stevenson, H. M. Lee, M. M. Olmstead, C. Kozikowski, P. Stevenson and A. L. Balch, *Chem. A Eur. J.*, 2002, 8, 4528-4535.
- H. Kurihara, X. Lu, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase and T. Akasaka, J. Am. Chem. Soc., 2012, 134, 3139-3144.
- B. Q. Mercado, M. A. Stuart, M. A. Mackey, J. E. Pickens, B. S. Confait, S. Stevenson, M. L. Easterling, R. Valencia, A. Rodríguez-Fortea, J. M. Poblet, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 2010, 132, 12098-12105.
- N. Chen, C. M. Beavers, M. Mulet-Gas, A. Rodríguez-Fortea, E. J. Munoz, Y.-Y. Li, M. M. Olmstead, A. L. Balch, J. M. Poblet and L. Echegoyen, *J. Am. Chem. Soc.*, 2012, **134**, 7851-7860.