Supporting Information of

$W(CO)_3(Ph_2PC_2H_4PPh_2)(\eta^2\text{-}Sc_3N@I_h\text{-}C_{80}/Sc_3N@D_{5h}\text{-}C_{80})$: Regioselective synthesis and crystallographic characterization of air-stable mononuclear complexes of endohedral fullerenes

Lipiao Bao,[a] Bin Liu,[b] Xiaofang Li,[b] Changwang Pan,[a] Yunpeng Xie,[a] and Xing Lu*[a]

[a]State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China.

[b]Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201 China.

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Section 1: General reagents and instruments

All commercial reagents were used without further purification except toluene which was freshly distilled before use. $W(CO)_4(Ph_2PC_2H_4PPh_2)$ (**1**) was synthesized according to the literature.[S1] $Sc_3N@I_h\text{-}C_{80}$ and $Sc_3N@D_{5h}\text{-}C_{80}$ were produced with a home-made arc-discharge furnace and were isolated with high-performance liquid chromatography (HPLC). The reaction process was monitored with analytical HPLC (FL2200, Zhejiang Fuli Analytical Instruments Co. Ltd.) equipped with an analytical 5PYE column (ø4.6×250 mm) and the separation was conducted on a preparative HPLC machine (LC-908; Japan Analytical Industry Co. Ltd.) equipped with a preparative Buckyprep column (ø20×250 mm) with toluene as the eluent. IR spectra were recorded on a Bruker VERTEX 70 spectrometer. The Vis-NIR experiments were carried out on a PE Lambda 750S UV-vis-NIR spectrophotometer. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were measured in 1,2-dichlorobenzene with 0.1 M of $(n\text{-}Bu)_4NPF_6$ as supporting electrolyte at a Pt working electrode with a CHI660E workstation. Crystal data of **2a** and **2b** was collected at 100 K using the radiation wavelength at 0.82653 Å with an ADSC q315 CCD detector at beamline BL17U1 of the Shanghai Synchrotron Radiation Facility (China). Multi-scan method was used for absorption corrections. The structures were solved with direct method and were refined with SHELXL-2014.[S2]

Section 2: Packing structure of 2a and 2b

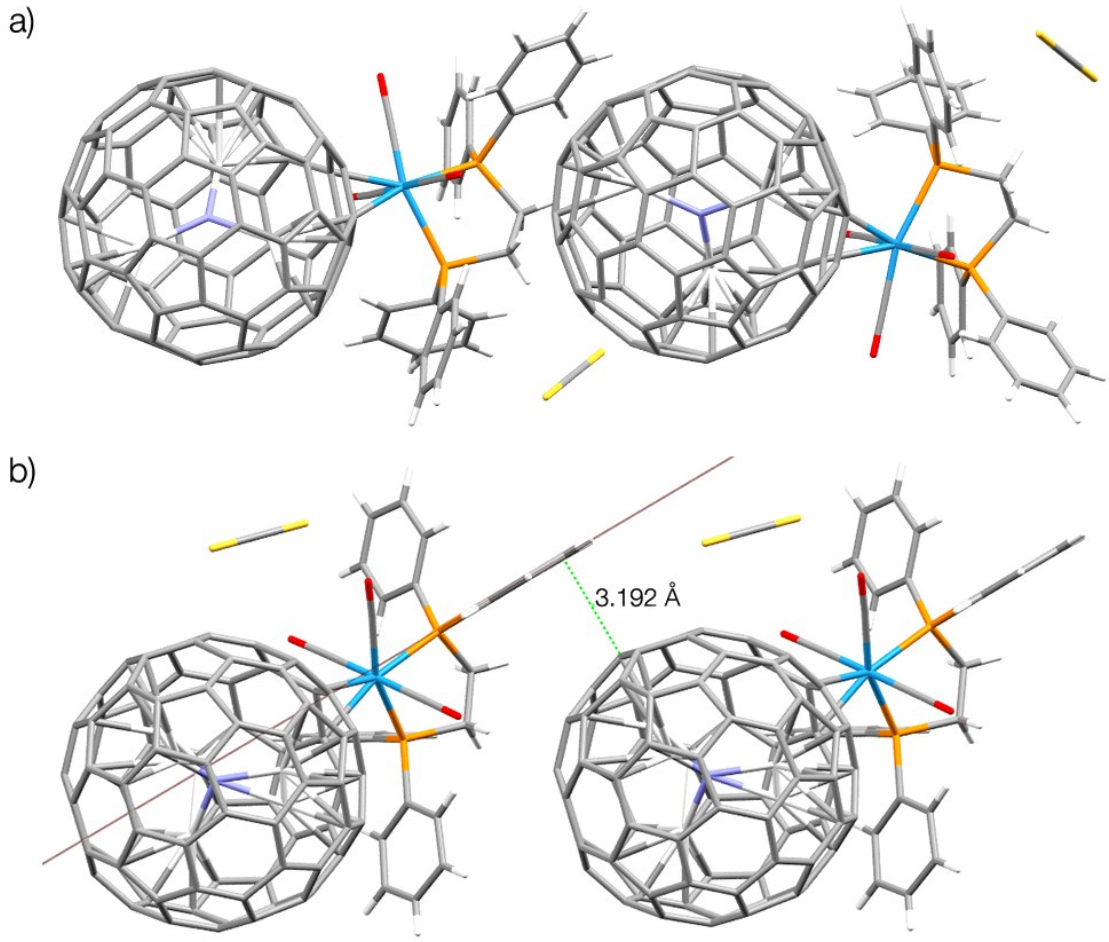

Fig. S1 Drawing showing the packing structure of a) **2a** and b) **2b**. The number in the figure shows the closest distance (Å) between the plane of one exohedral phenyl ring of one molecule and the closest carbon atom of the other fullerene cage.

Section 3: CV and DPV curves of 2a and 2b

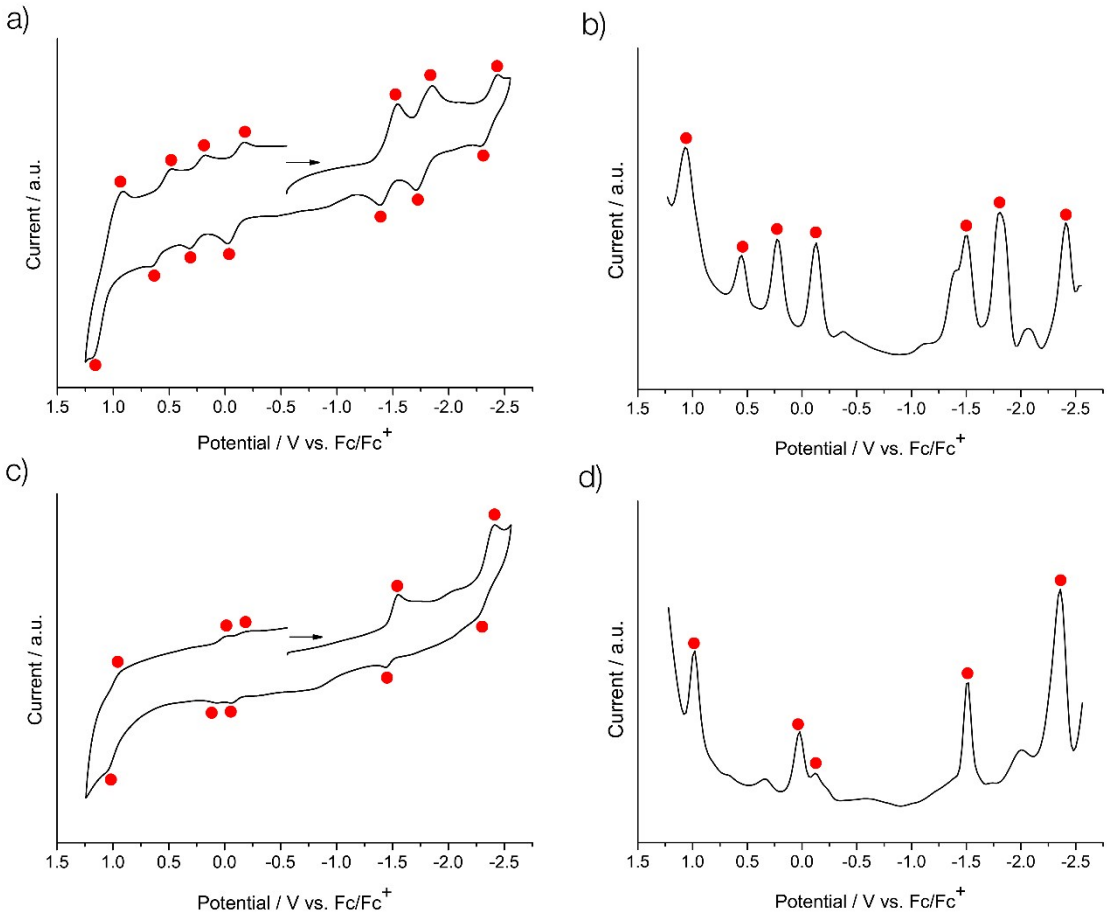

Fig. S2 CV curves of a) **2a** and c) **2b**. DPV curves of b) **2a** and d) **2b**. Conditions: working electrode, Pt disc; counter electrode, Pt wire; reference electrode, Ag wire; supporting electrolyte, 0.1 M *n*-Bu_4NPF_6 in 1,2-dichlorobenzene. Scan rate of CV: 20 mV/s. Conditions of DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms.

REFERENCES

(S1) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13* (5), 1095.

(S2) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64* (1), 112.