

Supporting Information

MS#:

MS Title: Positional Control of Encapsulated Atoms inside Fullerene Cage by Exohedral Addition

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Complete ref. 6

Yamada, M.; Feng, L.; Wakahara, T.; Tsuchiya, T.; Maeda, Y.; Lian, Y.; Kako, M.; Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S. *J. Phys. Chem. B* **2005**, *109*, 6049.

Complete ref. 12

Wakahara, T.; Kobayashi, J.; Yamada, M.; Maeda, Y.; Tsuchiya, T.; Okamura, M.; Akasaka, T.; Waelchli, M.; Kobayashi, K.; Nagase, S.; Kato, T.; Kako, M.; Yamamoto, K.; Kadish, K. *M. J. Am. Chem. Soc.* **2004**, *126*, 4883–4887.

Materials and Methods

Toluene was distilled over benzophenone sodium ketyl under argon atmosphere prior to use for the reactions. 1,2-dichlorobenzene was distilled over P₂O₅ under vacuum prior to use. CS₂ was distilled over P₂O₅ under argon atmosphere prior to use. HPLC isolation was performed on a LC-918 (Japan Analytical Industry Co., Ltd.). Toluene was used as the eluent and the eluants were monitored by UV absorption at 330 nm. Mass spectrometry was performed on a Bruker BIFLEX III with 9-nitroanthracene as matrix. The Vis-near-IR spectra were measured between 400 nm and 1600 nm in toluene solution by using a SHIMADZU UV-3150 spectrophotometer. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were recorded on a BAS CV50W electrochemical analyzer. A

platinum disk and a platinum wire were used as the working electrode and the counter electrode, respectively. The reference electrode was a saturated calomel reference electrode (SCE) filled with 0.1 M (*n*-Bu)₄NPF₆ in 1,2-dichlorobenzene. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc⁺) as the standard. CV: scan rate, 20 mV/s. DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s. NMR spectra were obtained with Bruker AVANCE 500 and AVANCE 300. The ¹H chemical shifts of **1** were calibrated with dichloromethane as an internal reference (δ = 5.23). ¹³C chemical shifts of Ce₂@C₈₀ were calibrated with acetone as an external reference (δ = 29.3). ¹³C chemical shifts were calibrated with CS₂ as an internal reference (δ = 195.0).

Preparation and isolation of Ce₂@C₈₀

Soot containing Ce-metallofullerenes were produced by the standard arc vaporization method using a composite anode containing graphite and cerium oxide in an atomic ratio of Ce/C = 0.008.¹ The composite rod was then subjected to an arc discharge as an anode under a helium atmosphere of 50 Torr. The raw soot was collected and extracted using 1,2,4-trichlorobenzene at its boiling temperature for 16 h. The soluble fraction was injected into the HPLC; a 5PYE column (ϕ 20 mm \times 250 mm; Cosmosil, Nacalai Tesque, Inc.) was used

in the first step and a Buckyprep column (ϕ 20 mm \times 250 mm; Cosmosil, Nacalai Tesque, Inc.) in the second step to give pure $\text{Ce}_2@\text{C}_{80}$.

1) Wakahara, T.; Kobayashi, J.; Yamada, M.; Maeda, Y.; Tsuchiya, T.; Okamura, M.; Akasaka, T.; Waelchli, M.; Kobayashi, K.; Nagase, S.; Kato, T.; Kako, M.; Yamamoto, K.; Kadish, K. M. *J. Am. Chem. Soc.* **2004**, *126*, 4883–4887.

Spectral data for $\text{Ce}_2@\text{C}_{80}$

^{13}C NMR (125 MHz, CS_2 with acetone- d_6 capillary, 298 K) δ 148.6(60C), 124.7(20C); MS m/z 1238 (M).

Synthesis of the silylated adduct 1

A toluene solution of 84 ml containing $\text{Ce}_2@\text{C}_{80}$ (6.0 mg, 5.8×10^{-5} M) was heated at 80 °C for 2 h with 50 equiv of 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane under argon atmosphere to achieve the adduct **1**. Adduct **1** can be readily isolated by the preparative HPLC using a Buckyprep column (ϕ 20 mm \times 250 mm; Cosmosil, Nacalai Tesque, Inc.).

Synthesis of the silylated adduct 1

Spectral data for 1

^1H NMR (300 MHz, $\text{CD}_2\text{Cl}_2/\text{CS}_2 = 1/3$, 293 K) δ 9.66 (s, 2H), 9.41 (s, 2H), 9.06 (s, 2H),

8.84 (s, 2H), 8.51 (s, 6H), 7.31 (s, 2H), 6.38 (s, 6H), 5.44 (s, 6H), 4.99 (s, 6H), 3.83 (s, 6H), 2.91 (s, 6H); ^{13}C NMR (125 MHz, $\text{CD}_2\text{Cl}_2/\text{CS}_2 = 1/3$, 293 K) δ 394.5 (2C), 275.0 (2C), 270.8 (2C), 243.5 (2C), 228.9 (2C), 223.4 (2C), 211.0 (2C), 185.9 (2C), 176.4 (2C), 173.9 (2C), 172.1 (2C), 171.2 (2C), 162.8 (4C), 161.2 (4C), 159.7 (2C), 158.6 (2C), 156.1 (2C), 155.3 (2C), 152.2 (4C), 151.6 (6C), 150.8 (2C), 145.9 (2C), 146.7 (2C), 145.6 (4C), 143.1 (2C), 142.4 (2C), 140.9 (2C), 138.8 (2C), 136.6 (2C), 135.0 (2C), 133.0 (2C), 123.4 (2C), 117.9 (2C), 117.6 (2C), 117.2 (2C), 111.2 (2C), 101.8 (2C), 100.1 (4C), 90.8 (2C), 92.6 (2C), 70.8 (2C), 69.1 (2C), 66.3 (2C), 64.4 (2C), 43.6 (2C), 37.6 (2C), 28.6 (2C), 24.7 (2C), 23.8 (2C), 18.8 (1C). Another peak was overlapped with the signal of hexane. Vis-near-IR (toluene) λ_{max} 819 nm; MALDI-TOF MS m/z 1786 (M^+), 1240 ($\text{M}^+ - [\text{Mes}_4\text{Si}_2\text{CH}_2]$).

X-ray crystallographic analysis of 1

Black crystals of **1** were obtained by slow evaporation of the solution in mixed solvent of CS_2 and dichloromethane. Single crystal X-ray diffraction data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo $\text{K}\alpha$ radiation in the scan range $1.11^\circ < \theta < 26.37^\circ$. Crystal data of **1**·3(CS_2): $\text{C}_{120}\text{H}_{46}\text{Ce}_2\text{S}_6\text{Si}_2$, $M_w = 2016.35$, orthorhombic, space group $P2_12_12_1$, $a = 11.2325(6)$ Å, $b = 23.7339(13)$ Å, $c = 28.7821(16)$ Å, $\alpha = \beta = \gamma = 90.00^\circ$, $V = 7673.0(7)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.745 \text{ Mg/m}^3$, $\mu = 1.429 \text{ mm}^{-1}$, $T = 90 \text{ K}$, crystal size $0.42 \times 0.10 \times 0.05 \text{ mm}^3$. 89123 reflections, 15678 unique reflections; 11990 with $I > 2\sigma(I)$; $R_1 = 0.0432$ [$I > 2\sigma(I)$], $wR_2 = 0.1079$ (all data), GOF (on F^2) = 1.004. The maximum residual electron density is equal to $0.826 \text{ e}\text{\AA}^{-3}$.

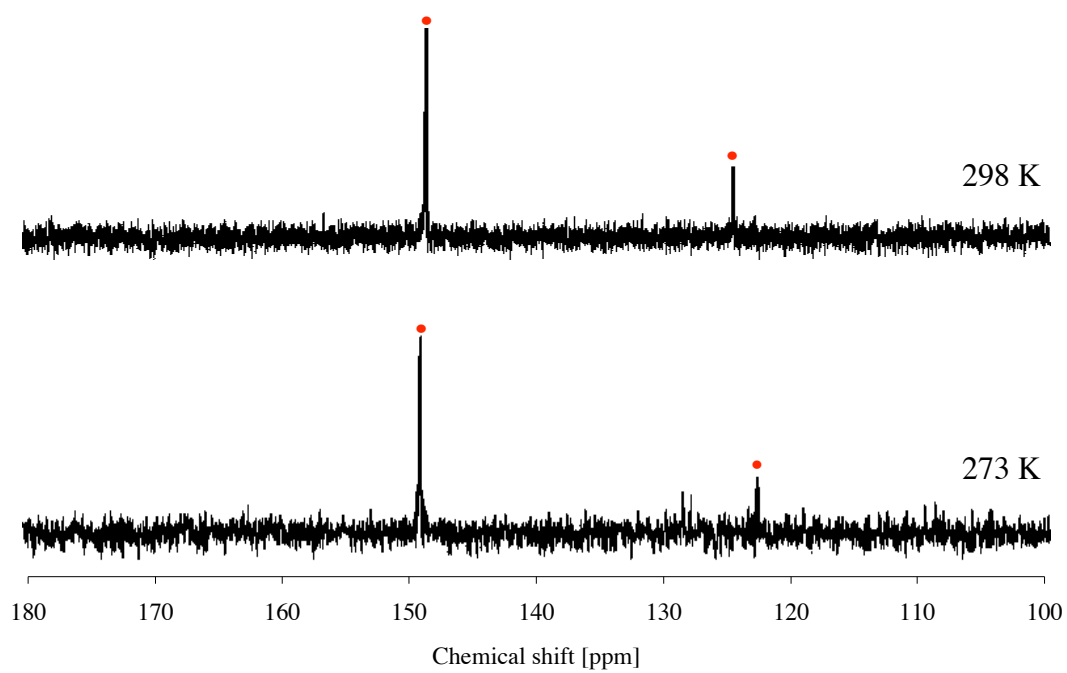


Figure S1. ^{13}C NMR spectra (125 MHz) of $\text{Ce}_2@C_{80}$ in CS_2 solvent with acetone- d_6 as an external lock.

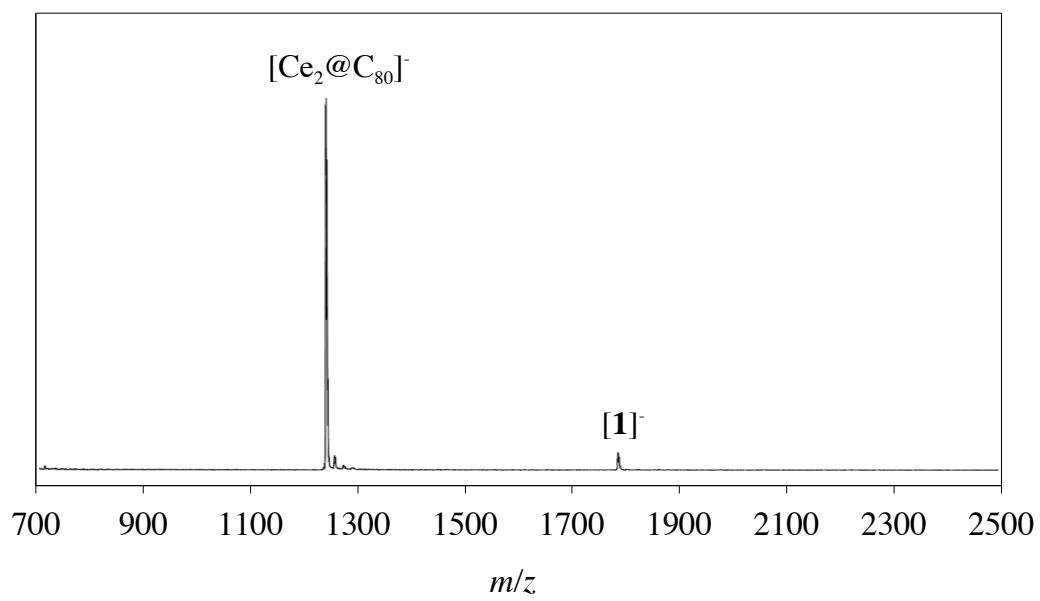


Figure S2. MALDI-TOF mass spectrum of isolated **1**.

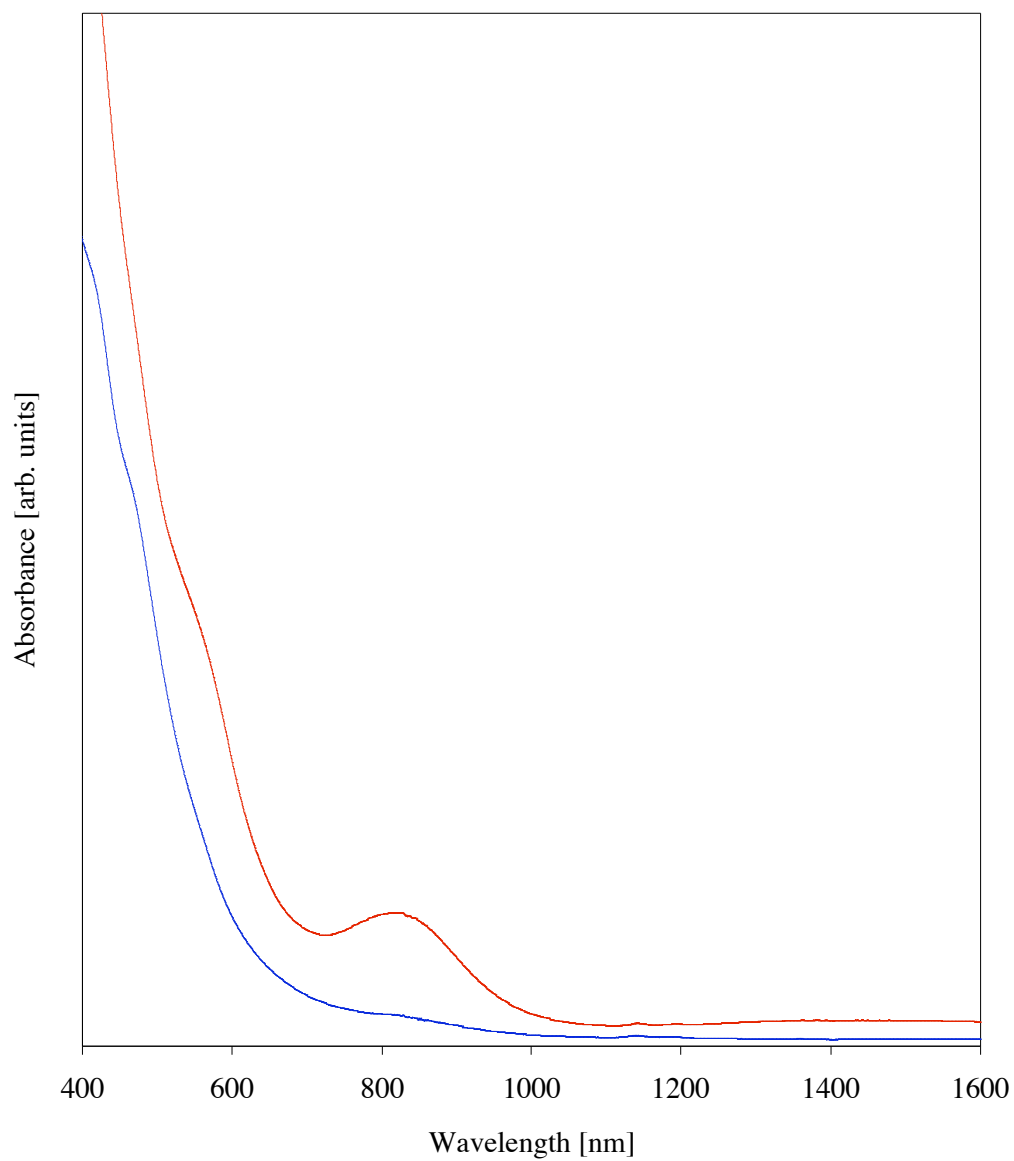


Figure S3. Vis-near-IR absorption spectra of $\text{Ce}_2@C_{80}$ and **1**.

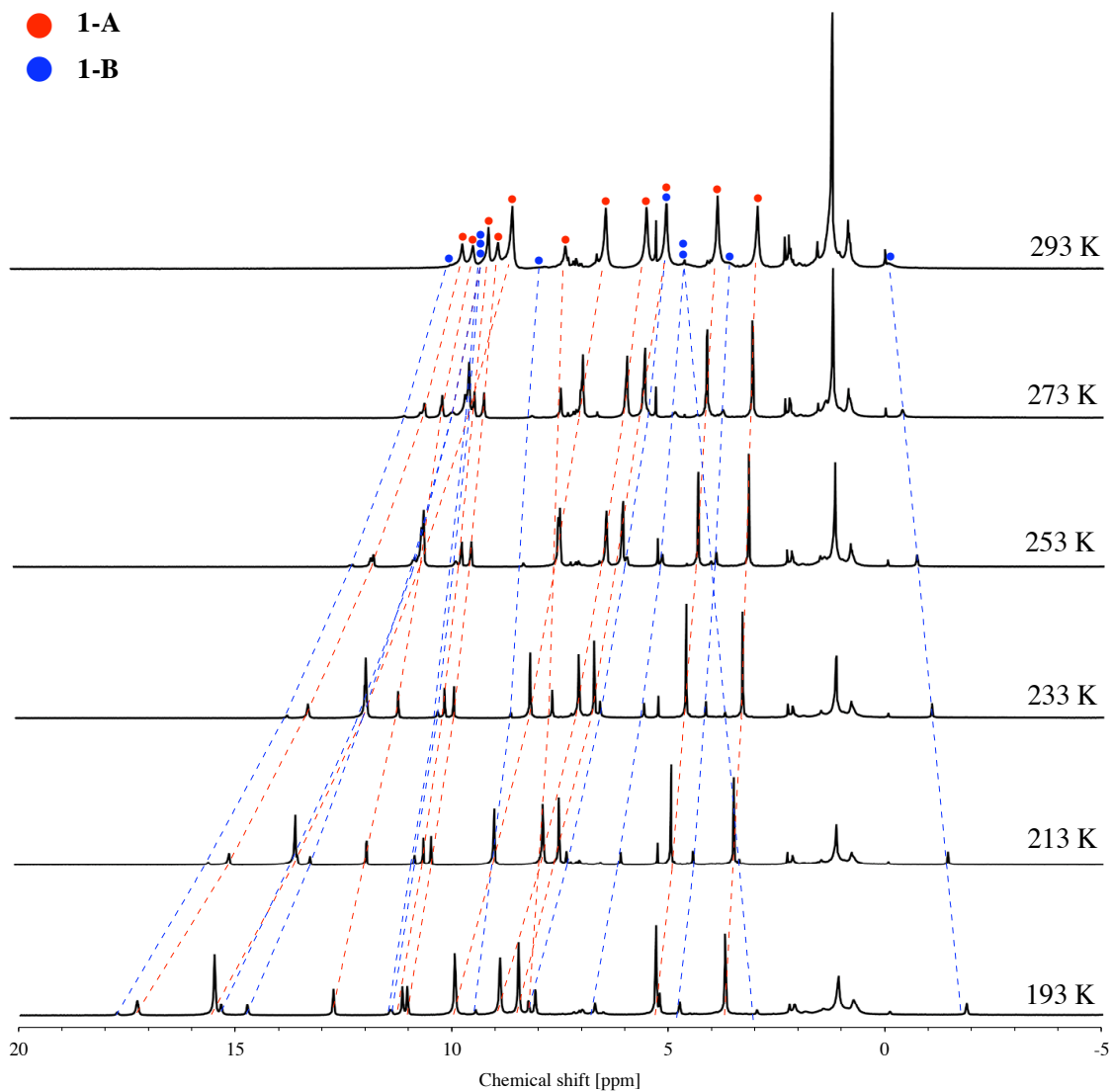
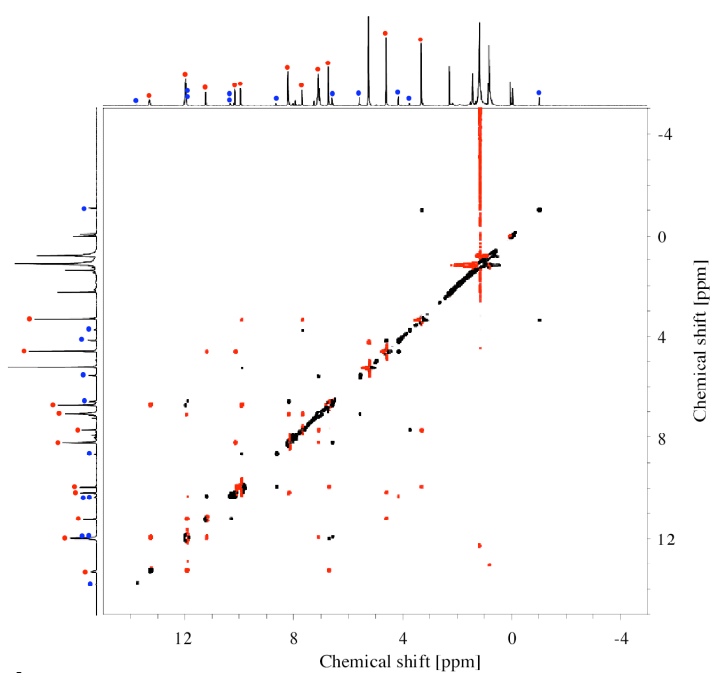


Figure S4. ^1H NMR spectra of **1**. The blue circle shows the peak corresponding to **1-A**, and the red circle shows the peaks corresponding to **1-B**.

c



d

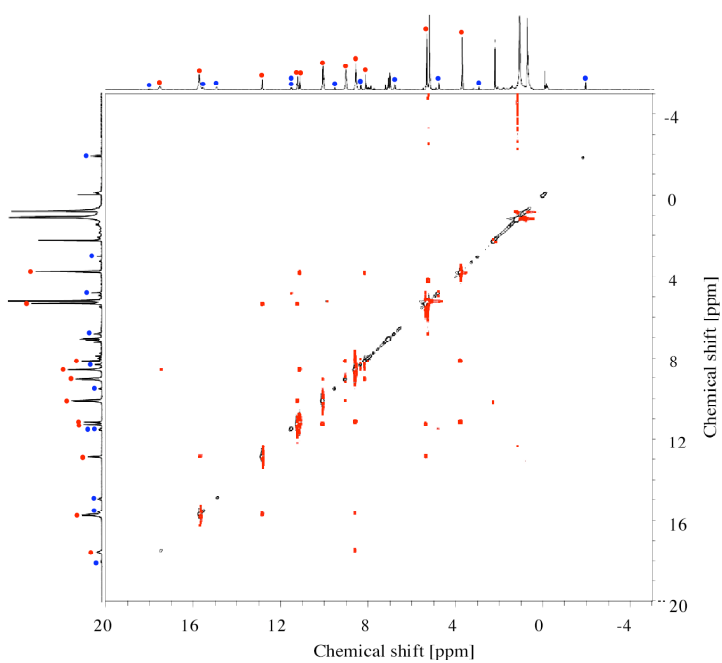


Figure S5. ROESY NMR spectra of **1**; (a) 273 K, (b) 253 K, (c) 233 K, and (d) 193 K. Positive and negative intensity are shown as red and black, respectively. The blue and red circle show the peak corresponding to **1-A** and **1-B**, respectively.

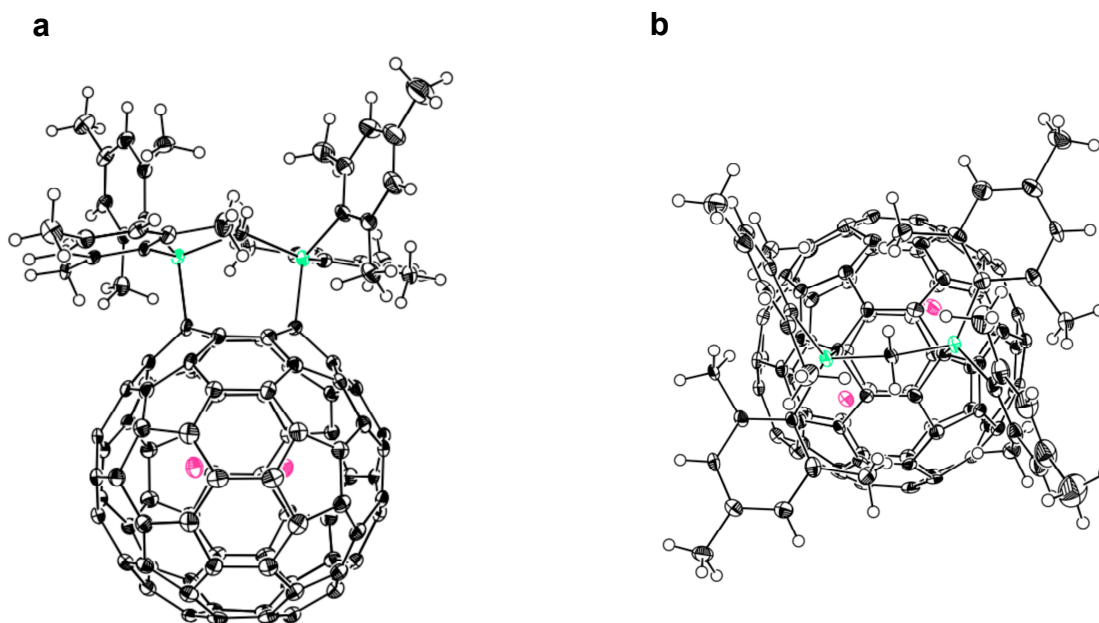


Figure S6. (a) Side view and (b) top view of ORTEP drawing of X-ray crystal structure of **1-B** at 90 K with thermal ellipsoids at 50% probability level, in which CS₂ molecule is omitted for clarity.

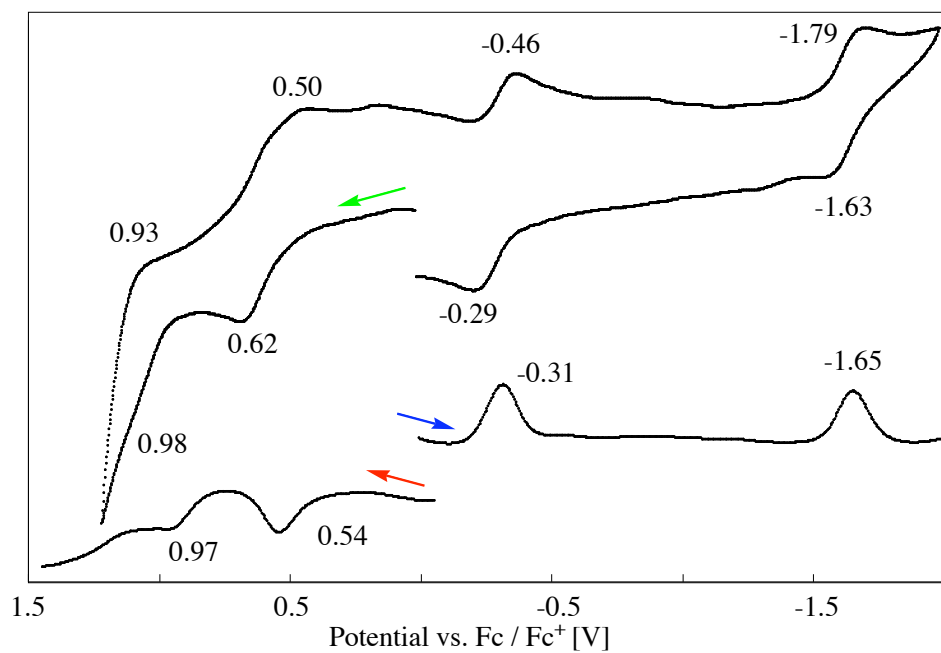


Figure S7. Cyclic and differential pulse voltammograms of $\text{Ce}_2@\text{C}_{80}$.

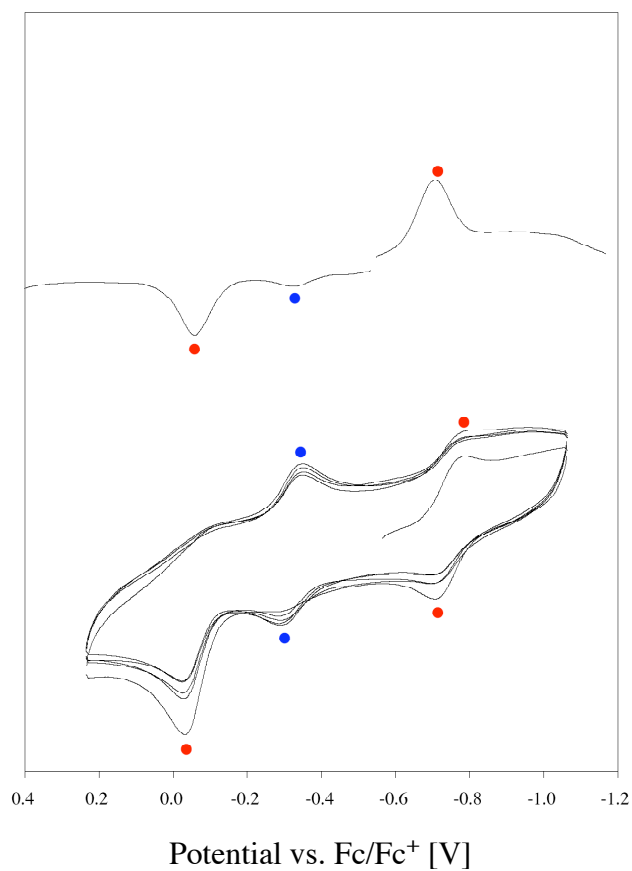


Figure S8. Cyclic and differential pulse voltammograms of **1**. The peaks of **1** and the peaks of Ce₂@C₈₀ decomposed from **1** are marked as red and blue circles, respectively.

Table S1. Redox Potentials^a of Ce₂@C₈₀ and **1**

Compd.	^{ox} <i>E</i> ₂	^{ox} <i>E</i> ₁	^{red} <i>E</i> ₁	^{red} <i>E</i> ₂
1		-0.07 ^{b, c}	-0.73	
Ce ₂ @C ₈₀	+0.95	+0.57	-0.39	-1.71

^aHalf-cell potentials unless otherwise stated. Values are in volts relative to ferrocene/ferrocenium couple. ^bIrreversible. ^cValues are obtained by DPV.