Supporting Information for

Metal-Encapsulation Induces a Highly Regioselective Bingel-Hirsch Reaction of the Labile Y@C_s(6)-C$_{82}$

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General reagents and instruments.

All commercial reagents were used without further purification before use. The reaction process was monitored with analytical HPLC (FL2200, Zhejiang Fuli Analytical Instruments Co. Ltd.) equipped with a Buckyprep column (ø = 4.6×250 mm, Cosmosil Nacalai Tesque). The separations were conducted on preparative HPLC (LC-908; Japan Analytical Industry Co. Ltd.) equipped with a Buckyprep column (ø = 20×250 mm, Cosmosil Nacalai Tesque) with toluene as the eluent. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was measured on a Bruker BIFLEX III spectrometer (Bruker Daltonics, Germany) using 1,1,4,4-tetraphenyl-1,3-butadiene as matrix. The vis-NIR experiments were carried out on a PE Lambda 750S UV-vis-NIR spectrophotometer.

Synthesis and isolation of Y@C_s(6)-C_{82}.

Carbon soot containing yttrium-EMFs was synthesized using a direct current arc discharge method. Briefly, a core-drilled graphite rod filled with graphite/Y_2O_3 (molar ratio: Y/C=1:17) was burned under 225 Torr helium atmosphere with a power of 100 A × 20 V. The soot was collected and refluxed in *N,N*-dimethylformamide (DMF) under a nitrogen atmosphere for 15 h. After removal of DMF, the residue was redissolved in toluene and the solution was subjected to HPLC separations. The pure Y@C_s(6)-C_{82} sample was isolated by a three-stage HPLC separation process. In the first stage, the extract mixture was isolated and fraction F7 was collected (Figure S1a). F7 was then subjected to the second-stage recycling HPLC separation, which afforded fraction F7-1 after three cycles (Figure S1b). Y@C_s(6)-C_{82} was obtained in the final stage of separation with F7-1 (Figure S1c).
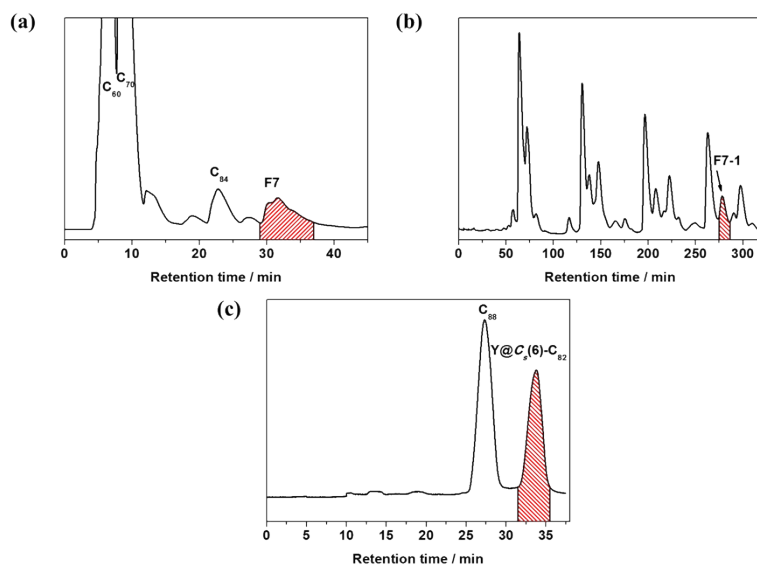
Figure S1. (a) HPLC profile of the fullerene extract mixture synthesized from Y_2O_3 (20 mm × 250 mm 5PYE column; flow rate 10 mL/min; injection volume 20 ml; toluene as eluent; room temperature). (b) Recycling HPLC profile of fraction F7 (20 mm × 250 mm Buckyprep column; flow rate 10 mL/min; injection volume 20 ml; toluene as eluent; room temperature). (c) HPLC profile of fraction F7-1 (20 mm × 250 mm Buckyprep M column; flow rate 10 mL/min; injection volume 20 ml; toluene as eluent; room temperature).

Synthesis of 2a, 2b and 2c.

Y@C_s(6)-C_{82} (2.72 mg, 2.5 μmol) and diethyl bromomalonate (1.05 mg, 4.4 μmol) were dissolved in 30 mL of anhydrous toluene in the presence of DBU (0.38 mg, 2.5 μmol). The reaction proceeded under an argon atmosphere at the room temperature and was monitored by analytical HPLC on a Buckyprep column (ø 4.6 mm × 250 mm). After the solution was stirred for 20 min, three new peaks appeared at 7.8, 8.3 and 9.4 min, which are identified as mono-adducts (**2a**, **2c** and **2b**). The reaction was terminated after 60 minutes when the peak at 18.8 min corresponding to pristine Y@C_s(6)-C_{82} disappeared. The reaction mixture was filtered and injected into an HPLC for analysis and isolation (ø 20 mm × 250 mm Buckyprep column, toluene, flow rate= 10.0 mLmin^{-1}, room temperature).
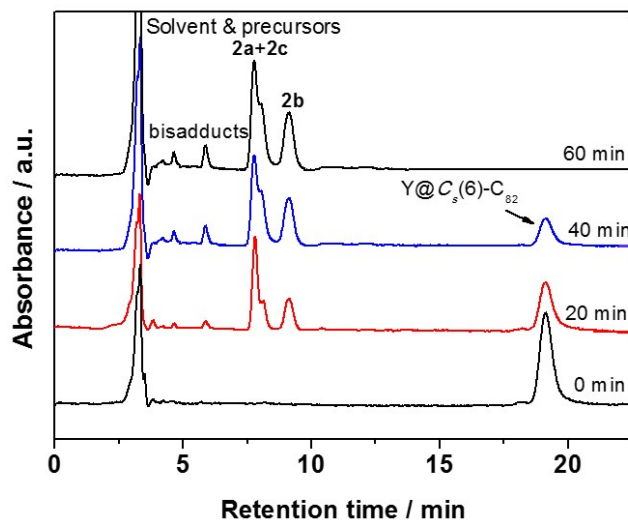
Figure S2. HPLC profiles of the reaction mixture containing **1** and Y@C_s(6)-C$_{82}$ probed at different times. Conditions: 5PYE column (ø 4.6 mm × 250 mm), 1.0 mL min^{-1} toluene flow; room temperature; 330 nm detection.
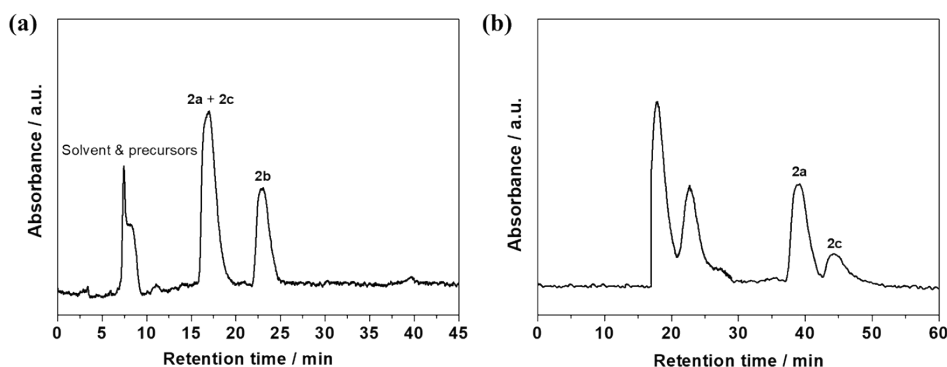
Figure S3. HPLC separations of **2a**, **2b** and **2c** from the reaction mixture of Y@C_s(6)-C$_{82}$ with **1**. a) First-stage HPLC chromatogram on a 5PYE column (ø 20 mm × 250 mm); b) second-stage HPLC chromatogram on a Buckyprep column (ø 20 mm × 250 mm). Conditions: 20 mL injection volume, 10 mL/min toluene flow, 330 nm detection wavelength, room temperature.

Single-crystal XRD measurement of 2b.

Crystal of **2b** was obtained by layering anhydrous n-hexane over a nearly saturated solution of **2b** in CS$_2$ in a glass tube. Over a 20-day period, the solution diffused together and black crystals formed. Crystallographic characterization of **2b** was performed at 173 K on a Bruker D8 QUEST machine equipped with a CMOS camera (Bruker AXS Inc., Germany). The

multiscan method was used for absorption corrections. The structure was solved by the direct method and were refined with SHELXL-2014/7[S1].

Crystal data of 2b.

Black block, 0.100×0.090×0.070 mm, monoclinic, space group $P2_1$/c, a = 11.2309(6) Å, b = 22.0675(12) Å, c = 20.7788(11) Å, β = 98.817(2)°, V = 5088.9(5) Å^3, Z = 4, D_{calc} = 1.911 Mg m^{-3}, μ = 2.170 mm^{-1}, T = 173(2) K; 70665 reflections, 9841 independent included in the refinement; R_1 = 0.0851[$I > 2\sigma(I)$], wR_2 = 0.2265 (all data). Crystallographic data have been deposited in the Cambridge Crystallographic Data Center (CCDC 2018002).
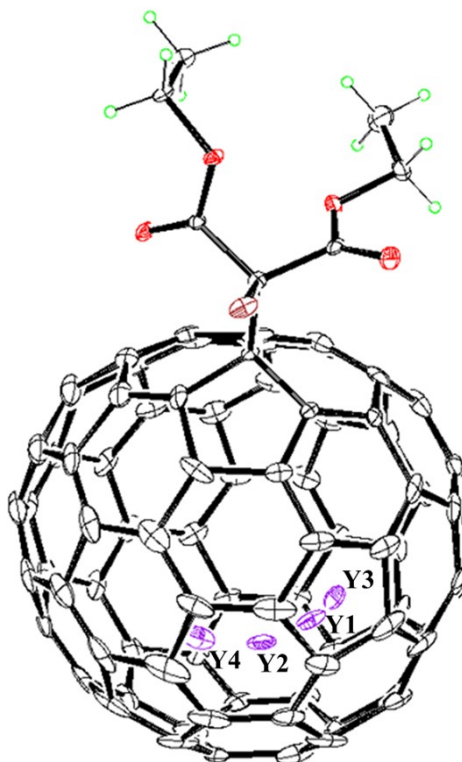

Figure S4. ORTEP drawing shows the disordered yttrium positions in **2b**. The thermal ellipsoids shown at the 20% probability level (the solvent molecules have been omitted for clarity).

Theoretical calculations.

Density functional theory (DFT) calculations were carried out by using the M06-2X functional[S2] in conjunction with the Stuttgart/Dresden relativistic effective core potential and corresponding basis set for Y and the standard 6-31G* basis set for other elements (denoted as M06-2X/6-31G*~SDD), as implemented in the Gaussian 09 software package[S3–S5].

2a (0.0)   **2b (2.8)**   **2c (3.9)**

(5.0)   **(5.1)**   **(5.8)**   **(6.8)**
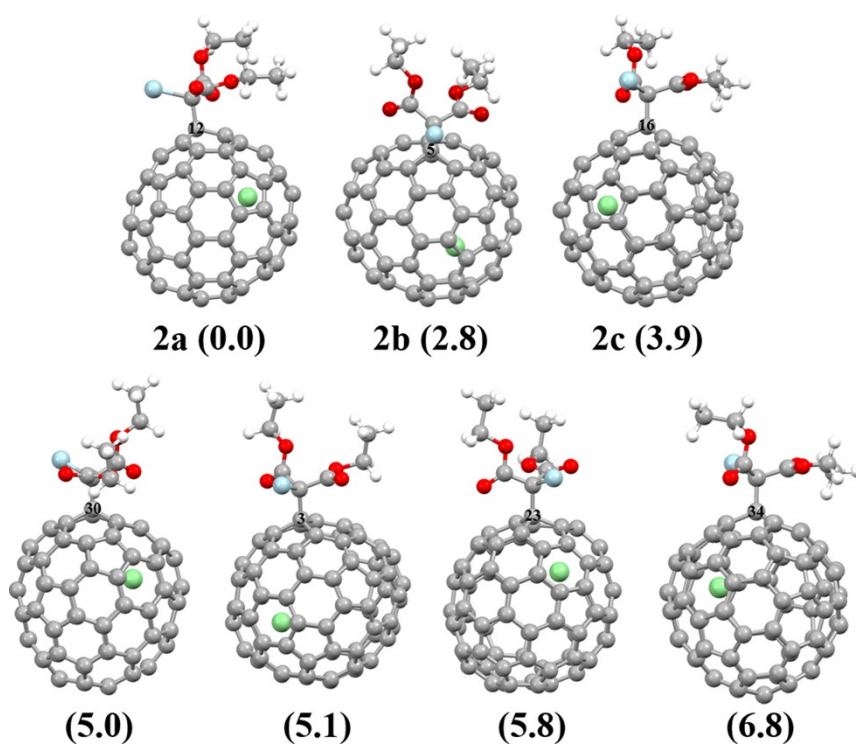
Figure S5. Optimized structures and relative energies (kcal/mol) of several low-energy singly bonded adducts.

(0.0)   **(5.3)**   **(8.8)**   **(17.7)**

(18.8)   **(19.7)**   **(24.0)**   **(26.0)**
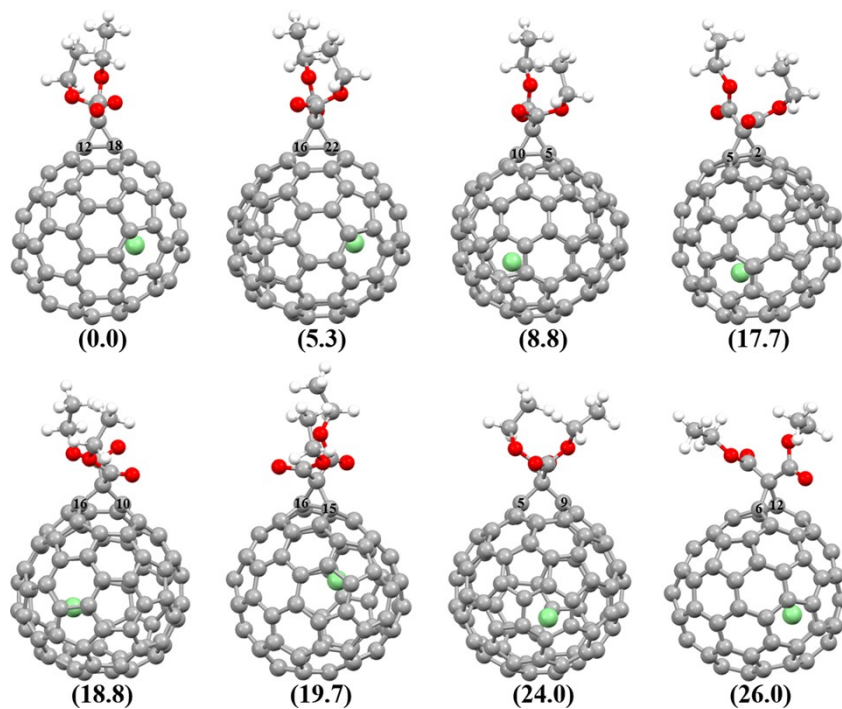
Figure S6. Optimized structures and relative energies (kcal/mol) of several low-energy Bingel-Hirsch cycloadducts.

References.

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