Electronic Supplementary Information (ESI)

Retro-reaction of singly bonded La@C$_{82}$ derivatives

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Experimental Section

General. All chemicals and solvents were obtained from Wako Inc. and used without further purification unless otherwise stated. Toluene was distilled over benzophenone sodium ketyl under an argon atmosphere prior to use in reaction. Analytical high performance liquid chromatography (HPLC) was performed on a JASCO HPLC apparatus using a Buckyprep column (4.6 x 250 mm, Nakarai Tesque) with monitoring UV absorption at 350 nm. Toluene was used as the eluent. Mass spectrometry was performed on a Bruker BIFLEX III or a Bruker UltrafleXtreme, using 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. Electron paramagnetic resonance (EPR) spectra were recorded by a Bruker EMXPlus9.5/2.7. The spectrometer was operated at 9.8 GHz with a microwave power of 0.2 mW (30 dB), a modulation frequency of 100 kHz, and modulation amplitude of 300 mG. The g values were determined by the readout function of the spectrometer with the weak pitch as a standard, while the hyperfine splitting constants were measured using a Hall unit for calibration of the magnetic field. Simulation of the spectra was carried out on a WINEPR SimFonia program attached to the Bruker EMX spectrometer.

Synthesis of the radical adducts of La@C₈₂ (1 and 2).

La@C₈₂CH₂C₆H₅ (1) and La@C₈₂CHClC₆H₃Cl₂ (2) were prepared according to previously reported synthetic procedures,¹ and identified with the spectroscopic data thereof.

General procedure of thermal reactions.

To a 0.20 mL aliquot of 5.0 x 10⁻⁴ M toluene solution of the substrates (1b, 1d, 2b, 2d or La@C₈₂, 1.0 x 10⁻⁶ mol), appropriate equivalent 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was added, respectively. The solutions were placed in a Pyrex grass tubes (or quartz tubes for EPR measurements) individually, degassed by three freeze-pump-thaw cycles under reduced pressures, and then sealed and heated in the conditions shown in Table 1 or Fig S1.

The reaction mixtures were analyzed by HPLC, and yields of La@C₈₂ were determined by peak areas of the HPLC profiles.

Reference:

Fig. S1 HPLC profiles of the reaction mixtures. The labels on the graphs show the conditions of heating temperature and duration. (a) 1b, (b) 1d, (c) 1d with 30 equiv of TEMPO, (d) 2d, (e) 2d with 25 equiv of TEMPO, and (f) La@C$_{82}$ with 25 equiv of TEMPO. HPLC conditions: column, Buckyprep ($\phi$4.6 mm × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; monitored wavelength, 350 nm; temp., 40°C.
Fig. S2 MALDI-TOF mass (negative mode) spectrum of 1b in an absence of TEMPO after heating at 115°C for 7 h in degassed toluene.
**Fig. S3** (Upper) EPR spectra of 1b in degassed toluene, (black line) before and (red line) after heating in an absence of TEMPO, and (lower) simulated EPR spectra for the reaction mixture. The simulated spectra show the existence of La@C_{82} (Spectrum 1), and two paramagnetic adducts (Spectra 2 & 3), expected to be benzyl bis-adducts.
**Fig. S4** MALDI-TOF mass (positive mode) spectra of (black line) the matrix (TPB) solely, and (red line) the reaction mixture of 1d in a presence of 30 equiv of TEMPO after heating at 100°C for 7 h using the matrix. The spectra are normalized with the biggest peaks in the presenting region respectively. Inset shows calculated isotropic distribution pattern of TEMPO-CH₂Ph, which was formed as the result of coupling of TEMPO and benzyl radical.

**Fig. S5** MALDI-TOF mass (negative mode) spectrum of La@C₈₂ in a presence of 25 equiv of TEMPO after heating at 100°C for 7 h in degassed toluene.
Fig. S6 EPR spectra of 2d in degassed toluene, (black line) before and (red line) after heating at 80°C for 4 h in a presence of 25 equiv of TEMPO.