Electronic Supplementary Information (ESI)

Experimental
All moisture sensitive reactions were carried out under an atmosphere of argon using dried glassware. 1,2-Dichlorobenzene was freshly distilled from P2O5 before use. Compounds 1a, 3a, and 5a were purchased from Tokyo Chemical Industry CO., LTD. and were used without further purification. 1H and 13C NMR spectra were measured on a JEOL JNM-ECX-400P spectrometer. Chemical shifts (δ) for 1H and 13C NMR spectra are given in ppm relative to tetramethylsilane (TMS) and are referenced to internal TMS or residual non-deuterated solvent. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker Daltonics autoflex III smartbeam with 1,1,4,4-tetraphenylbuta-1,3-diene (TPB) as the matrix. Absorption spectra were recorded on JASCO V-670 spectrophotometer. The electrolysis process was carried out with a BAS ALS 630DT potentiostat/galvanostat and performed in a divided glass cell (K-3) consisting of two platinum plate electrodes that was obtained from Techno Sigma Co.

Procedure for preparation and reaction of C60 radical anion
General procedure for preparation and reaction of C60 radical anion
C60 radical anion (18.0 mg, 0.025 mmol) was prepared by bulk electrolysis of C60 (18.0 mg, 0.025 mmol) in 1,2-dichlorobenzene (15 mL) containing tetrabutylammonium perchlorate (TBAP: 0.684 g, 2.0 mmol). The applied potential was chosen based on in situ CV measurements and was more negative than Ered for the C60/C60 radical anion redox pair. The production and consumption of the C60 radical anion was confirmed by vis NIR absorption spectra. Alkyl halide was added to the generated C60 radical anion, and the solution was stirred at room temperature. After evaporation of the solvent, CS2 was added and removed TBAP by filtration. Purification and isolation of recovered C60 and the corresponding C60 adducts were accomplished by FC or preparative HPLC (Buckyprep φ20 x 250 mm; Cosmsil; Nacalai Tesque Inc., toluene. Flow rate 9.9 mL min⁻¹).

Entry 1: 2a was prepared in 40% yield (17.6 mg, 0.020 mmol) from C60 (36.0 mg, 0.05 mmol) and 1a (119.1 mg, 0.50 mmol) in 1,2-dichlorobenzene (30 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1a. HPLC gave pure 2a and C60 in 48% (17.4 mg, 0.024 mmol).

Entry 2: 2b was prepared in 38% yield (8.1 mg, 0.0096 mmol) from C60 (18.1 mg, 0.025 mmol) and 1b (52.4 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1b. Flash chromatography (SiO2 toluene/hexane 1:1,
toluene, then toluene/AcOEt 1:1) gave pure 2b and C₆₀ in 52% (9.5 mg, 0.013 mmol).

Entry 3: 2c was prepared in 42% yield (9.5 mg, 0.010 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 1c (67.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1c. Flash chromatography (toluene/hexane 1:1, then toluene) gave pure 2c and C₆₀ in 55% (9.9 mg, 0.014 mmol).

Entry 4: 2d was prepared in 34% yield (7.5 mg, 0.0085 mmol) from C₆₀ (18.1 mg, 0.025 mmol) and 1d (60.3 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1d. Flash chromatography (toluene, then toluene/AcOEt 1:1) gave pure 2d and C₆₀ in 60% (10.8 mg, 0.015 mmol).

Entry 5: 2e was prepared in 30% yield (7.1 mg, 0.0075 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 1e (75.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1e. HPLC gave pure 2e and C₆₀ in 58% (10.5 mg, 0.015 mmol).

Entry 6: 2a was prepared in 29% yield (6.3 mg, 0.0072 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 1f (79.0 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1f. Flash chromatography (SiO₂ toluene/hexane 1:1, toluene, then toluene/AcOEt 1:1) gave pure 2a and C₆₀ in 58% (10.4 mg, 0.014 mmol).

Entry 7: 2a was prepared in 38% yield (8.3 mg, 0.0094 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 1f (5.0 mg, 0.016 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 1f. Flash chromatography (SiO₂ toluene/hexane 1:1, toluene, then toluene/AcOEt 1:1) gave pure 2a and C₆₀ in 40% (7.2 mg, 0.010 mmol).

Entry 8: 4 was prepared in 11% yield (2.5 mg, 0.0028 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 3a (42.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 20 h at room temperature after the addition of 3a. HPLC gave pure 4 and C₆₀ in 39% (7.1 mg, 0.0099 mmol).

Entry 9: 4 was prepared in 17% yield (3.8 mg, 0.0042 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 3a (213 mg, 1.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 18 h at room temperature after the addition of 3a. HPLC gave pure 4 and C₆₀ in 61% (11.0 mg, 0.015 mmol).

Entry 10: 4 was prepared in 31% yield (6.9 mg, 0.0076 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 3b
(54.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 3b. HPLC gave pure 4 and C₆₀ in 44% (8.0 mg, 0.011 mmol).

Entry 11: 6 was prepared in 41% yield (8.5 mg, 0.010 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 5a (66.1 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 72 h at room temperature after the addition of 5a. HPLC gave pure 6 and C₆₀ in 56% (10.1 mg, 0.014 mmol).

Entry 12: 6 was prepared in 33% yield (6.7 mg, 0.0081 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 5b (89.3 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of 5b. HPLC gave pure 6 and C₆₀ in 63% (11.3 mg, 0.016 mmol).

Entry 13: 6 was prepared in 39% yield (8.1 mg, 0.0098 mmol) from C₆₀ (18.0 mg, 0.025 mmol) and 5b (5.4 mg, 0.015 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 1 h at room temperature after the addition of 5b. HPLC gave pure 6 and C₆₀ in 44% (8.0 mg, 0.011 mmol).

Spectral data (2d)

^1^H NMR (400 MHz, CS₂:CDCl₃=1:1)
δ 2.75 (s, 3H), 7.58-7.61 (m, 2H), 7.68-7.73 (m, 1H), 8.53-8.56 (m, 2H)

^1^C NMR (100 MHz, CS₂:CDCl₃=1:1)
δ 27.75, 66.99, 73.36, 129.38, 130.07, 134.00, 134.97, 137.23, 138.44, 141.04, 141.87, 142.10, 142.85, 142.89, 143.00, 143.04, 143.65, 143.69, 144.40, 144.55, 144.61, 144.68, 145.07, 145.12, 145.44, 145.75, 186.31, 193.69

MALDI-TOF-MS (TPB) calcd for C₇₀H₈O₂ [(M)]: m/z (%): 880.052; found 879.894.

Synthesis of 1b, 1c, 1d, 1e, 1f, 3b, and 5b was conducted according to literature procedures.

1b, 1c, 1d, 1e: Synlett., 2006, 14, 2287.

Synthetic procedure:

1c. A mixture of ethyl benzoyleacetate (1.29 mL, 7.5 mmol), KBr (4.46 g, 37.5 mmol), 1 M aq HCl (37.5 mL), and 30% H₂O₂ (17 mL) in toluene (37.5 mL) was stirred for 2 h at room temperature. The organic layer was washed with a saturated aqueous solution of sodium bicarbonate, a saturated aqueous solution of sodium thiosulfate, and brine. The organic layer was dried over MgSO₄ and
concentrated under reduced pressure. Flash chromatography afforded pure 1c (1.83 g, 90%) as a pale-yellow oil.

1f. Bromine (0.9 mL, 17.5 mmol) was added to a solution of sodium hydroxide (2.2 g, 55 mmol) in water (25 mL) at -6 °C. The mixture was stirred for 30 min then added dropwise to a solution of diethyl malonate (0.92 mL, 6.1 mmol) in acetone (25 mL) and glacial acetic acid (10 mL) at -8 °C. The reaction mixture was stirred for 1 h at 0 °C, then extracted with CH₂Cl₂. The organic layer was washed with a saturated aqueous solution of sodium thiosulfate, a saturated aqueous solution of sodium bicarbonate, and brine. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. Flash chromatography afforded pure 1f (1.74 g, 5.5 mmol) as a pale-yellow oil in 90% yield.

3b. Benzyl bromide (0.6 mL, 5 mmol) and NaI (1.5 g, 10 mmol) were dissolved in acetone (7 mL). The mixture was stirred for 24 h at room temperature in the dark. The reaction was quenched with water (20 mL) and extracted with diethyl ether. The organic layer was dried over MgSO₄ and concentrated under reduced pressure to afford pure 3b as a colorless oil in 93% yield (1.02 g, 4.7 mmol).

5b. 1,2-bis(bromomethyl)benzene (0.66 g, 2.5 mmol) and NaI (1.5 g, 10 mmol) were dissolved in acetone (7 mL). The mixture was stirred for 24 h at room temperature in the dark. The reaction was quenched with water (20 mL) and extracted with diethyl ether. The organic layer was dried over MgSO₄ and concentrated under reduced pressure to afford pure 5b as a pale-yellow solid in 96% yield (0.86 g, 2.4 mmol).

![Applied potential](image)

Figure S1. In situ cyclic voltammogram of C₆₀ at 100 mV/s in 1,2-DCB containing 0.13 M TBAP before bulk electrolysis.
Figure S2. Absorption spectra of C₆₀ radical anion before and after the addition of alkyl halides.
Figure S3. HPLC profiles of reaction mixtures. Conditions: Column, Buckyprep φ4.6 x 250 mm; temp., 40°C; flow rate, 1 mL min$^{-1}$; eluent, toluene; monitor, 330 nm detection.
Figure S4. HPLC profiles of isolated fullerene derivatives. Conditions: Column, Buckyprep φ4.6 x 250 mm; temp., 40°C; flow rate, 1 mL min⁻¹; eluent, toluene; monitor, 330 nm detection.
Figure S5. MALDI-TOF mass spectra of isolated fullerene derivatives in negative-ion mode.
Figure S6. Absorption spectra of isolated fullerene derivatives in CS$_2$. 
Figure S7. $^1$H NMR spectrum of C$_{61}$(CO$_2$Et)$_2$ (2a) in CDCl$_3$/CS$_2$=1:1.

Figure S8. $^{13}$C NMR spectrum of C$_{61}$(CO$_2$Et)$_2$ (2a) in CDCl$_3$/CS$_2$=1:1.
Figure S9. $^1$H NMR spectrum of C$_{61}$(COMe)(CO$_2$Et) (2b) in CDCl$_3$/CS$_2$=1:1.

Figure S10. $^{13}$C NMR spectrum of C$_{61}$(COMe)(CO$_2$Et) (2b) in CDCl$_3$/CS$_2$=1:1.
Figure S11. $^1$H NMR spectrum of $C_{61}(COPh)(CO_2Et)$ (2c) in CDCl$_3$/CS$_2$=1:1.

Figure S12. $^{13}$C NMR spectrum of $C_{61}(COPh)(CO_2Et)$ (2c) in CDCl$_3$/CS$_2$=1:1.
Figure S13. $^1$H NMR spectrum of C$_6$(COPh)(COCH$_3$)$_2$ (2d) in CDCl$_3$/CS$_2$=1:1.

Figure S14. $^{13}$C NMR spectrum of C$_6$(COPh)(COCH$_3$)$_2$ (2d) in CDCl$_3$/CS$_2$=1:1.
Figure S15. $^1$H NMR spectrum of C$_{61}$(COPh)$_2$ (2e) in CDCl$_3$/CS$_2$=1:1.

Figure S16. $^{13}$C NMR spectrum of C$_{61}$(COPh)$_2$ (2e) in CDCl$_3$/CS$_2$=1:1.
Figure S17. $^1$H NMR spectrum of C$_{60}$(CH$_2$Ph)$_2$ (4) in CDCl$_3$/CS$_2$=1:1.

Figure S18. $^{13}$C NMR spectrum of C$_{60}$(CH$_2$Ph)$_2$ (4) in CDCl$_3$/CS$_2$=1:1.
Figure S19. $^1$H NMR spectrum of C$_{60}$C$_8$H$_8$ (6) in CDCl$_3$/CS$_2$=1:1.

Figure S20. $^{13}$C NMR spectrum of C$_{60}$C$_8$H$_8$ (6) in CDCl$_3$/CS$_2$=1:1.