Selective Synthesis of [60]Fullerene Multiadducts through Dicyclohexylcarbodiimide (DCC) Mediated Reactions

Hao Zhang, Yanbang Li, Liangbing Gan*

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All reagents were used as received. All solvents were used as received. The reactions were carried out under atmosphere condition. The NMR spectra were obtained at 25 °C with 400, 500 MHz spectrometers (1H and 13C NMR spectra for the same compound were obtained with different spectrometers and different solvents in some cases). Chemical shifts are given in ppm relative to TMS or CDCl3 (for 13C NMR) or CDCl2CDCl2 (for 13C NMR). ESI-FT-ICR-HRMS spectra were recorded in positive mode. Chromatographic purifications were carried out with silica gel of mesh 200-300.

Note: common impurities such as residue solvent toluene and grease from silica gel are sometimes impossible to be removed from the fullerene derivatives by routine flash column chromatography. Further purification by a diffusion-precipitation procedure was usually required to obtain pure samples. The diffusion-precipitation solvents are CS2/hexane or CHCl3/hexane.

**Preparation of Compound 1**

A solution of C60 (72 mg, 0.1 mmol) in 5 mL of oDCB (orthodichlorobenzene) was stirred at 35 °C. Then DCC (dicyclohexylcarbodiimide) (824 mg, 4 mmol) and 4-methylpiperidine (MePi) (0.24 mL, 2 mmol) were added into the solution. The resulting mixture was stirred at 35 °C for 40 min. The solution was directly chromatographed on a silica gel column eluting with petroleum ether (60-90 °C) to remove oDCB. Eluting with toluene/ethyl acetate (100:1) gave a little orange by-product as the known tetraamino fullerene epoxide C60(MePi)4(O) and another main orange band as compound 1 (85.7 mg, 0.065 mmol, 65%).

Characterization data for 1:

1H NMR (500 MHz, CDCl2CDCl2) δ 3.92-3.71 (m, 8H), 2.87-2.68 (m 8H), 2.19 (d, J = 9.6 Hz, 2H), 1.92 (d, J = 5.2 Hz, 4H), 1.83-1.79 (m, 16H), 1.51-1.30 (m, 20H), 1.07-1.02 (m, 12H). 13C NMR (126 MHz, CDCl2CDCl2) δ 152.25, 149.42, 148.93, 148.63, 148.55, 148.07, 147.73, 147.52, 147.41, 147.39, 147.05, 146.88, 146.56, 145.54, 145.27, 145.84, 145.82, 145.58, 145.45, 145.16, 144.52, 143.51, 143.43, 143.32, 142.44, 142.37, 77.58, 75.93, 71.41, 68.46, 55.74 (N-CH), 53.33 (N-CH), 52.20 (N-CH2), 51.33 (N-CH2), 50.38 (N-CH2), 35.84 (CH2), 35.37 (CH2), 35.30 (CH2), 35.04 (CH2), 34.87 (CH2), 30.76 (CH), 30.61 (CH), 25.97 (CH2), 25.71 (CH2), 25.52 (CH2), 25.24 (CH2), 21.96 (CH3). (signals for the four CH groups in the 4-methylpiperidinyl rings and the CH2 groups in the 23-25 ppm region could not be assigned conclusively because of presence of minor impurities (see attached spectrum, impurity signals δ 30.92, 29.71, 25.63, 24.75, 21.17, 21.13 ppm.)

ESI-FT-ICR-HRMS-Positive C97H71N6 (M + H+) calculated 1319.5757, found
Preparation of Compounds 3a, 3b

A solution of compound 1 (36.6 mg, 0.028 mmol) in 10 mL of toluene was stirred at 60 °C. Then ethanethiol (0.04 mL, 0.54 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 5 h. The solution was directly chromatographed on a silica gel column eluting with toluene to give the orange band as compound 3a (22.8 mg, 0.022 mmol, 80%).

Characterization data for 3a

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.12 (s, 1H), 3.37-3.23 (m, 10H), 1.48-1.43 (m, 15H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.25, 153.10, 151.12, 150.22, 148.88, 148.77, 148.61, 148.40, 148.26, 148.23, 148.06, 147.71, 146.96, 146.90, 146.67, 145.29, 144.45, 144.41, 144.37, 144.27, 144.21, 144.02, 143.43, 143.37, 143.29, 143.25 (C$_{60}$ ?), 60.46 (CH), 56.70, 56.06, 54.15, 28.40 (CH$_2$), 27.87 (CH$_2$), 27.73 (CH$_2$), 15.15 (CH$_3$), 15.13 (CH$_3$), 14.51 (CH$_3$).

A solution of compound 1 (54.8 mg, 0.042 mmol) in 12 mL of toluene was stirred at 60 °C. Then cyclohexanethiol (0.1 mL, 0.82 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 4 h. The solution was directly chromatographed on a silica gel column eluting with toluene to give the orange band as compound 3b (22.5 mg, 0.017 mmol, 42%).

Characterization data for 3b

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (s, 1H), 3.91-3.86 (m, 1H), 3.80-3.76 (m, 2H), 3.64-3.59 (m, 2H), 2.24-2.14 (m, 10H), 1.79-1.78 (m, 10H), 1.62-1.61 (m, 20H), 1.45-1.41 (m, 4H), 1.34-1.31 (m, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.71, 153.11, 151.65, 150.75, 148.82, 148.70, 148.56, 148.39, 148.24 (1C), 148.19, 148.03, 147.66, 146.95 (1C), 146.92, 146.67, 145.32, 145.19, 144.65, 144.49, 144.36, 144.33, 144.19, 144.13, 143.58, 143.37, 143.24, 61.23 (CH), 57.20, 56.13, 54.08, 45.96 (S-CH), 45.39 (S-CH), 45.33 (S-CH), 35.99 (CH$_2$), 35.76 (CH$_2$), 35.70 (CH$_2$), 35.56 (CH$_2$), 35.44 (CH$_2$), 26.37 (CH$_2$), 26.33 (CH$_2$), 26.23 (CH$_2$), 25.71 (CH$_2$), 25.63 (CH$_2$).

(all signals represent 2C except noted).

Preparation of Compounds 4a, 4b, 4c

A solution of compound 1 (224.2 mg, 0.17 mmol) in 50 mL of toluene was stirred at 60 °C. Then phenol (320 mg, 3.3 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 2 d. The solution was directly chromatographed on a silica gel column eluting with toluene to give the brown band as compound 4a (48.1 mg, 0.048 mmol, 28%), several other minor
by-products could not be separated.

Characterization data for 4a

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (dd $J = 0.9, 7.5$ Hz, 1H), 7.44-7.41 (m, 1H)
7.25 (d, $J = 8.1$ Hz, 1H), 7.11-7.08 (m, 1H), 4.00 (d, $J = 11.0$ Hz, 1H), 3.95 (d, $J = 10.5$ Hz, 1H), 3.74 (d, $J = 10.7$ Hz, 1H), 3.65 (d, $J = 10.8$ Hz, 1H), 3.08-3.04 (m, 1H), 2.93-2.81 (m, 3H), 1.95-1.93 (m, 1H), 1.82-1.80 (m, 2H), 1.68-1.65 (m, 3H), 1.56-1.54 (m, 2H), 1.38-1.36 (m, 2H), 1.04 (d, $J = 5.8$ Hz, 3H), 1.00 (d, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_2$CDCl$_2$) $\delta$ 157.91, 153.74, 152.52, 152.30, 151.50, 150.48, 150.04, 149.82, 149.44, 149.20, 149.08, 148.87, 148.77, 147.98, 147.70, 147.63, 147.49, 147.17, 146.94, 146.85, 146.62, 146.58, 146.33, 145.91, 145.79, 145.73, 145.52, 145.38, 145.16, 145.02, 144.97, 144.82, 144.73, 144.69, 144.52, 144.24, 144.08, 144.04, 143.89, 143.85, 143.69, 143.33, 143.14, 143.12, 142.72, 142.59, 142.37, 141.70, 140.96, 139.83, 138.98, 136.73, 134.57, 134.18, 130.60 (CH), 126.81, 124.90 (CH), 121.97 (CH), 111.32 (CH), 100.75, 77.49, 74.65, 71.21, 65.54, 51.52 (N-CH$_2$), 51.07 (N-CH$_2$), 50.27 (N-CH$_2$), 49.28 (N-CH$_2$), 35.41 (CH$_2$), 35.27 (CH$_2$), 35.14 (CH$_2$), 35.11 (CH$_2$), 30.86 (CH), 30.77 (CH), 22.14 (CH$_3$), 22.04 (CH$_3$).

ESI-FT-ICR-HRMS-Positive C$_{78}$H$_{29}$N$_2$O (M + H$^+$) calculated 1009.2255, found 1009.2274.

A solution of compound 1 (89.3 mg, 0.068 mmol) in 20 mL of toluene was stirred at 60 °C. Then 4-tertbutylphenol (203 mg, 1.4 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 12 h. The solution was directly chromatographed on a silica gel column eluting with toluene to give the brown band as compound 4b (18.0 mg, 0.017 mmol, 25%), several other minor by-products could not be separated.

Characterization data for 4b

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 2.0$ Hz, 1H), 7.45 (dd, $J = 2.0, 8.6$ Hz, 1H), 7.14 (d, $J = 8.5$ Hz, 1H), 4.00 (d, $J = 10.3$ Hz, 1H), 3.94 (d, $J = 10.5$ Hz, 1H), 3.73 (d, $J = 9.8$ Hz, 1H), 3.62 (d, $J = 9.8$ Hz, 1H), 3.08-3.04 (m, 1H), 2.92-2.82 (m, 3H), 1.94-1.92 (m, 2H), 1.82-1.79 (m, 2H), 1.66-1.63 (m, 2H), 1.56-1.54 (m, 4H), 1.33 (s, 9H), 1.04 (d, $J = 5.8$ Hz, 3H), 1.00 (d, $J = 6.3$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.74, 153.02, 152.50, 151.89, 150.60, 150.39, 150.02, 149.62, 149.42, 149.26, 148.95, 148.18, 148.04, 147.90, 147.72, 147.33, 147.22, 147.13, 147.04, 146.76, 146.74, 146.53, 146.11, 145.99, 145.94, 145.90, 145.66, 145.59, 145.49, 145.42, 145.21, 145.15, 145.03, 144.98, 144.87, 144.69, 144.44, 144.32, 144.20, 144.16, 143.99, 143.88, 143.36, 143.32, 142.95, 142.93, 142.73, 142.62, 141.93, 141.18, 139.99, 139.15, 136.87, 134.69, 134.37, 127.91 (CH), 126.27, 121.36 (CH), 110.71 (CH), 74.87, 71.39, 66.04, 51.62 (N-CH$_2$), 51.36 (N-CH$_2$), 50.41 (N-CH$_2$),
A solution of compound 1 (94.1 mg, 0.071 mmol) in 25 mL of toluene was stirred at 60 °C. Then 4-methoxyphenol (177 mg, 1.4 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 12 h. The solution was directly chromatographed on a silica gel column eluting with toluene to give the brown band as compound 4c (16.2 mg, 0.016 mmol, 22%), several other minor by-products could not be separated.

Characterization data for 4c
1H NMR (500 MHz, CDCl3) δ 7.12 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 2.6 Hz, 1H), 6.97 (dd, J = 2.6, 8.8 Hz, 1H), 4.02 (d, J = 5.0 Hz, 1H), 3.94 (d, J = 11.6 Hz, 1H), 3.81 (s, 3H), 3.73 (d, J = 9.9 Hz, 1H), 3.66 (d, J = 9.8 Hz, 1H), 3.08-3.04 (m, 1H), 2.92-2.86 (m, 3H), 1.94-1.93 (m, 1H), 1.82-1.80 (m, 2H), 1.70-1.67 (m, 3H), 1.56-1.54 (m, 2H), 1.41-1.39 (m, 2H), 1.04 (d, J = 5.8 Hz, 3H), 1.00 (d, J = 6.2 Hz, 3H).

13C NMR (126 MHz, CDCl3) δ 155.33, 150.05, 149.64, 149.45, 149.31, 148.98, 148.22, 148.11, 147.87, 147.72, 147.33, 147.13, 147.03, 146.79, 146.75, 146.52, 146.13, 146.00, 145.91, 145.71, 145.61, 145.38, 145.22, 145.03, 145.00, 144.94, 144.69, 144.47, 144.31, 144.24, 144.01, 143.93, 142.97, 142.94, 142.73, 142.57, 141.97, 141.18, 140.02, 139.15, 136.76, 134.77, 127.50, 116.80 (CH), 111.65 (CH), 109.92 (CH), 74.87, 71.41, 66.07, 56.25 (O-CH3), 51.67 (N-CH2), 51.37 (N-CH2), 50.43 (N-CH2), 49.44 (N-CH2), 35.35 (CH2), 35.18 (CH2), 31.01 (CH), 30.94 (CH), 22.14 (CH3), 22.02 (CH3).

ESI-FT-ICR-HRMS-Positive C79H31N2O2 (M + H+) calculated 1039.2368, found 1039.2380.

Preparation of Compound 5
A solution of compound 4a (59.6 mg, 0.059 mmol) in 15 mL of toluene was stirred at 60 °C. Then TBHP (tertbutyl hydroperoxide) (0.8 mL, 65.0% aqueous solution, 5.4 mmol) was added into the solution. The resulting mixture was stirred at 60 °C for 40 min. The solution was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1) to give the orange band as compound 5 (22.3 mg, 0.019 mmol, 32%).

Characterization data for 5
1H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 7.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.00-6.97 (m, 1H), 3.76 (d, J = 11.2 Hz, 1H), 3.68 (d, J = 10.0 Hz, 2H), 3.33 (d, J = 9.5 Hz, 1H), 3.01-2.96 (m, 1H), 2.82-2.77 (m, 1H), 2.52 (m, 2H), 1.92-1.89 (m, 2H), 1.80-1.76 (m, 2H), 1.68-1.62 (m, 2H), 1.50-1.49 (m, 4H), 1.43 (s, 9H), 1.02 (d, J = 6.0 Hz, 3H), 1.00 (s, 9H), 0.90 (d, J
$= 5.7$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.39, 149.47, 149.24, 149.19, 149.09, 148.89, 148.84, 148.60, 148.44, 148.24, 148.07, 147.77, 147.72, 147.59, 147.53, 147.46, 147.31, 147.26, 147.21, 146.86, 146.40, 145.99, 145.78, 145.76, 145.64, 145.47, 144.76, 144.58, 144.12, 144.09, 143.99, 143.72, 143.46, 142.89, 142.59, 142.46, 140.42, 138.35, 135.95, 130.33 (CH), 129.90, 129.18, 129.15, 128.73, 128.37, 127.13, 127.10, 125.44, 124.42 (CH), 121.40 (CH), 111.26 (CH), 82.33, 81.66, 81.41, 81.01, 74.72, 74.67, 71.56, 61.71, 51.80 (N-CH$_2$), 51.52 (N-CH$_2$), 51.43 (N-CH$_2$), 50.51 (N-CH$_2$), 35.36 (CH$_2$), 35.22 (CH$_2$), 30.82 (CH), 30.72 (CH), 26.90 (C(CH$_3$)$_3$), 26.37 (C(CH$_3$)$_3$), 22.16 (CH$_3$), 21.89 (CH$_3$).

ESI-FT-ICR-HRMS-Positive C$_{86}$H$_{47}$N$_2$O$_5$ (M + H$^+$) calculated 1187.3495, found 1187.3479.
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Comment:

Acquisition Date: 11/11/2017 9:28:51 PM
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Operator: Peking University

[Graph showing mass spectra with annotations]

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- N-Rule: ok
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Comment: 
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Instrument: Bruker Solarix XR FTMS
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[Graph showing mass spectrometry data]

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