Supporting information

Head to tail and back to back dimerization of an open-cage fullerene derivative through π-π interaction-based self-assembly

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**Experimental Section**

All reagents were used as received. Dichloromethane (DCM) was distilled from phosphorus pentoxide. Other solvents were used as received. The reactions were carried out in air. The NMR spectra were obtained at 25 °C unless noted. Compound 1 was prepared as previously reported (Q. Y. Zhang, Z. S. Jia, S. M. Liu, G. Zhang, Z. Xiao, D. Z. Yang, L. B. Gan, Z. M. Wang and Y. L. Li, *Org. Lett.*, **2009**, *11*, 2772).

*Caution: A large amount of peroxides is involved in some of the reactions. Care must be taken to avoid possible explosion.*

**Compound 2:**

To a 60 mL DCM solution of compound 1 (54 mg, 0.049 mmol), 40 mg of water was added. After the mixture was stirred for 30 min at 15 °C, 60 mg (0.349 mmol) of TsOH was added. Progress of the reaction was monitored by TLC. After compound 1 was consumed completely in about 8 hours, the reaction mixture was chromatographed on a silica gel column eluting with DCM-ethyl acetate = (50:1) to give some unknown byproducts. Then a dark green band of 2 was eluted with DCM-methanol = (50:1) and evaporated to give 2 as a dark solid (18mg, 0.017mmol, 35%).

$^1$H NMR (CDCl$_3$, 300MHz) $\delta$ 7.73 (d, $j = 6.0$ Hz , 4H), 7.52 (d, $j = 6.0$ Hz , 4H), 1.40 (s, 18H). $^{13}$C NMR (CDCl$_3$, 125MHz) all signals represent 2C except noted.$\delta$ 185.82, 183.79(1C), 150.52, 150.30, 149.88(1C), 149.66, 149.43, 149.10, 148.82(1C), 146.85, 146.79, 146.41, 146.27, 146.11, 145.83, 145.22, 143.68, 143.36, 143.22, 143.11, 142.72, 142.62, 141.84, 137.33, 136.97, 136.08, 133.89, 132.45, 127.60, 125.95, 125.83, 125.69(4C), 124.76(4C), 124.44, 120.09, 34.60, 31.42 (6C). FT–IR (microscope): 2960, 2865, 1746, 1657, 1561, 1494, 1460, 1363, 1268, 1214, 1183, 1154, 1130, 1108, 1030, 979, 929, 840 cm$^{-1}$. ESI-HRMS: m/z calcd for C$_{79}$H$_{27}$N$_2$O$_4$ (M+H$^+$) 1067.1965, found 1067.1982. X-ray structure.
Compound 3:

To a 20 mL DCM solution of compound 2 (9 mg, 0.008 mmol), 40 mg of PCl₅ was added. The color of the mixture changed from green into red at once. The mixture was stirred overnight at 15 °C. Progress of the reaction was monitored by TLC. After compound 2 was consumed completely, the reaction mixture was chromatographed on a silica gel column eluting with DCM-methanol = (50:1). The brown band of the 3 was collected and evaporated to give 3 (7 mg, 0.007 mmol, 78%).

¹H NMR (CDCl₃, 500MHz) δ 8.11(d, J = 8.0 Hz, 2H), 7.77(d, J = 8.0 Hz, 2H), 7.16(d, J = 8.0 Hz, 2H), 6.84(d, J = 8.0 Hz, 2H), 1.49(s, 9H), 1.06(s, 9H). ¹³C NMR (CDCl₃, 125MHz) all signals represent 1C except noted. δ 185.23, 184.67, 183.99, 165.38, 153.10, 150.49, 150.14, 150.03, 149.65, 149.40(2C), 149.24, 149.13(2C), 148.99, 148.47, 148.11, 146.92, 146.52(2C), 146.49(2C), 146.37, 146.24, 146.18, 146.09, 146.03, 146.00(2C), 145.90, 145.48, 145.61, 145.45, 145.16, 143.51, 143.48, 143.35, 143.27, 143.13, 142.83(2C), 142.78, 142.61, 142.59, 142.55, 141.88, 140.53(2C), 138.73, 138.28, 137.66, 137.42, 137.34, 137.15, 133.79, 133.63, 131.61, 131.51, 131.09, 130.42, 130.17, 127.79(2C), 126.26, 126.11(2C), 125.55(2C), 123.00, 120.39(2C), 34.66, 33.92, 31.34(3C), 31.00(3C). FT-IR (microscope): 2959, 2924, 2855, 1743, 1652, 1562, 1515, 1494, 1460, 1391, 1267, 1159, 1132, 1110, 1030, 839, 757, 716 cm⁻¹. ESI-HRMS: m/z calcd for C₇₀H₂₇N₂O₄ (M+H⁺) 1067.1965, found 1067.1912.
SI 7

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12051237_20120931_000001.d
Sample: 7Gm-4BuOeOH Dimer
Comment: ESI Positive
Acquisition Date: 5/31/2012 10:32:00 AM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Ar \quad Ar = 4^\cdot BuC_6H_4

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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12051237_20120831_000001.d
Sample: tcm-4BuO Dimer
Comment: ESI Positive
Acquisition Date: 5/31/2012 10:32:00 AM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

![Mass Spectrum Graph]

Ar = 4-BuC6H4

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$\text{Ar} = 4^t\text{BuC}_6\text{H}_4$
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 11110622_20111115_000001.d
Sample: Ism-GreenDeCHPCISMajor
Comment: ESI Positive

Acquisition Date: 11/15/2011 2:13:12 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

![Mass Spectrum Chart]

Ar = 4-BuC6H4

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X-ray structure of 1a. For clarity solvent molecules CS$_2$ were not drawn in the crystal packing structure. Ellipsoids were at 50%. Color scheme: grey = C, blue = N, red = O.