Supplementary Information

Two new Types of \( \pi \)-Conjugation between a Fullerene Sphere and an Addend.

Floris B. Kooistra, Tessa M. Leuning, Enrique Maroto Martinez, and Jan C. Hummelen

Molecular Electronics, Zernike Institute for Advanced Materials & Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Table of Contents:

General Procedure p 1
UV/VIS Spectroscopy p 3
\(^1\)H NMR Spectroscopy p 10
\(^{13}\)C NMR Spectroscopy p 15
Mass Spectroscopy p 16

**Figure 1:** General Synthetic Scheme (a: R=H, b: R=NO2)

**General Procedure for Diazirine addition:**

A flame-dried three-necked flask equipped with thermometer, condensor, N\(_2\)-inlet, and stirring egg was charged with a solution of C\(_{60}\) in ODCB (20 mg/ml). This solution was thoroughly degassed by 3 N\(_2\)/vacuum purges. The diazirine (5 eq.) was added at once to this solution. The resulting reaction mixture was heated to 60 °C. The reaction was followed by HPLC and stopped at the following conversion: C\(_{60}\): 50%, [6,6]-adduct: 32% and [5,6]-adduct: 5%. The different products were then isolated by preparative HPLC using a Buckycatcher column and cyclohexane/toluene (1:1) as the eluent.
General Procedure for the HCl elimination reaction:
A flame dried flask was charged with a solution of fullerene in ODCB (1mg/ml). This solution was heated to 50 °C and KOtBu (2 eq) was then added at once. The reaction was followed by HPLC. When a conversion of around 85% was reached, the reaction was stopped and the products were purified by the same preparative HPLC procedure as before.

1-benzyl-1-chlorohomofullerene 5a: IR (KBr) = ν (cm⁻¹): 3425 (s), 3060 (m), 3028 (s), 2923 (s), 2851 (m), 1722 (m), 1601 (m), 1495 (s), 1454 (s), 1433 (s), 1380 (m), 1260 (w), 1174 (w), 1033 (m), 747 (s), 697 (s), 527 (s). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 537, 602. Mass m/z calcd. for C₆₈H₇Cl: 858.02. Found: 858.8

1-(p-nitrobenzyl)-1-chlorohomofullerene 5b: UV/Vis (toluene/cyclohexane 1:1); λ (nm): 540, 603. Mass m/z calcd. for C₆₈H₆ClNO₂: 903.01, Found: 903.8

1-benzyl-1-chlorocyclopropafullerene 6a: IR (KBr) = ν (cm⁻¹): 3426 (s), 3026 (w), 1602 (w), 1494 (m), 1465 (m), 1452 (m), 1429 (m), 1385 (w), 1186 (m), 698 (m), 577 (m), 526 (s). ¹H NMR (CS₂ with D₂O insert, 300 MHz); δ (ppm): 7.78 (d, J = 6.9 Hz, 2H), 7.47–7.56 (m, 3H), 4.67 (s, 2H). ¹³C NMR (D₂O/CS₂, 300 MHz); δ (ppm): 39.1, 57.3, 78.8, 127.3, 128.4, 129.7, 130.1, 135.2, 137.0, 138.7, 140.6, 142.7, 142.9, 143.2, 144.0, 144.1, 144.2, 144.4, 144.5, 144.6, 144.7, 144.8, 145.3, 145.6. UV/Vis (toluene/cyclohexane 1:1); λ (nm): 431, 497, 692. Mass m/z calcd. for C₆₈H₇Cl: 858.02. Found: 858.6

1-(p-nitrobenzyl)-1-chlorocyclopropafullerene 6b: IR (KBr) = ν (cm⁻¹): 3424 (s), 1601 (m), 1517 (s), 1430 (m), 1340 (s), 854 (w), 578 (w), 526 (s). ¹H NMR (CS₂ with D₂O insert, 400 MHz); δ (ppm): 8.45 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 4.58 (s, 2H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 438, 490, 685. Mass m/z calcd. for C₆₈H₆ClNO₂: 903.01. Found: 903.3

Benzylidenehomofullerene 7a: UV/Vis (toluene/cyclohexane 1:1); λ (nm): 548, 603, 664. Mass m/z calcd. for C₆₈H₆: 822.04. Found: 822.7

p-Nitrobenzylidenehomofullerene 7b: UV/Vis (toluene/cyclohexane 1:1); λ (nm): 547. Mass m/z calcd. for C₆₈H₆NO₂: 867.03. Found: 867.8

Benzylidendecyclopropafullerene 8a: IR (KBr) = ν (cm⁻¹): 3026 (s), 1538 (w), 1496 (w), 1466 (m), 1452 (m), 1429 (s), 1259 (m), 1188 (s), 1076 (m), 915 (w), 879 (w), 752 (m), 743 (m), 688 (s), 525 (s), 518 (s). ¹H NMR (CS₂ with D₂O insert, 400 MHz); δ (ppm): 8.1 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 6.9 Hz, 2H), 7.54–7.58 (m, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 427, 515, 690. Mass m/z calcd. for C₆₈H₆: 822.04. Found: 822.7

p-Nitrobenzylidendecyclopropafullerene 8b: IR (KBr) = ν (cm⁻¹): 3446 (s), 1597 (m), 1516 (s), 1429 (m), 1340 (s), 1109 (m), 526 (s). ¹H NMR (CS₂ with D₂O insert, 400 MHz); δ (ppm): 8.49 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H), 7.58 (s, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 511. Mass m/z calcd. for C₆₈H₅NO₂: 867.03. Found: 867.7
**UV/VIS spectroscopy**

**Compound 5a**
Compound 5b
Compound 6a
Compound 6b
Compound 7a
Compound 7b
Compound 8a
Compound 8b
$^1$H NMR Spectroscopy

Compound 6a
Compound 8a
Compound 6b
Compound 8b
13C NMR spectroscopy

Compound 6a
Mass Spectrometry

Compound 5a

[Image of mass spectrometry graph with peaks at 704, 728, and 988]
Compound 5b

Print of window 80: MS Spectrum
Compound 6a
Bucky LC-MS Positive APCI Mode

MS Spectrum
"MSD2 SPC, time=5.488,5.623 of FLOR10F0030009.D" APC, P2a, Scan, Flag 30, "Scan"

Max: 4.9679e+006
Compound 6b
Compound 7a
Compound 7b
Compound 8a

Bruker LC-MS Positive APCI Mode

MS Spectrum

Max: 1.4617e+06
Compound 8b