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Supplementary Information

Two new Types of π -Conjugation between a Fullerene Sphere and an Addend.

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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, N₂-inlet, and stirring egg was charged with a solution of C₆₀ in ODCB (20 mg/ml). This solution was thoroughly degassed by 3 N₂/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: C₆₀ : 50%, [6,6]-adduct : 32 % and [5,6]-adduct : 5%. The different products were then isolated by preparative HPLC using a Buckyclutcher 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), 7.47–7.7.56 (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, 140.9, 141.4, 141.7, 141.8, 141.9, 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 C₆₈H₅NO₂: 867.03. Found: 867.8.

Benzylidenecyclopropafullerene 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, 300 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), 7.47 (s, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 427, 515, 690. Mass m/z calcd. for C₆₈H₆: 822.04. Found: 822.7.

p-Nitrobenzylidenecyclopropafullerene 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

^1H NMR Spectroscopy

Compound 6a

Compound 8a

Compound 6b

Compound 8b

¹³C NMR spectroscopy

Compound 6a

Mass Spectrometry

Compound 5a

(modified after loading/
Bucky LC-MS Positive APCI Mode

Compound 5b

Print of window 80: MS Spectrum

Compound 6a

Bucky LC-MS Positive APCI Mode

Compound 6b

Compound 7a

of window 80: MS Spectrum

Compound 7b

of window 80: MS Spectrum

Compound 8a

Bucky LC-MS Positive APCI Mode

Compound 8b