

# Adduct removal from methanofullerenes via reductive electrochemistry

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**Electrochemical reduction of different spiromethanofullerenes leads to adduct removal, opening the way to new protecting–deprotecting groups in fullerene chemistry.**

The Bingel reaction has been used as a synthetic tool for the addition of di(alkoxycarbonyl)methano bridges to fullerenes for several years.<sup>1</sup> The resulting Bingel adducts are relatively stable thermally<sup>2</sup> and under a variety of chemical environments. However, Diederich and Echegoyen recently reported the retro-Bingel reaction, an electrochemical reduction reaction which efficiently removes the cyclopropane ring adduct, resulting in the formation of the parent C<sub>60</sub>.<sup>3</sup> This electrochemical reduction reaction has also been employed successfully on other fullerene systems.<sup>4,5</sup> Before the work reported here, to our knowledge the only fullerene adducts that were removable *via* electrochemical reduction were the Bingel adducts.

Fullerenes substituted with electron-donating and electron-accepting addends have been studied extensively, mainly within the context of developing optically and electronically active systems for potential applications.<sup>6</sup> Previously, Wudl and coworkers described the electrochemical properties of the methanofullerenes **1** and **2**, which bear quinone type addends (Fig. 1).<sup>7</sup> These compounds exhibit irreversible electrochemistry, presumably resulting from the cleavage of one of the cyclopropane bonds connecting the addend to C<sub>60</sub> upon reduction.<sup>8</sup> These observations, coupled with those of the retro-Bingel reaction, motivated the work reported here, to observe the behavior of compounds **1–4** under controlled potential electrolysis (CPE) for potential adduct removal. Compound **3** is similar to the Bingel adduct owing to the presence of the two carbonyls  $\alpha$  to the methano bridge carbon. **4** is structurally and electronically very different from the others, and was used mainly for comparison.

The synthesis of the spiromethanofullerenes **1** and **2** was carried out according to the method previously reported in the literature.<sup>9</sup> Compound **3** was synthesized in two steps from indan-1,3-dione which was transformed into 2-diazoindan-1,3-dione by reaction with tosyl azide under basic conditions. Further reaction of 2-diazoindan-1,3-dione with C<sub>60</sub> in ODCB (*o*-dichlorobenzene) at 120 °C for 4 h afforded spiromethanofullerene **3**<sup>10</sup> in 33% yield (62% based on consumed C<sub>60</sub>). Compound **3** showed the presence of the carbonyl groups as a single signal at  $\delta$  191.7 in the <sup>13</sup>C NMR spectrum, which shows

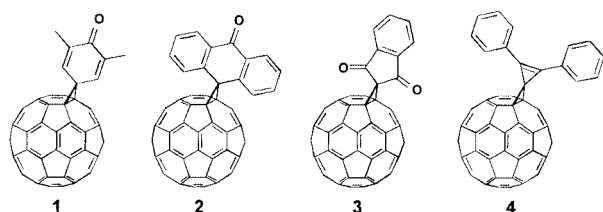


Fig. 1 Novel spiromethanofullerenes for reductive electrochemistry.

the presence of 17 signals, suggesting a C<sub>2v</sub> symmetry. Spiromethanofullerene **4** was obtained from diphenylcyclopropene in two steps, by formation of the tosylhydrazone and further *in situ* generation of the intermediate diazo compound under basic conditions,<sup>11</sup> which reacted with C<sub>60</sub> by heating in ODCB to lead to **4** in 20% yield (46% based on consumed C<sub>60</sub>). Spiromethanofullerene **4** shows a characteristic signal in the FTIR spectrum at 1712 cm<sup>-1</sup> due to the cyclopropene double bond.

The electrochemistry of **1–4** in dichloromethane was studied by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) (Fig. 2 and Table 1).<sup>12,13</sup> The methanofullerenes **1** and **2** both exhibit, besides several reversible electrochemical processes, an irreversible electrochemical reduction wave between the first and third reductions. Compound **3** undergoes a two-electron reduction, followed by two one-

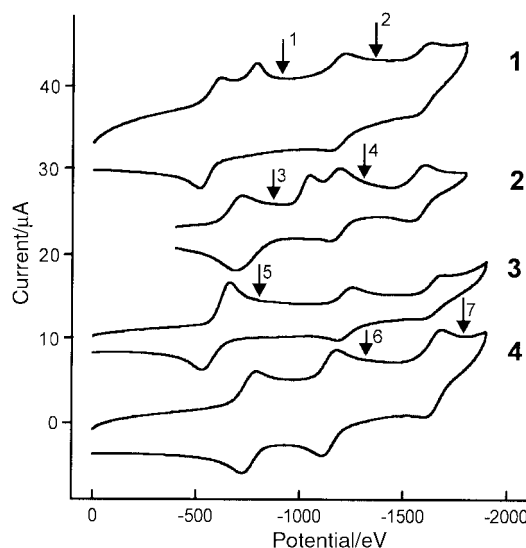


Fig. 2 Cyclic voltammograms of the methanofullerenes **1–4**.

Table 1 Redox potentials of **1–4** vs. ferrocene in dichloromethane<sup>a</sup>

	E <sub>1</sub> /mV	E <sub>2</sub> /mV	E <sub>3</sub> /mV	E <sub>4</sub> /mV
<b>3</b>	–859	–1119 <sup>b</sup>	–1522	–1926
<b>4</b>	–1038	–1383 <sup>b</sup>	–1492	–1893
<b>5</b>	–971 <sup>c</sup>	–1598	–2015	
<b>6</b>	–1035	–1426	–1929	

<sup>a</sup> Electrochemical measurements were performed using a BAS 100W Electrochemical Analyzer (Bioanalytical system), GC working electrode, a Ag wire pseudo-reference electrode and a Pt-mesh counter electrode. NBu<sub>4</sub>PF<sub>6</sub> was used as supporting electrolyte. <sup>b</sup> Electrochemically irreversible. <sup>c</sup> Two-electron process.

electron reductions. By contrast, the reference methanofullerene **4**, which bears no electron accepting addends, has three reversible redox waves.

Typically 2–5 mg of each compound were subjected to CPE. CPE of **1** was performed at a potential *ca.* 100–150 mV more cathodic than the second, irreversible, reduction wave (Fig. 2, arrow 1). This electrolysis consumed *ca.* 3.9 electrons molecule<sup>-1</sup> and induced clear changes in the CV and OSWV, indicating that a chemical reaction had taken place. Subsequent reoxidation at 0 V and purification of the product mixture by column chromatography (eluent toluene) yielded fullerene products in *ca.* 60% yield. Analysis of this mixture by HPLC, UV–VIS spectroscopy and MALDI-TOF spectrometry showed the complete disappearance of the starting material, but no C<sub>60</sub> was isolated. Unfortunately, the structure of the products could not be assigned.<sup>14</sup>

CPE of methanofullerene **2** was initially performed after the first reduction wave in order to completely dissolve methanofullerene **2** in CH<sub>2</sub>Cl<sub>2</sub> (arrow 3, Fig. 2; 1.0 electron molecule<sup>-1</sup>). No changes in the CV or OSWV were observed after electrolysis. Subsequent electrolysis after the third reduction wave (arrow 4, Fig. 2) consumed *ca.* 3.7 electrons molecule<sup>-1</sup>. At that point the cyclic voltammogram had completely changed. This voltammogram exhibited three reversible electrochemical waves. After reoxidation and purification, analysis of the reaction mixture by HPLC and UV–VIS clearly proved the formation of C<sub>60</sub> in a 65% yield. Thus electrolysis leads to the clean and efficient removal of the spiroanthraquinone adduct.

Electrolysis of methanofullerene **3** was performed after the first, two-electron, reduction (arrow 5, Fig. 2; 2.3 electrons molecule<sup>-1</sup>). CV and OSWV clearly showed that chemical processes accompanied the electrochemical reductions.

Reoxidation, purification and subsequent analysis showed the formation of the parent C<sub>60</sub> in a 58% yield.<sup>15</sup>

CPE of methanofullerene **4** after the second reduction (arrow 6, Fig. 2) consumed 2.0 electrons molecule<sup>-1</sup> and is fully reversible: no changes in the cyclic or OSWV voltammogram were observed. Electrolysis after the third reduction wave (arrow 7, Fig. 2; 7.3 electrons molecule<sup>-1</sup>) leads to passivation of the working electrode and to the formation of insoluble and intractable products.

In conclusion, the electrochemical measurements described above show that for all ‘quinone’ type methanofullerenes **1–3**, a chemical reaction occurs after reduction. This reaction leads to the parent C<sub>60</sub> for compounds **2** and **3**, in a ‘retro-Bingel’ like reaction. Thus the range of fullerene adducts that can be removed *via* electrochemical reduction is here extended beyond the Bingel adducts.

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- 9 T. Ohno, N. Martín, B. Knight, F. Wudl, T. Suzuki and H. Yu, *J. Org. Chem.*, 1996, **61**, 1306.
- 10 *Selected spectroscopic data for 3*: FTIR (KBr) 1712, 1515, 1345, 1265, 1232, 739, 529 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.22 (2H, m), 8.02 (2H, m); <sup>13</sup>C NMR [CDCl<sub>3</sub>-CS<sub>2</sub> (1:1), 75 MHz] δ 191.7 (CO), 144.9, 144.8, 144.6, 144.4, 143.7, 143.4, 142.9, 142.0, 141.5, 141.4, 141.3, 140.8, 135.7, 123.2, 77.1, 76.3; UV–VIS (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>(log ε) 290 (4.70), 338 (4.64), 432 (3.34), 510 (3.12) nm; MS (FAB<sup>-</sup>) *m/z*: 864 (M<sup>+</sup>, 55), 720 (C<sub>60</sub>, 80). **4**: FTIR (KBr) 1712, 1461, 1154, 761, 720, 702, 691, 546 cm<sup>-1</sup>; <sup>1</sup>H NMR [CDCl<sub>3</sub>-CS<sub>2</sub> (3:1), 300 MHz] δ 7.65–7.63 (4H, m, ArH), 7.45–7.41 (6H, m, ArH); UV–VIS (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>(log ε) 290 (4.73), 336 (4.58), 438 (3.70), 702 (3.03) nm.
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- 14 HPLC measurements indicated that the polarity of the products is in the range of that for the parent C<sub>60</sub>, rather than around that of the starting methanofullerene **1**. UV–VIS spectroscopy measurements showed a broad band around 450 nm. Furthermore, the main peak in the MALDI-TOF mass-spectrum of the reaction mixture is at *m/z* 890. A separate electrolysis experiment performed after the third reduction potential of methanofullerene **1** (Fig. 2, arrow 2; 4.3 electrons molecule<sup>-1</sup>), leads to a similar result: yield = 65%, main peak in the MALDI-TOF is at *m/z* 890.
- 15 Besides the retro-Bingel product C<sub>60</sub>, 22% of starting material, methanofullerene **3** was also isolated.