Synthesis of \textit{trans}-1, \textit{trans}-2, \textit{trans}-3, and \textit{trans}-4 Bisadducts of C\textsubscript{60} by Regio- and Stereoselective Tether-Directed Remote Functionalization

Sergey Sergeyev, Michael Schär, Paul Seiler, Olena Lukoyanova, Luis Echegoyen, and François Diederich*
Figure 10 (SI). Absorption spectra of (±)-9 (black), (±)-10 (green), (±)-14 (grey), (±)-19 (blue), and (±)-23a (red) in CHCl₃.
Figure 11 (SI). CD spectra of a) (S,S)-2 (red) and (R,R)-2 (black); b) (S,S)-1 (red) and (R,R)-1 (black) in CHCl₃.
**Figure 12 (SI).** CD spectra of (S,S)-22 (red) and (R,R)-22 (black) in CHCl₃.
Figure 13 (SI). $^1$H-NMR spectrum (300 MHz, CDCl$_3$) of (S,S,$^{fs}$A)-9 at 298 K.
Figure 14 (SI). $^{13}$C-NMR spectrum (75 MHz, CDCl$_3$) of (S,S$^{t_s}$A)-9 at 298 K, C(sp$^2$)-region.
Figure 15 (SI). Crystal structure of malonate (±)-13. Atomic displacement parameters obtained at 220 K are drawn at the 30% probability level.
**Figure 16 (SI).** Crystal structure of malonate (±)-22. Atomic displacement parameters obtained at 200 K are drawn at the 30% probability level.
Controlled Potential Electrolysis

The experiments were conducted in CH\textsubscript{2}Cl\textsubscript{2} containing 0.1 M Bu\textsubscript{4}NPF\textsubscript{6} in an H-cell with a glass frit separating the two compartments. The electrolyte and compounds were kept under vacuum. Solvent was independently degassed by 4 freeze- pump-thaw cycles over CaH\textsubscript{2} before it was vapour-transferred directly into the cell. The cell compartment that contained the compound was fitted with a glassy carbon working electrode and a Pt mesh electrode. A silver wire was separated from the solution by a Vycor tip and served as the reference electrode. The other compartment was fitted with a Pt mesh counter electrode.

**Electrolysis of bisadducts (±)-9, (±)-14, and (±)-19**

The experimental results were similar for all three compounds. The fullerene bisadducts were initially reduced using bulk electrolysis around the first reduction wave. The net charge transferred was equivalent to one electron per molecule. The CV and OSWV of the electrochemically produced monoanions were similar to those of the original compounds, with different rest potentials. Electrolysis was continued at the reduction potential for the formation of the dianion. Upon reduction at the second wave, the current did not reach the background level, after transfer of two electrons per molecule. However, the electrolysis was interrupted at that point and the solution was investigated by CV and OSWV. The obvious changes indicated that a chemical reaction had taken place, in agreement with earlier electrochemical studies. The electroreduction of the solution was continued at the same potential and stopped after addition of five electrons. The appearance of new waves can be explained by the
formation of intermediates during the course of the transformation of the bisadducts into C\textsubscript{60}. To complete the reaction, the solution was electrolyzed further at the potential that corresponded to the formation of a trianionic species. After discharging 5 electrons per molecule, the electrolysis was stopped. In the case of \textit{trans}-4 bisadduct (±)-14, the solution turned purple, characteristic for C\textsubscript{60}. The CVs of \textit{trans}-1 and \textit{trans}-2 bisadducts (±)-19 and (±)-9 showed evidence of the presence of species in solution besides C\textsubscript{60}, suggesting that the retro-Bingel reaction proceeds to completion most easily for (±)-14. Upon reoxidation at 0 V and product analysis by TLC, C\textsubscript{60} was recovered as the main product in all cases.
Figure 17 (SI). CVs of 0.15 mM trans-1 bisadduct (±)-19 in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPf$_6$, under vacuum and at room temperature, scan rate 100 mV s$^{-1}$) of the original compound, upon addition of up to 5 e$^-$, and after re-oxidation of the solution.
Figure 18 (SI). OSWVs of 0.15 mM *trans*-1 adduct (±)-19 in CH₂Cl₂ (0.1 M Bu₄NPF₆, under vacuum and at room temperature, scan rate 100 mV s⁻¹) of the original compound, upon addition of up to 5 e⁻, and after re-oxidation of the solution.
Figure 19 (SI). CVs of 0.32 mM trans-2 bisadduct (±)-9 in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, under vacuum and at room temperature, scan rate 100 mV s$^{-1}$) of the original compound, upon addition of up to 5 e$^-$, and after re-oxidation of the solution.
Figure 20 (SI). OSWVs of 0.32 mM trans-2 bisadduct (±)-9 in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, under vacuum and at room temperature, scan rate 100 mV s$^{-1}$) of the original compound, upon addition of up to 5 e$^-$, and after re-oxidation of the solution.
Figure 21 (SI). CVs of 0.45 mM trans-4 bisadduct (±)-14 in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, under vacuum and at room temperature, scan rate 100 mV s$^{-1}$) of the original compound, upon addition of up to 5 e$^-$, and after re-oxidation of the solution.
Figure 22 (SI). OSWVs of 0.45 mM \textit{trans}-4 bisadduct (±)-14 in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, under vacuum and at room temperature, scan rate 100 mV s$^{-1}$) of the original compound, upon addition of up to 5 e$^-$, and after re-oxidation of the solution.