TETHER-DIRECTED REGIOSELECTIVE SYNTHESIS OF AN \textit{EQUATORIALFACE} BISADDUCT OF AZAFULLERENE USING \textit{CYCLO-[2]-OCTYLMALONATE}

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We have synthesized and fully characterized the first bisadduct of heterofullerene C\textsubscript{59}N, exploiting a tether-directed remote functionalization strategy. \textit{Cyclo-[2]-octylmalonate} tether was added on the C\textsubscript{59}N cage via a Mannich-type reaction, followed by an intramolecular iodine-catalyzed Bingel cyclopropanation reaction, which afforded a single bisadduct. \textsuperscript{13}C NMR spectroscopy unveiled the \textit{C\textsubscript{1}} symmetry of the formed bisadduct, while X-ray single crystal analysis revealed an \textit{equatorialface} addition pattern which is inherently chiral. The \textit{equatorialface} bisadduct has distinct absorption features, which constitute signatures for the identification of such a bisaddition pattern along the C\textsubscript{59}N cage.

Interestingly, the addition of the second malonate unit upshifts the LUMO level of the bisadduct above that of the parent (C\textsubscript{59}N)\textsubscript{2} by 0.08 eV. The latter is a remarkable change on the electron accepting properties of the C\textsubscript{59}N cage. Despite C\textsubscript{59}N is the most explored heterofullerene, it lacks designing strategies towards the regioselective synthesis of bisadducts with desired electronic properties. The regioselective synthesis of C\textsubscript{59}N bisadducts addresses the quest for molecular manipulation towards efficient fullerene-based electron acceptors. The influential benefits of this strategy could be further exploited to manipulate the band structure of heterofullerene cages by the integration of different addition patterns.