TETHER-DIRECTED REGIOSELECTIVE SYNTHESIS OF AN EQUATORIAL_{FACE} BISADDUCT OF AZAFULLERENE USING CYCLO-[2]-OCTYLMALONATE

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We have synthesized and fully characterized the first bisadduct of heterofullerene $C_{59}N$, exploiting a tether-directed remote functionalization strategy. *Cyclo*-[2]-octylmalonate tether was added on the $C_{59}N$ cage *via* a Mannich-type reaction, followed by an intramolecular iodine-catalyzed Bingel cyclopropanation reaction, which afforded a single bisadduct. ¹³C NMR spectroscopy unveiled the C_1 symmetry of the formed bisadduct, while X-ray single crystal analysis revealed an *equatorial_{face}* addition pattern which is inherently chiral. The *equatorial_{face}* bisadduct has distinct absorption features, which constitute signatures for the identification of such a bisaddition pattern along the $C_{59}N$ cage.



Interestingly, the addition of the second malonate unit upshifts the LUMO level of the bisadduct above that of the parent $(C_{59}N)_2$ by 0.08 eV. The latter is a remarkable change on the electron accepting properties of the $C_{59}N$ cage. Despite $C_{59}N$ is the most explored heterofullerene, it lacks designing strategies towards the regioselective synthesis of bisadducts with desired electronic properties. The regioselective synthesis of $C_{59}N$ 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.

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