

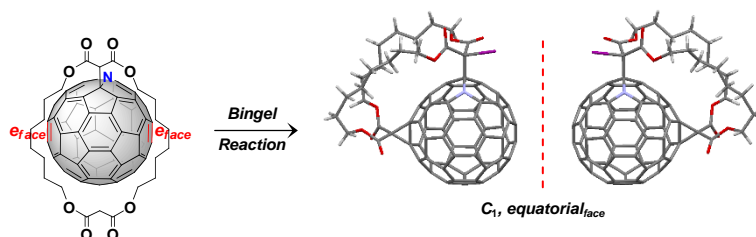
TETHER-DIRECTED REGIOSELECTIVE SYNTHESIS OF AN *EQUATORIAL*_{FACE} BISADDUCT OF AZAFULLERENE USING *CYCLO*-[2]-OCTYLMALONATE

Anastasios Stergiou^a, Karam Asad^b, Andreas Kourtellaris^b, Nikos Tagmatarchis^a,
and Nikos Chronakis^b

^aTheoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
11635 Athens, Greece

^bDepartment of Chemistry, University of Cyprus, 2109 Nicosia, Cyprus

We have synthesized and fully characterized the first bisadduct of heterofullerene C₅₉N, exploiting a tether-directed remote functionalization strategy. *Cyclo*-[2]-octylmalonate tether was added on the C₅₉N 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 C₁ 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 C₅₉N cage.



Interestingly, the addition of the second malonate unit upshifts the LUMO level of the bisadduct above that of the parent (C₅₉N)₂ by 0.08 eV. The latter is a remarkable change on the electron accepting properties of the C₅₉N cage. Despite C₅₉N is the most explored heterofullerene, it lacks designing strategies towards the regioselective synthesis of bisadducts with desired electronic properties. The regioselective synthesis of C₅₉N 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.

[1] A. Stergiou, K. Asad, A. Kourtellaris, N. Chronakis,* and N. Tagmatarchis,* *Chem.-Eur. J.*, doi: 10.1002/chem.201900273.