# Controlling Ground-State Multiplicity of Polycyclic Aromatic Hydrocarbons by Topological Design

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The topologically tailored degrees of freedom in the spin configuration of π-conjugated systems enable the stabilization of either highest or intermediate spin states through an appropriate structural design of the σ-framework of polycyclic aromatic hydrocarbons (PAHs). As demonstrated in recent work in our group [1-4], increasing the delocalization energy within specific electronic configurations — achieved by incorporating additional (pro)aromatic rings into the polyradical(oid) framework without altering the underlying topology — can promote the emergence of a high-spin ground state (GS) [3]. At the same time, the peculiar topology of alternant versus non-alternant π-systems exerts a decisive influence on the GS electronic structure and the resulting low-energy spin spectrum, making topology an essential design parameter. Building on these principles, we formulate a general-purpose topological model —the Topologically Rational Assembly of Polyradicals (TRAP) method [3,4] — which establishes rules for π-conjugated hydrocarbons that enable the controlled design of the number of unpaired electrons, ground-state multiplicity, and ordering of spin states in the spin spectrum. This framework provides a unifying strategy for rational molecular engineering of fully π-conjugated organic polyradicals, applicable to both alternant and non-alternant systems. The TRAP approach provides an interesting tool for the creation of nanostructured graphenic systems —including nanostripes and nanoflakes— with electronic and magnetic properties difficult to rationalise in terms of classical rules of alternancy and aromaticity. Such systems are of potential interest for organic electronics, spintronics, biosensing, and single-molecule functional devices, where tailored open-shell character and controlled spin multiplicity are key design targets. A variety of non-alternant and quasi-alternant polyradicals with well-defined ground states have already been designed as illustrative applications of the model.[4]

References

[1] Betkhoshvili, S.; de P. R. Moreira, I.; Poater, J.;Bofill, J. M. Pathway to Polyradicals: A Planar and Fully π-Conjugated Organic Tetraradical(oid). J. Phys. Chem. Lett. 15, (2024) 5243

[2] Betkhoshvili, S.; de P. R. Moreira, I.; Poater, J.;Bofill, J. M. Leap from Diradicals to Tetraradicals by Topological Control of π-Conjugation. J. Org. Chem. 89 (2024)14006.

[3] Betkhoshvili, S.; de P. R. Moreira, I.; Poater, J.;Bofill, J. M.Algorithmic Design of Metal-Free Fully π-Conjugated Organic Polyradicals with Any Ground-State Multiplicity. J. Phys. Chem. C 129 (2025) 4464.

[4] Betkhoshvili, S.; de P. R. Moreira, I.; Poater, J.;Bofill, J. Fully Conjugated Heteroatomic Non- and Quasi-Alternant Polyradicals. Chemistry, 7(2025) 1.