Singlet-triplet energy gaps modulation of Diindeno [1,2-b: 1'2'-g] anthracene molecular family

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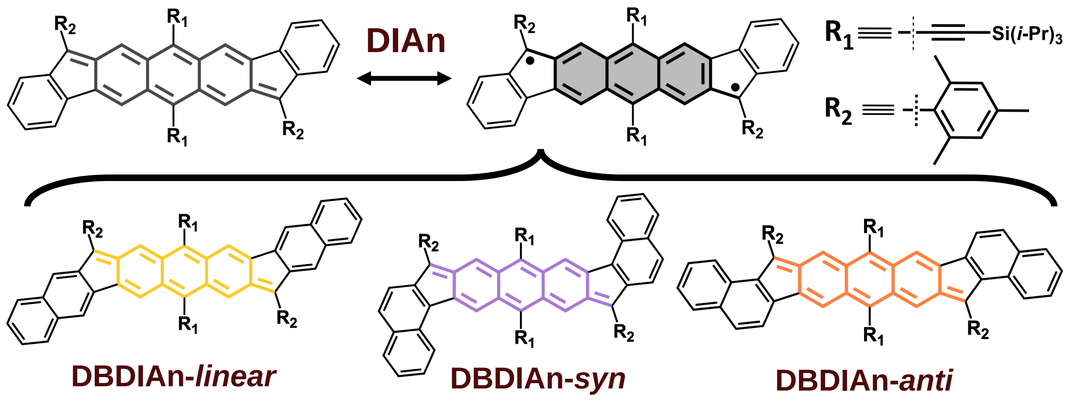
XVIII SIMPOSIO DE JÓVENES INVESTIGADORES QUÍMICOS SEVILLA 2022

INTRODUCTION



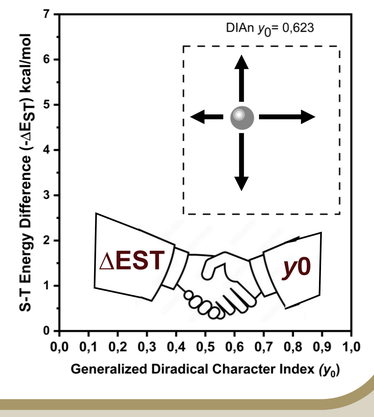
Diradical polycyclic aromatic hydrocarbons (PAHs) offer unique properties to be use in organic electronic and magnetic materials. DIAn close shell form has a characteristic antiaromatic moiety. The diradical formation produces the core aromatization that exhibit remarkable stability [1].

TARGET

Modulation of the ΔEST

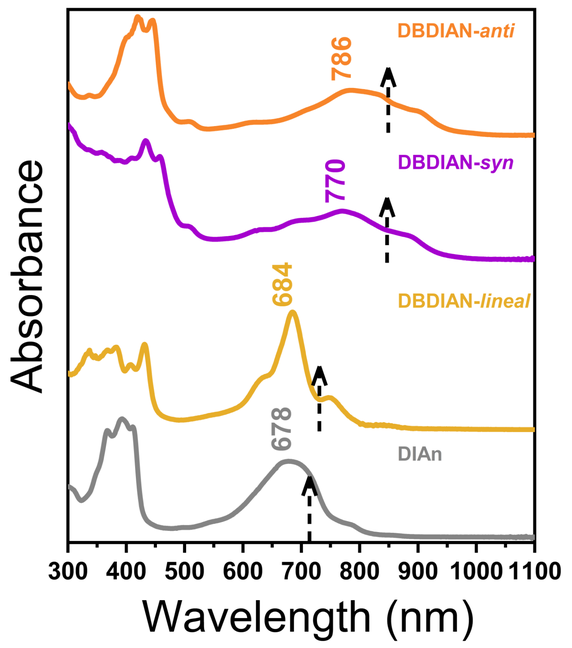
1) Extension of the molecule with another fused benzene (i.e., forming terminal napthalenes)

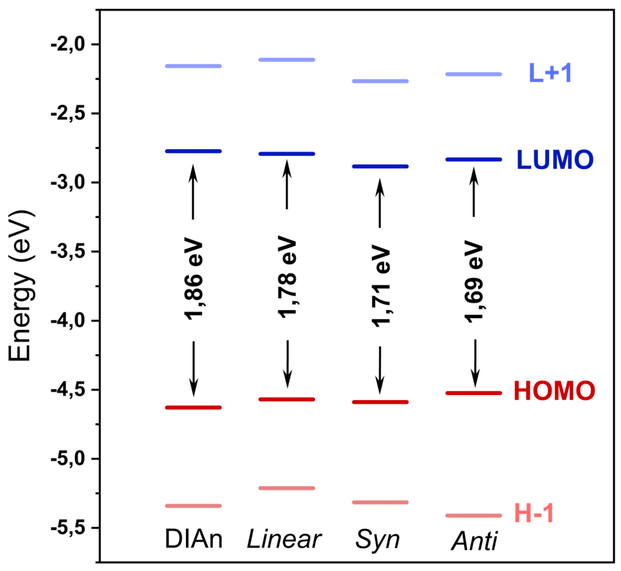
2) Isomerization resulting from the fusion topology of these terminal benzenes [2].

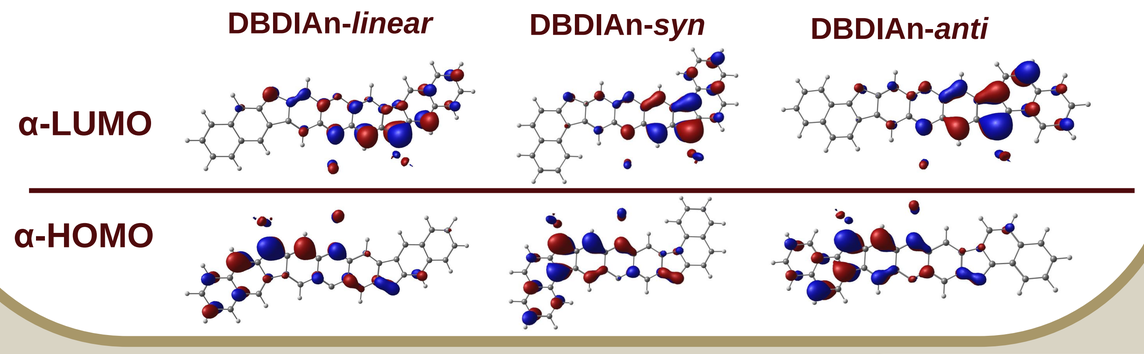


ELECTRONIC STRUCTURAL CHARACTERIZATION

UV-VIS-NIR ELECTRONIC ABSORBTION, ENERGY DIAGRAM AND TOPOLOGY OF FRONTIER MOLECULAR ORBITALS.



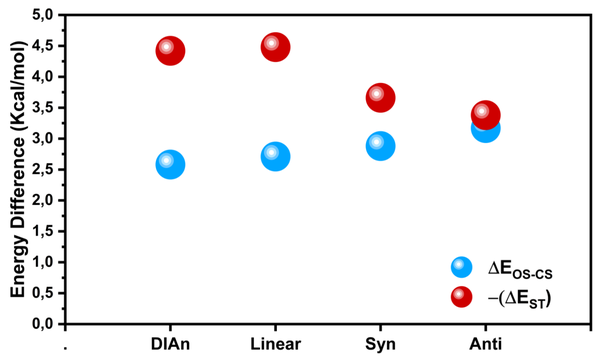


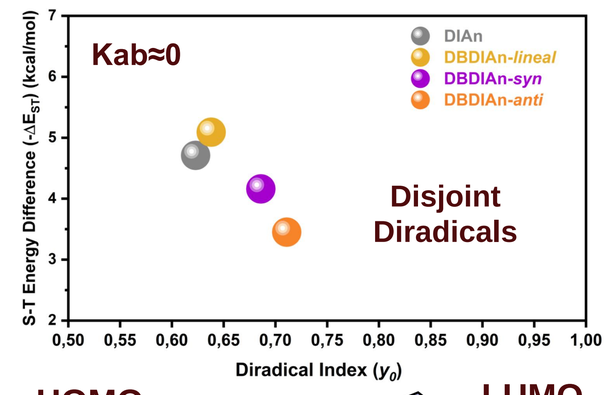


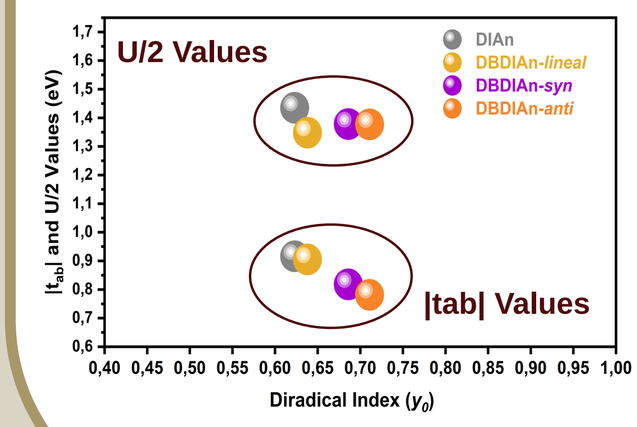
THE "TWO ELECTRONS IN TWO SITES" MODEL

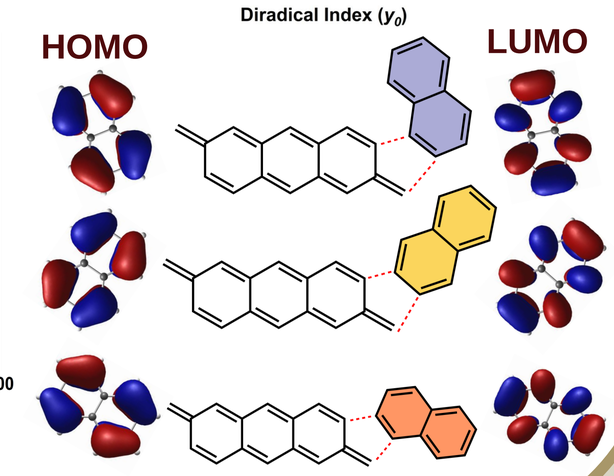
$$y_0 = 1 - \frac{1}{\sqrt{1 + (\frac{U}{4t_{ab}})^2}}$$

$$\Delta E_{ST} = \frac{U}{2}\left[1 - \frac{1}{\sqrt{y_0(2 - y_0)}}\right] + 2K_{ab}$$



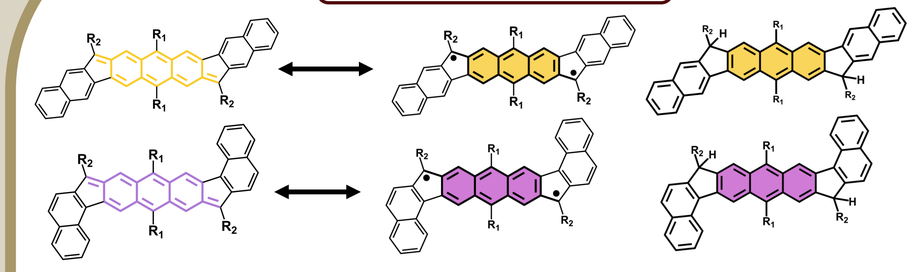


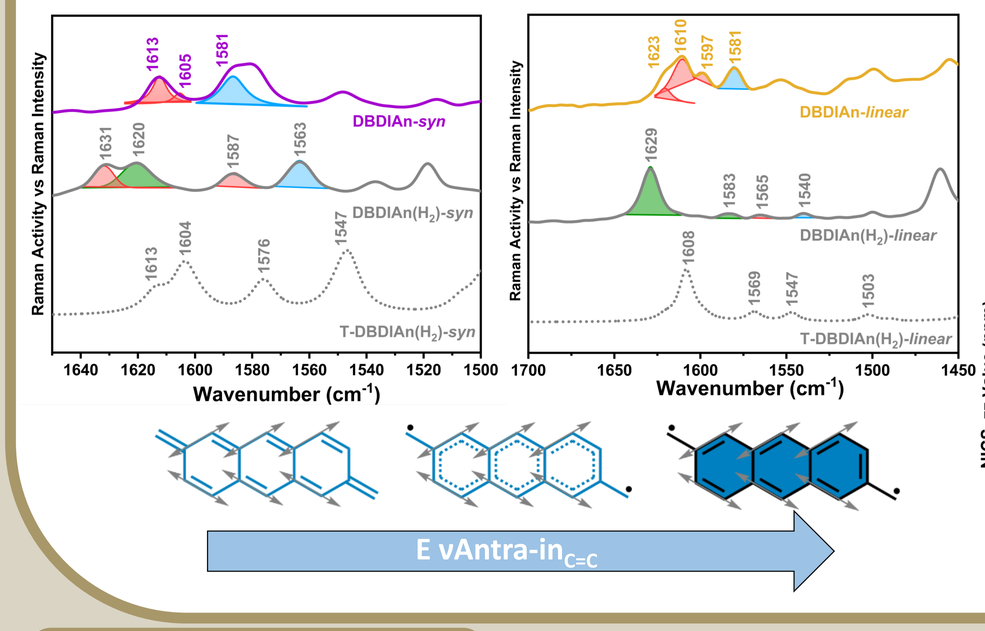




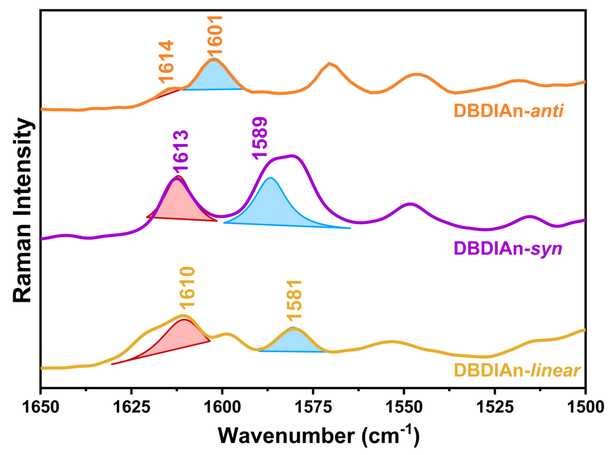
MOLECULAR STRUCTURAL CHARACTERIZATION

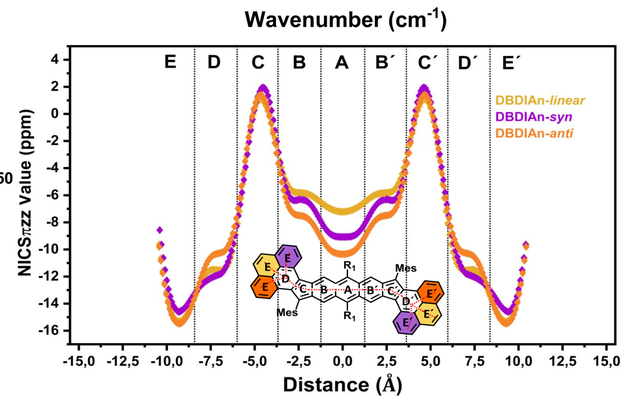
RAMAN ASSIGNMENT



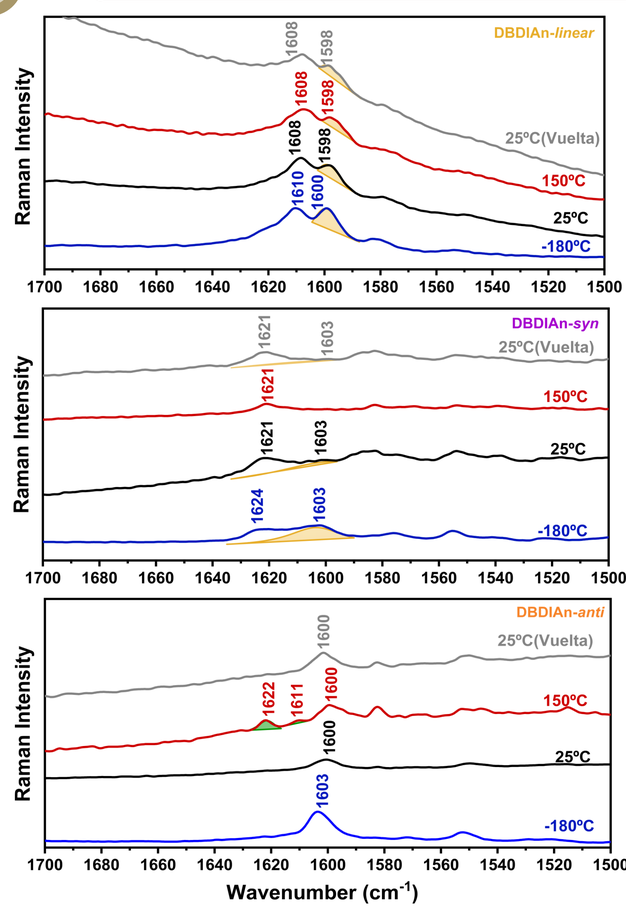


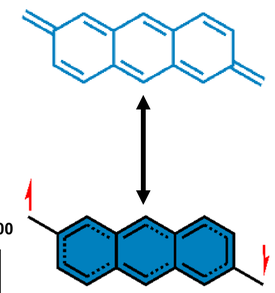
RAMAN SPECTRA AND NICS VALUES



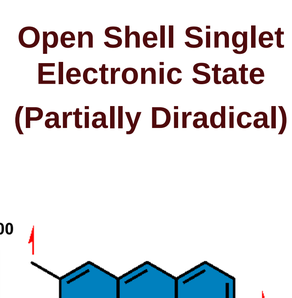


TEMPERATURE INFLUENCE IN THE VIBRATIONAL RAMAN SPECTROSCOPY





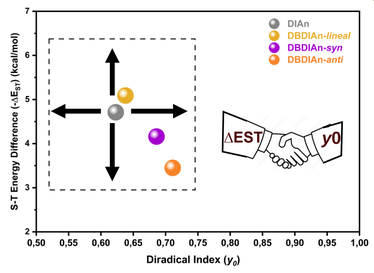
Open Shell Singlet Electronic State (Partially Diradical)



Triplet Electronic State (Fully Diradical)

CONCLUSIONS

In conclusion we carry out a complete study of the electronic and molecular structure characterization together with model quantum chemical calculations. Based on the 2 electron in 2 sites model, the diradical character is dictated by two electronic parameters, the repulsion term U and the transfer integral, tab. Here, we have shown how to design new diradicaloids based on the fine-tuning of the transfer integral term using structure refinement of a series of molecules containing a common 2,6-anthracene conjugation of the two radical centers. We were able to incrementally and rationally tune the singlet-triplet energy gap of the DBDIAn series over a narrow 1.6 kcal·mol-1 range. As demonstrated by this study, we are aiming to produce real, synthesizable compounds with tailored singlet-triplet energy gaps for specific organic electronic applications.



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[1] Diindeno-fusion of an anthracene as a design strategy for stable organic biradicals. Gabriel E. Rudebusch, José L. Zafra, Kjell Jorner,, Jonathan L. Marshall, Iratxe Arrechea-Marcos, Guzmán L. EKotaro Fukudaspejo, Rocío Ponce Ortiz, Carlos J. Gómez-García, Lev N. Zakharov, Masayoshi Nakano Henrik Ottosson Juan Casado and Michael M. Haley, Nature Chem.,2016,

[2] Diindenoanthracene Diradicaloids Enable Rational, Incremental Tuning of Their Singlet- Triplet Energy Gaps, J.J Dressler, A. Cardenas Valdivia, R. Kishi, G.E. Rudebusch, A.M. Ventura, B.E. Chastain, C.J. Gomez-Garcia, L.N. Zakharov, M. Nakano, J. Casado, M.M. Haley, Chem, 2020, 6, 1353−1368.