Tuning the Diradical Character and Singlet-Triplet Energy Gap in Diindenoanthracene Derivatives

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Over the last few years we have been utilizing the indenofluorene scaffold[1] and, more recently, pi-extended derivatives[2] to explore diradical character on a fundamental level. Altering either the center acene core or the outer arene unit results in molecules with varying diradical character values (y) while also changing the singlet-triplet energy gap (ΔE_{ST}) of the resultant diradicaloids. Although the literature in recent years has seen a huge increase in the number of new diradicaloids with unique properties, there are very few cases in which modifications are made to the original scaffolds after their initial publication to refine or change the singlet-triplet energy gap or the y index. This is often due to the inherent instability and complex synthesis of such molecules, which makes modification of the original molecule difficult. If the posited applications for organic diradicals are to come to fruition, the ability to incrementally change these properties while maintaining stability will be crucial. To that end computations on a series of modified diindenoanthracene derivatives illustrate the potential to tune these properties incrementally (Figure 1). In the interest of exploring these small changes in y and singlet-triplet gap from an experimental standpoint, the synthesis of these molecules and examination of their chemical, magnetic, and optoelectronic properties will be presented.

Linear Dibenzo-DIAn
BO = 1.33
y = 0.63
ΔE_{ST} = 5.27 kcal mol^{-1}

DIAn
BO = 1.5
y = 0.62
ΔE_{ST} = 5.42 kcal mol^{-1}

Syn Dibenzo-DIAn
BO = 1.66
y = 0.68
ΔE_{ST} = 4.99 kcal mol^{-1}

Anti Dibenzo-DIAn
BO = 1.66
y = 0.70
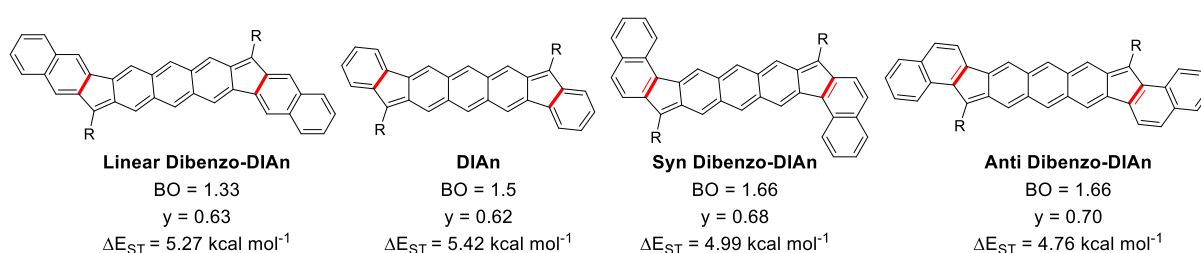ΔE_{ST} = 4.76 kcal mol^{-1}

Figure 1. Diindenoanthracene derivatives examined in this study.

1. Frederickson, C. K.; Rose, B. D.; Haley, M. M. *Acc. Chem. Res.* **2017**, *50*, 977-987.
2. Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce-Ortiz, R.; Gomez-Garcia, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. *Nat. Chem.* **2016**, *8*, 753-759.