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TOWARD π -EXTENDED PORPHYRIN, ALTERNATIVE ROUTE TO FUSED UNACTIVATED AROMATIC RINGS BY THERMAL CYCLODEHYDROGENATION

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Abstract: π -extended molecular systems are of great interest according to their optical properties and more specifically due to their strong absorption and emission in NIR region. These systems may find applications in organic electronic (solar cells, photodetectors, light-emitting-diodes, thin film transistors, etc.). To reach a bathochromic shift, it is required to fuse precursors' aromatic rings which is usually performed by standard Scholl reaction using oxidative agents such as FeCl₃, AuCl₃ etc. However, this method presents some limitations such as partial fusion, chlorination or in some cases do not proceed as in the case for pyridyl-disubstituted dibenzo[5]helicene¹. Fused-porphyrins are good candidates for NIR optical application as the porphyrin core intrinsically presents a strong absorption in visible region. Although, the fusion of porphyrin with Polycyclic Aromatic Hydrocarbons (PAHs) undergoes direct red-shift to NIR region. However, the Scholl reaction on such porphyrins succeed only under very specific conditions. Indeed, as demonstrated by Yamane et al. in 2004, the fusion occurred only when porphyrin is metallated with nickel and PAHs activated with donor groups². Unfortunately, the metalation of porphyrin with nickel causes fast deactivation of the porphyrin excited stated while the substitution with donor groups drastically limits to tune the periphery of the molecule. In 2012, Thompson et al. proposed an alternative method to fuse porphyrin with PAHs in a single step by thermal cyclodehydrogenation³ without nickel metalation or donor substituents on the aromatic moieties. The solubility and processability of fused compounds were conserved but a mixture of syn/anti isomers was reported due to asymmetric PAH studied.

The interesting optical properties of tetraanthracenylporphyrin (TAP) has been described by Anderson et al. with the fusion of [5,10,15,20-[4,5-bis-(2,4,6-trimethylphenoxy)anthracene]porphyrinato]nickel(II)⁴. Nevertheless, the fusion was achieved by Scholl reaction and proceeded only under the very specific conditions mentioned above.

I present the results obtained for the fusion of nickel free and unactivated TAP using the alternative thermal cyclodehydrogenation method (figure 1). The use of symmetric anthracene moieties fused with porphyrin allows to encompass the problem of syn/anti isomers which leads to a single fused product. Finally, thermal cyclodehydrogenation could be used as alternative method to prepare graphene quantum dots from polyphenylene molecules, which do not react under standard Scholl condition.

References

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