



HAL
open science

Toward π -extended porphyrin, alternative route to fused unactivated aromatic rings by thermal cyclodehydrogenation

Joffrey Pijeat, Stéphane Campidelli

► To cite this version:

Joffrey Pijeat, Stéphane Campidelli. Toward π -extended porphyrin, alternative route to fused unactivated aromatic rings by thermal cyclodehydrogenation. Chem2DMat, Aug 2017, Strasbourg, France. cea-02340904

HAL Id: cea-02340904

<https://cea.hal.science/cea-02340904>

Submitted on 31 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Toward π -extended porphyrin, alternative route to fused unactivated aromatic rings by thermal cyclodehydrogenation

J. PIJEAT and **S. CAMPIDELLI**

Laboratoire d'Innovation en Chimie des Surfaces et Nanosciences (LICSEN), NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette cedex, France
Joffrey.pijeat@cea.fr

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 FeCl_3 , AuCl_3 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 state 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.

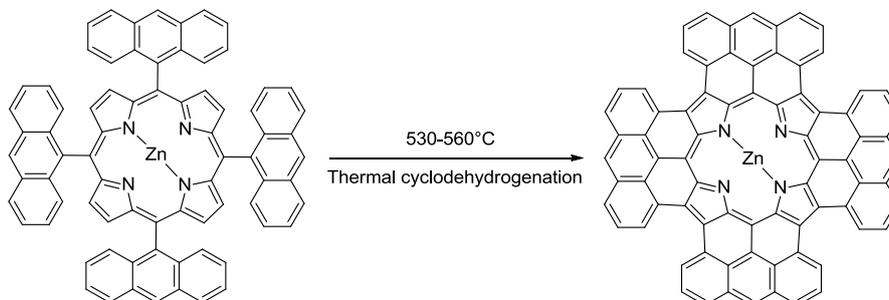


Figure 1 : Thermal cyclodehydrogenation of tetraanthracenylporphyrin (TAP)

1. O. Yamane, K. Sugiura, H. Miyasaka, et al. *Chemistry letters*, **2003**, 33 (1), 40–41.
2. A.L. Pinardi, J.I. Martinez, A. Jancaric et al. *Chemical Communications*, **2014**, 50 (13), 1555.
3. V.V. Diev, C.W. Schlenker, K. Hanson et al. *The Journal of Organic Chemistry*, **2012**, 77 (1), 143–159.
4. N.K.S. Davis, A.L. Thompson, and H.L. Anderson, *Journal of the American Chemical Society*, **2011**, 133 (1), 30–31.