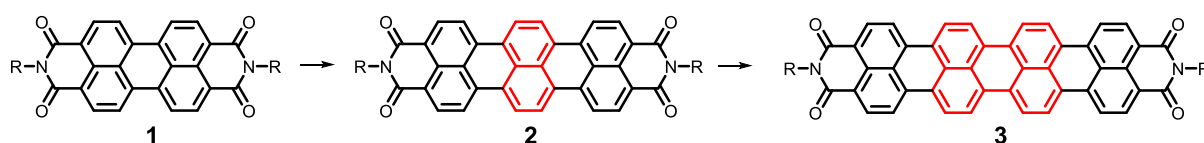


Towards the larger rylenes



Perylene 3,4,9,10 tetracarboxylate derivatives, like the perylenebisimide (**1**) depicted above, are fantastic molecules with excellent physicochemical properties. They are the most stable organic chromophores known to (and made by) man and they are highly fluorescent with fluorescence quantum yields close to unity.¹ Due to various commercial applications, the starting material for their synthesis is affordable and readily available. Most synthetic challenges, linked to limited solubility and non-specific substitution at bay and peri positions, have been resolved.²

For many applications, both energy and bio related, inducing a shift in absorption and emission wavelength towards the near IR, while retaining the excellent physicochemical properties, is highly desirable. For that reason the “higher rylenes”, being terrylene (**2**) and quarterrylene (**3**) are in high demand, provided there is a decent synthesis for them.³

This proposal aims at finding an efficient and affordable synthetic scheme for terrylene and quarterrylene tetracarboxylic acid derivatives like **2** and **3**. Care will be taken to assure good solubility during all stages of the synthesis of **2** and **3**, and to gain control over the substitution pattern of these compounds.

This proposal contains challenging organic synthesis and spectroscopy. For this reason it is best suited for a MSc project.

¹ Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386–2407.

² (a): Highly Efficient Synthesis of Regioisomerically Pure 1,7-Dibromo Perylene-3,4,9,10-Tetracarboxylic Acid Derivatives. Sengupta, S; Dubey, R. K.; Hoek, R. W. M.; van Eeden, S. P. P.; Gunbaş, D. D; Grozema, F. C.; Sudhölter, E. J. R.; Wolter F. Jäger. *J. Org. Chem.* **2014**, *79*, 6655-6662. (b): Novel Derivatives of 1,6,7,12-Tetrachloroperylene-3,4,9,10-Tetracarboxylic Acid: Synthesis, Electrochemical and Optical Properties. Rajeev K. Dubey, Nick Westerveld, Ernst J. R. Sudhölter, Ferdinand C. Grozema and Wolter F. Jäger. *Org. Chem. Frontiers*, **2016**, *3*, 1481-1492.

³ *Quarterrylenetetracarbonsaurediimide*. Quant, H.; Müllen, K. *Angew. Chem.* **1995**, *107*, 1487-1489. *Terryleneimides: New NIR Fluorescent Dyes*. Holtrup, F.; Müller, G. R. J.; Quante, H.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **1997**, *3*, 219-225. *Pentarylene- and Hexarylenebis(dicarboximide)s: Near-Infrared-Absorbing Polyaromatic Dyes*. Pschirer, N. G.; Kohl, C.; Nolde, F.; Qu, J.; Müllen, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 1401-1404.