

A synthetic approach for the synthesis of a naphthalocyanine derivative self-prevented from aggregation

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Abstract

A synthetic approach for the synthesis of a naphthalocyanine derivative self-prevented from aggregation is described, using 3,4-dicyano-1,6-methano[10]annulene (**7**) and phthalonitrile **9** as building blocks.

Introduction

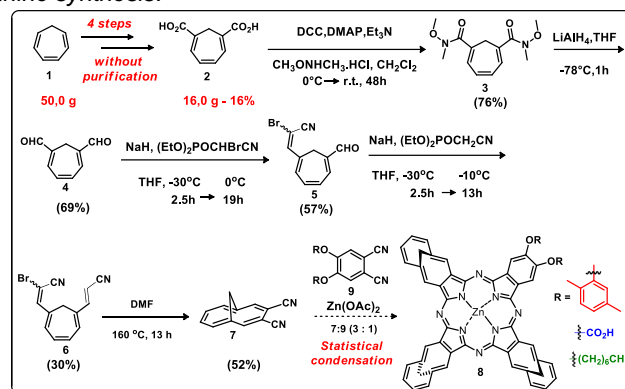
Naphthalocyanines are one of the major types of heterocyclic dyes with a highly π -conjugated system, allowing absorption in the near-infrared spectra.¹ Photosensitizers with absorption above 700 nm show a wide range of applications in materials science, medicine and catalysis.^{1,2}

Generally, methodologies for naphthalocyanine synthesis start from the traditional cyclotetramerization of building blocks such as naphthalonitriles and naphthalimides.² However, non-substituted naphthalocyanines present limitations for use in some applications, because of their tendency to undergo aggregation (π -stacking interactions), leading to poor solubility in most known organic solvents and poor photochemical properties.

Compounds such as 3,4-dicyano-1,6-methano[10]annulene (**7**) should present similar behavior to naphthalocyanine precursors, with the advantage of the methylene bridge presence, which should avoid aggregation, thus increasing the solubility. Numerous non-symmetrical naphthalocyanine derivatives present low aggregation, and improved photophysical and photochemical properties compared to symmetrical ones. Herein, we propose to obtain a new non-symmetrical naphthalocyanine with absorption up to 700 nm, by using 3,4-dicyano-1,6-methano[10]annulene (**7**) and phthalonitrile **9** as building blocks.

Results and Discussion

Diacid **2** was synthesized on a decagram scale from cycloheptatriene (**1**) in 16% overall yield and with no need of purification (Scheme 1).³ The diacid **2** was then converted into the respective Weinreb diamide **3** in 76% yield, after column chromatography. Reduction of **3** with LiAlH_4 in THF furnished dialdehyde **4** on a 3.0 g scale, in 69% yield after crystallization.



Scheme 1. Synthetic route to non-aggregating naphthalocyanine derivative **8**.

Dialdehyde **4** was converted into the mono-aldehyde **5** by a chemoselective HWE olefination ($\text{NaH}/(\text{EtO})_2\text{POCHBrCN}$) in 57% yield after column chromatography. A second HWE olefination ($\text{NaH}/(\text{EtO})_2\text{POCH}_2\text{CN}$) furnished **6** in 30% yield. The annulene **7** was obtained after a one-pot electrocyclic cyclization followed by loss of HBr , in 52% yield after chromatography.⁴ Annulenenitrile **7** and phthalonitrile **9** are being submitted to cyclotetramerization to furnish a new non-aggregating unsymmetrical naphthalocyanine **8**.

Conclusion

Annulenenitrile **7** was successfully synthesized. We are now attempting to improve the yield of **6**, and carry out the remaining steps of the proposed synthesis to **8**.

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¹ Muranaka, A.; Yonehara, M.; Uchiyama, M.; *J. Am. Chem. Soc.* **2010**, *132*, 7844.

² Lukyanets, E. A.; Nemykin, V. N. *J. Porphyrins Phthalocyanines* **2010**, *14*, 1.

³ Vogel, E.; Schäfer-Ridder, M.; Wagner, A. "Neue cycloheptatrienverbindungen und verfahren zur herstellung von cyclo-heptatrienverbindungen" EP 0011669A1, Apr 30, 1979.

⁴ Sarmah, C. S.; Katak, J. C. S. *Indian J. Chem.* **1993**, *32B*, 1149.