



# Cross-coupling reactions as a strategy for Naphthalocyanine synthesis

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## INTRODUCTION

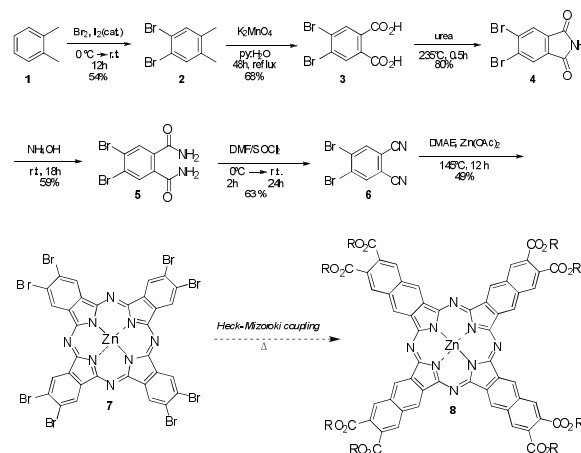
Naphthalocyanines are a third order class of photosensitizers with a highly  $\pi$ -conjugated system, allowing absorption in near-infrared spectra.<sup>1</sup> Photosensitizers with absorption over 700 nm are useful for applications in many areas such as photodynamic therapy (PDT), solar cells, semiconductors, catalysis and others.<sup>2,3</sup>

Due to these potential applications, methodologies for naphthalocyanine synthesis start from the traditional cyclotetramerization of building blocks such as naphthalonitriles and naphthalimides. This sometimes limits functionalizations, and results in poor yields due to the drastic conditions required. Therefore, the development of new methods which permit structural modifications, and also the enhancement of the photophysical and photochemical properties, are under study in our research group.<sup>4</sup> Herein we propose to obtain naphthalocyanines by cross coupling reactions of halogenated phthalocyanines and vinylic esters, followed by one-pot electrocyclic reactions.

## RESULTS AND DISCUSSION

Our approach started with the synthesis of the building block **6** (Scheme 1). First, selective bromination of *o*-xylene (**1**) ( $0^{\circ}\text{C} \rightarrow \text{r.t.}$ , overnight, 54% yield)<sup>5a</sup> to compound **2**, was followed by oxidation to diacid **3** ( $\text{K}_2\text{MnO}_4/\text{py}:\text{H}_2\text{O}$ , reflux, 48h) in 68% yield.<sup>5b</sup> Compound **3** was heated at  $235^{\circ}\text{C}$  in the presence of urea (no-solvent) furnishing the corresponding phthalimide **4** in 80% yield.<sup>5c</sup> Diamide **5** was obtained from **4** using a concentrated ammonium hydroxide solution at room temperature (59% yield).<sup>5d</sup> Finally, phthalonitrile **6** was obtained in 63% yield by reacting **5** with  $\text{DMF}/\text{SOCl}_2$  ( $0^{\circ}\text{C} \rightarrow \text{r.t.}$ ).<sup>5e</sup>

Heating phthalonitrile **6** in standard conditions in *N,N*-dimethylethanolamine (DMAE) and with zinc acetate, furnished octabromophthalocyanine **7** in 49% yield.<sup>5f</sup> We are now investigating cross-coupling reactions involving compound **7** and vinylic esters.



Scheme 1. Synthetic route for naphthalocyanines.

## CONCLUSION

Octabromophthalocyanine **7** has been synthesized successfully. Cross-coupling reactions with one pot electrocyclic reactions are under study in order to synthesize naphthalocyanines by an original methodology.

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