



Synthesis of non-peripherally substituted phthalocyanines with alkylsulfanyl groups

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INTRODUCTION

Phthalocyanines (Pcs) are planar aromatic macrocyclic compounds that can be widely used in various fields for their unique photochemical and photophysical properties. This work is focused on synthesis of new non-peripherally substituted Pcs with different alkylsulfanyl groups (*tert*-butyl, *n*-butyl, pentan-3-yl) (Figure 1.). Comparison of their properties was the next task of this work.

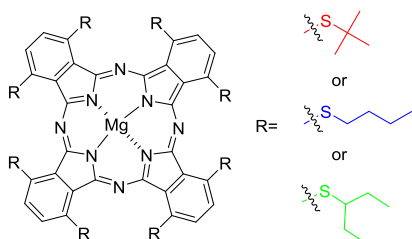


Figure 1. Non-peripheral substitution of phthalocyanines with alkylsulfanyl groups.

RESULTS AND DISCUSSION

The synthesis of precursors for cyclotetramerization was the first step of this work. They were prepared by nucleophilic substitution of 3,6-ditosylphthalonitrile by appropriate alkylthiol. 3,6-ditosylphthalonitrile originated from 3,6-dihydroxyphthalonitrile after esterification of hydroxyl groups by tosylchloride. Cyclotetramerization of prepared precursors was accomplished by magnesium butoxide as an initiator of reaction. Magnesium Pcs prepared in this way were converted to the metal-free derivatives by using 1% hydrochloric acid. Subsequently, metal-free Pcs reacted with anhydrous zinc acetate in pyridine to form corresponding zinc complexes. Conversion of Mg derivative of Pc with *tert*-butylsulfanyl substitution to its Zn complex was not successful. Magnesium Pcs were characterized by spectral methods (Figure 2.)

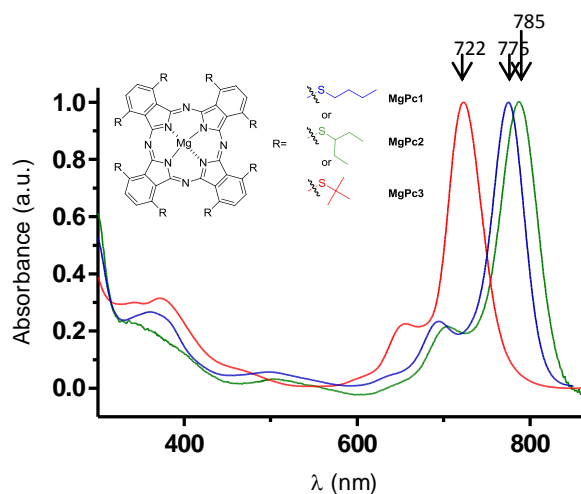


Figure 2. UV-Vis spectra of the magnesium Pcs with alkylsulfanyl substitution in THF

Position of Q-bands of Pcs bearing *n*-butylsulfanyl and pentan-3-ylsulfanyls lied at 775 and 785 nm, respectively. Unusual hypsochromic shift that can be explained by torsion of the macrocycle was observed in the case of Pc with *tert*-butylsulfanyl groups¹. The crystallographic analysis may, however, bring the further explanation.

CONCLUSION

Magnesium, metal-free and zinc Pcs were prepared. UV-Vis spectroscopy was performed in magnesium Pcs. Unusual hypsochromic shift in the UV-Vis spectrum that can be caused by torsion of the macrocycle was observed.

ACKNOWLEDGEMENTS

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REFERENCES

- ¹ Chambrier I., Cook J. M., Wood T. P. Chem. Commun., **2000**, 2133–2134.