

ABSTRACT

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Title of Thesis Synthesis of symmetrical azaphthalocyanines substituted with bulky aromatic substituents

In this work, I dealt with synthesis of two types of azaphthalocyanine (AzaPc) with bulky peripheral substituents attached through stable C-C bond. Synthesis was followed by investigation of their photophysical properties. Each AzaPc was prepared in the metal-free form and as complexes with zinc or magnesium cations.

The first AzaPc (**8**) carried eight peripheral phenolic groups sterically hindered by adjacent *tert*-butyl substituents in *ortho* positions. These acidic hydroxy groups can be ionized and the resulting negative charge can cause an intramolecular charge transfer (ICT) and quench the fluorescence of this compound. This behavior may find its potential in sensoric applications. Second AzaPc (**7**) carried eight peripheral methoxy groups with adjacent isopropyl substituents in *ortho* positions. This AzaPc served as the ICT-negative control.

The precursor for **8** was prepared *via* nucleophilic substitution of 5,6-dichloropyrazine-2,3-dicarbonitrile with 2,6-di(*tert*-butyl)phenolate. Bulky *tert*-butyls hindered the phenolate fully from *O*-substitution and strong M⁺ effect of the phenolate rendered the carbon in position 4 a sufficiently strong *C*-nucleophile. The precursor for **7** was synthesized *via* condensation of diaminomaleonitrile with corresponding vicinal diketone prepared from aldehyde by benzoin condensation and oxidation. The substituted pyrazin-2,3-dicarbonitriles were cyclotetramerized using magnesium butoxide. Photophysical properties of AzaPcs were studied.

Photophysical measurements confirmed that the phenolic group behaves as a weak donor. After the addition of a base, AzaPc **8** deprotonated, phenolate ion was formed and ICT became a more preferred process. Furthermore, dependence of AzaPc **8** on solvent polarity was confirmed. The quantum yield of fluorescence dropped nearly to zero in the most polar solvent.