Synthesis and Aggregation Behavior of Novel Tetrapyrazino-porphyrine Derivatives Containing Morpholine and tert-Butyl Group

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Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. Tetrapyrazinoporphyrine macrocycles tend towards higher aggregation compared to phthalocyanine molecules. These problems are usually solved through introduction of optimal substituents onto the periphery of the tetrapyrazinoporphyrine core that suppress the aggregation, which resulted in various applications such as chemical sensor, catalyst, etc.

2,3-Dicyanopyrazines for tetramerization (tetrapyrazino-porphyrines) are usually built up through condensation of α-diketones and diaminomaleonitrile, enabling peripheral substitutions typically not available for phthalocyanines.

We have studied the syntheses of functional dye materials based on 2,3-dicyanopyrazine chromophores, and correlated their physical properties with structure. In this paper, We designed and synthesized metal and metal-free tetrapyrazinoporphyrines derived from 2,3-dicyanopyrazine derivatives.

The 1-(4-bromophenyl)-2-(4-tert-butylphenyl)ethan-1,2-dione was synthesized by a method described in the literature. Using L-proline as a promoter, the coupling of 1-(4-bromophenyl)-2-(4-tert-butylphenyl)ethan-1,2-dione with morpholine (1.5 eq) in DMSO gave 1-(4-morpholinophenyl)-2-(4-tert-butylphenyl)ethan-1,2-dione in 36% yield. The tetrapyrazinoporphyrine precursor 2 was synthesized from reaction of the unsymmetrical α-diketone (1) and 2,3-diaminomaleonitrile.

Tetrapyrazinoporphyrine magnesium complexes were synthesized from 2,3-dicyanopyrazine derivatives 2 using freshly prepared solutions of magnesium butoxide in n-butanol. The corresponding metal-free derivatives were obtained by treatment with p-toluenesulfonic acid. Copper complexes were successfully synthesized using excess cuprous chloride and DBU (1,8-diazabicyclo[5,4,0]-7-undecene) as a catalyst in o-dichlorobenzene at reflux. The synthetic route of this work is summarized in Scheme 1.

The ground state electronic spectra of the metal complexes showed characteristic absorption in the Q-band region at 665 nm for 3 and 669 nm for 4. The metal-free phthalocyanine...
gives a doublet (Q/Q) with Q-bands as a result of the D₃h symmetry. However, the absorption spectra of 5 did not show split Q/Q bands, as shown in Figure 1, due to the electronic coupling between a pair (or more) of porphyrin units.

There has been a great deal of research focusing on the optical sensitivity of phthalocyanines due to their acidic and basic properties. The synthesized products also experienced an anion effect, especially with the F⁻ anion, which was added to the non-aqueous solvents in the form of a tetra-n-butylammonium salt. Strictly speaking, it either forms F⁻-coordinated complexes or causes deprotonation of the proton on the pyrrole group of metal-free phthalocyanines. In our case, Figure 3 showed the UV-visible spectral changes of 3 upon adding tetrabutylammonium fluoride monohydrate (TBAF). The spectra showed a sharp peak in the Q-band and molar absorptivity was higher than that for the initial solution.

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References
7. 1,4-dinitrostilbene-6-(4-morpholinophenyl)pyrazine-2,3-dicarbonitrile (2): A solution of distoben (1) (1.0 g, 2.845 mmol), 2,3-diaminomonocrotalate (0.34 g, 3.166 mmol) and a small amount of p-toluenesulfonylic acid as catalyst in methanol (10 mL) was refluxed for 2 h. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate-n-hexane (1:3) as eluent. Yield: 0.87 g (73%) as orange color powder, m.p.: 183-186 °C, IR (KBr pellet); ν(C=O): 2232 (CN); 1718.8 (C=O) cm⁻¹; 1,3.33, 1,3.26-2.79 (s, 9 proton), 5.26-3.86 (t, CH₃, J = 4.8 Hz, 4 proton), 3.83-3.86 (t, CH₂, J = 5.1 Hz, 4 proton); 6.79 (d, Ar-H, J = 9 Hz, 2 proton), 7.40 (d, Ar-H, J = 8.7 Hz, 2 proton), 7.55 (d, Ar-H, J = 8.7 Hz, 4 proton); Elemental Anal. Calcd. For C₁₂;H₂₈;N₂;O₂; C, 73.74; H, 5.05; N, 16.54. Found: C, 73.52; H, 5.80; N, 16.65.
8. Porphyrim magnesium complex (3): Absolute n-hexanol was refluxed with magnesium (0.15 g, 6.17 mmol) and a small crystal of iodine for 4 h, and then 2 (0.8 g, 154 mmol) was added and refluxing continued for next 3 h. Aqueous acetic acid (30% (v/v), 50 mL) was added after evaporation of the solvent, and the suspension was stirred for 30 min. Dark solid was filtered and washed with aqueous acetic acid, water and methanol. Crude 3 was purified by column chromatography over silica gel with chloroform-methanol (50:1) as eluent. Yield: 0.25 g (38%) as dark green powder, m.p.: > 300 °C, IR (KBr pellet); ν(C=O): 3.05-4.27 (v, CH₃, 32 proton), 7.06 (broad s, Ar-H, 8 proton), 7.61-8.16 (broad m, Ar-H, 24 proton); Elemental Anal. Calcd. For C₁₂H₁₆N₂O₂; C, 72.69; H, 5.87; N, 16.50. Found: C, 72.57; H, 5.71; N, 16.07.