

Synthesis and Aggregation Behavior of Novel Tetrapyrazino-porphyrazine 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. Tetrapyrazinoporphyrazine macrocycles tend towards higher aggregation compared to phthalocyanine molecules.¹ These problems are usually solved through introduction of optimal substituents onto the periphery of the tetrapyrazinoporphyrazine core that suppress the aggregation, which resulted in various applications such as chemical sensor,² catalyst,³ etc.

2,3-Dicyanopyrazines for tetramerization (tetrapyrazinoporphyrazines) are usually built up through condensation of α -diketones and diaminomaleonitrile, enabling peripheral substitutions typically not available for phthalocyanines.⁴

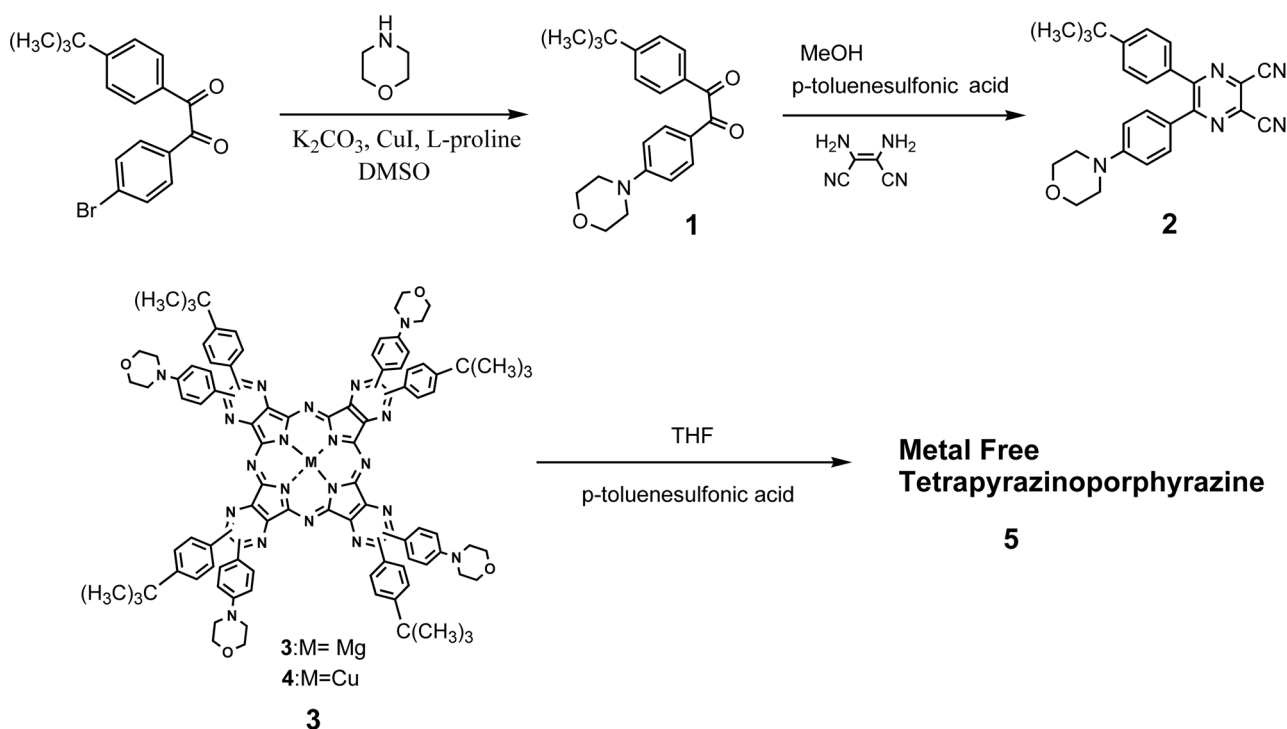
We have studied the syntheses of functional dye materials based on 2,3-dicyanopyrazine chromophores, and correlated their physical properties with structure.⁵ In this paper, We designed and synthesized metal and metal-free tetrapyrazinoporphyrazines derived from 2,3-dicyanopyrazine derivatives.

The 1-(4-bromophenyl)-2-(4-*tert*-butylphenyl)ethan-1,2-

dione was synthesized by a method described in the literature.⁶ 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 56% yield. The tetrapyrazinoporphyrazine precursor (**2**) was synthesized from reaction of the unsymmetrical α -diketone (**1**) and 2,3-diaminomaleonitrile.⁷

Tetrapyrazinoporphyrazine magnesium complexes were synthesized from 2,3-dicyanopyrazine derivatives (**2**) using freshly prepared solutions of magnesium butoxide in *n*-butanol.⁸ 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**.⁹ The metal-free phthalocyanine



Scheme 1. Reaction routes of tetrapyrazinoporphyrazine derivatives.

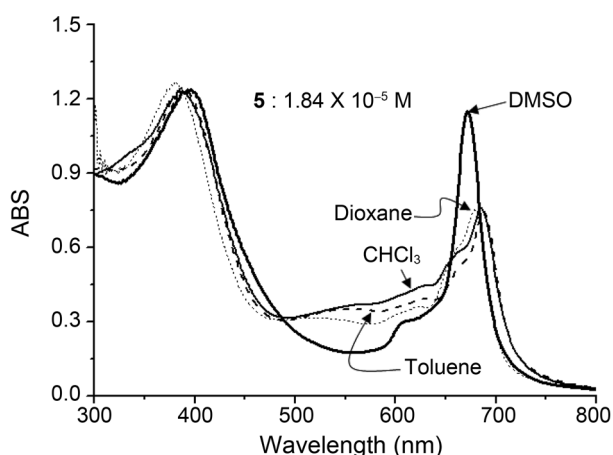


Figure 1. Absorption spectra of **5** in DMSO, CHCl_3 , Toluene, and 1,4-dioxane.

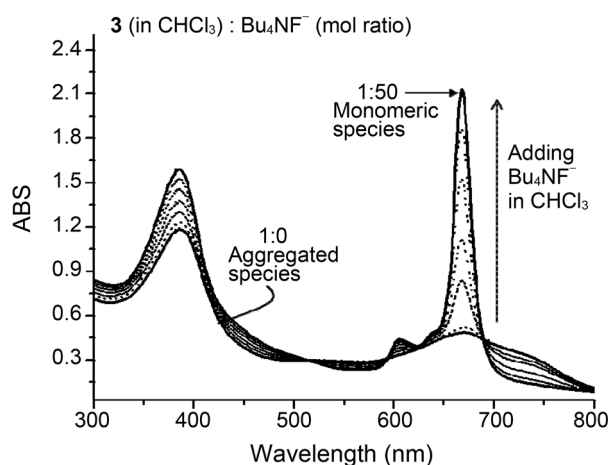


Figure 2. UV-visible absorption spectral change upon adding TBAF to **3** (1.84×10^{-5} M).

gives a doublet (Q_x/Q_y) with Q-bands as a result of the D_{2h} symmetry.¹⁰ However, the absorption spectra of **5** did not show split Q_x/Q_y bands, as shown in Figure 1, due to the electronic coupling between a pair (or more) of porphyrine units.¹¹

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 complexes¹² or causes deprotonation of the proton on the pyrrole group of metal-free phthalocyanines.¹³ 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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- 1-(4-*tert*-Butylphenyl)-6-(4-morpholinophenyl)pyrazine-2,3-dicarbonitrile (**2**): A solution of diketone (**1**) (1.0 g, 2.845 mmol), 2,3-diaminomaleonitrile (0.34 g, 3.186 mmol) and a small amount of *p*-toluenesulfonic acid as catalyst in methanol (10 mL) was refluxed for 2 hr. 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): $\nu(\text{cm}^{-1})$ 2232 (CN); $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.33 (s, $-\text{C}(\text{CH}_3)_3$, 9 protons), 3.26–3.29 (t, CH_2 , $J = 4.8$ Hz, 4 protons), 3.83–3.86 (t, CH_2 , $J = 5.1$ Hz, 4 protons), 6.79 (d, Ar-H, $J = 9$ Hz, 2 protons), 7.40 (d, Ar-H, $J = 8.7$ Hz, 2 protons), 7.55 (d, Ar-H, $J = 8.7$ Hz, 4 protons); Elemental Anal. Calcd. For $\text{C}_{26}\text{H}_{25}\text{N}_5\text{O}$: C, 73.74; H, 5.95; N, 16.54. Found: C, 73.52; H, 5.80; N, 16.65.
- Porphyrine magnesium complex (**3**): Absolute *n*-butanol was refluxed with magnesium (0.15 g, 6.17 mmol) and a small crystal of iodine for 4 hr, and then **2** (0.8 g, 1.54 mmol) was added and refluxing continued for next 3 hr. Aqueous acetic acid (50% (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; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.53 (broad s, $-\text{C}(\text{CH}_3)_3$, 36 protons), 3.06–4.27 (m, CH_2 , 32 protons), 7.06 (broad s, Ar-H, 8 protons), 7.61–8.16 (broad m, Ar-H, 24 protons); Elemental Anal. Calcd. For $\text{C}_{104}\text{H}_{100}\text{MgN}_{20}\text{O}_4$: C, 72.69; H, 5.87; N, 16.30. Found: C, 72.57; H, 5.71; N, 16.07; MALDI-TOF-MS spectra: m/z 1718.8 (calcd. 1718.34).
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