

Synthesis and Spectral Properties of Phenylene Dendrimers Based on Porphyrazines

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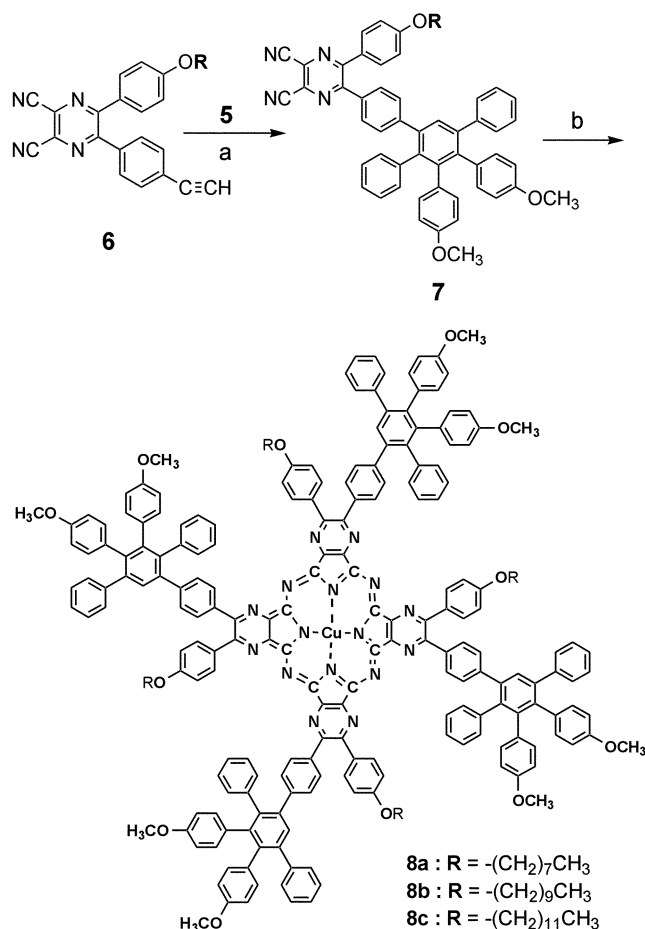
Key Words : Dendrimers, Porphyrazine, Absorption spectra, Aggregation

Owing to their potential applications as photosensitizers in solar energy conversion¹ and photodynamic therapy,² phthalocyanines and their metal complexes have recently received considerable attention. Their characterization was influenced by the nature of the peripheral substituents and the central metal ion. One of the intrinsic problems of using phthalocyanine macrocycles is their strong stacking tendency to form aggregated species in solution.³ It has been found that such stacking can lead to an efficient nonradioactive energy relaxation, reducing the triplet-state population and, consequently, significantly decreasing the photosensitizing efficacy.⁴

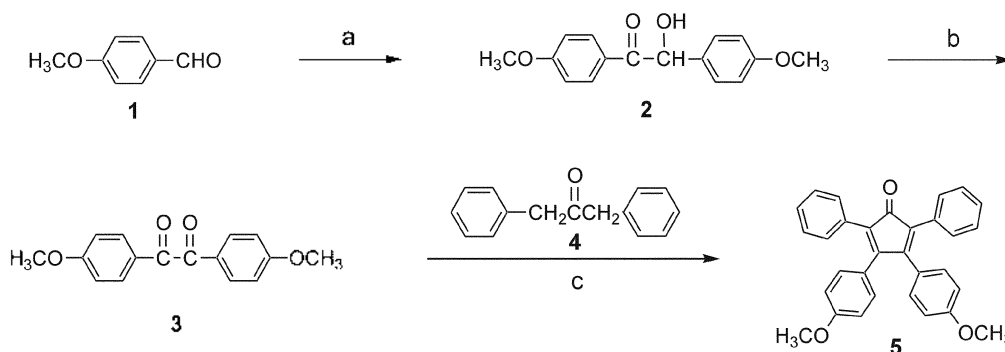
On the other hand, dendrimers are macromolecules with highly branched and regular structural units.⁵ The polyphenylene dendrons, characterized by their shape-persistent structure, and out-of-plane twisted phenyl components, have been successfully attached to various functions.^{6,7} In this paper, we report a general synthesis of 2,3-dicyanopyrazines and their conversion to copper porphyrazines equipped with polyphenylene dendrons, which show that the polyphenylene dendrimers increase the solubility of porphyrazine in common organic solvents. Their aggregation behaviors depending on the polarity of solvents were correlated with their chemical structures.

1,2-Bis-(4-methoxyphenyl)-ethane-1,2-dione (**3**) was prepared by the known method.⁸ Condensation reaction of compound **3** with one equivalent of 1,3-diphenylacetone (**4**) in the presence of one equivalent of tetrabutylammonium hydroxide under reflux conditions gave 3,4-bis-(4-methoxyphenyl)-2,5-diphenyl-cyclopenta-2,4-dienone (**5**) in a yield of 85% after recrystallization from methanol (Scheme 1).

Preparation of 5-(4-ethynylphenyl)-6-(4-alkoxyphenyl)-pyrazine-2,3-dicarbonitrile (**6**) has been described in the



Scheme 2. Reagents and conditions: (a) *p*-xylene, reflux, 20 h, 81–85%; (b) 1 equiv. Cu(I)Cl, (NH₄)₆Mo₇O₂₄·4H₂O, reflux, 6 h, 20–23%.



Scheme 1. Reagents and conditions: (a) 0.5 equiv. NaCN, MeOH/H₂O (13 : 10), reflux, 16 h; (b) 2 equiv. CuSO₄, pyridine/H₂O, 100 °C, 1 h; (c) 1 equiv. Bu₄NOH, *tert*-butylalcohol, reflux, 12 h, 85%.

literature.⁹ The treatment of compound **6** with one equivalent of **5** in degassed *p*-xylene afforded the corresponding 2,3-dicyanopyrazine derivatives (**7**). The ¹H NMR spectrum of compound **7c** indicated that -CH₃ protons appeared as a triplet at 0.88 ppm and that two -OCH₃ signals appeared as a singlet at 3.34 and 3.67 ppm. Tetrapyrazinoporphyrazinato copper complexes (**8**) were prepared by reacting compound **7** with one equivalent of cuprous chloride in *o*-dichlorobenzene in the presence of hexaammonium heptamolybdate tetrahydrate as catalyst, and were obtained in a yield of 20-23% after purification by silica-gel column chromatography (Scheme 2).¹¹

Figure 2 shows the effect of solvent polarity on the absorption spectra of porphyrazines **8c** when carbon-tetrachloride was added to the chloroform solution. With the increase in the ratio of carbon-tetrachloride to chloroform, the absorption at 640-670 nm and 590-610 nm decreased. The Q-band spectra in CCl₄ show the characteristic pattern of dimeric or/and polymeric species which are replaced at lower concentration with the spectral envelope. Isosbestic points were observed at around 410, 565, 640 and 682 nm,

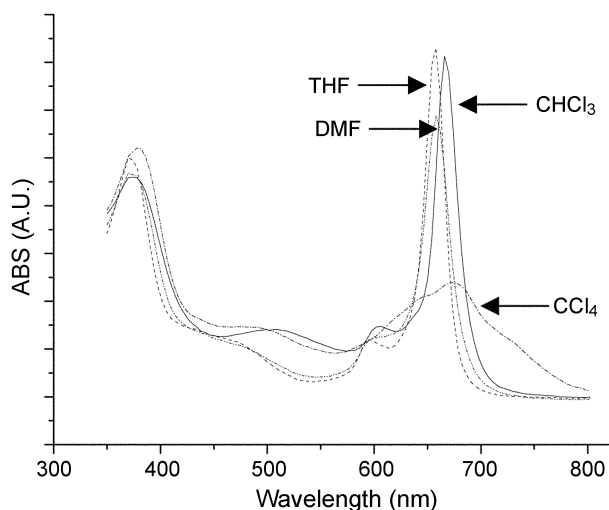


Figure 1. Absorption spectra of **8c** in several solvents.

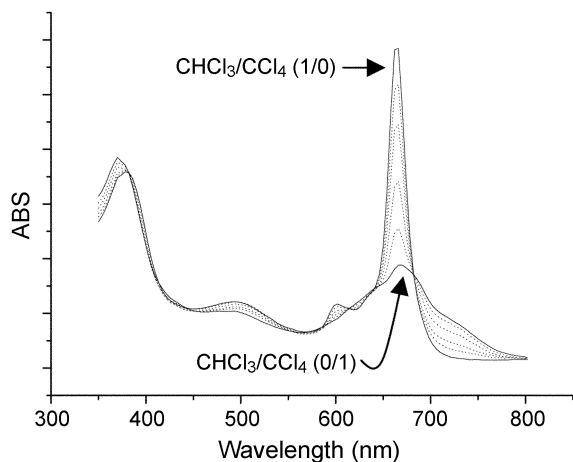


Figure 2. The effects of carbon-tetrachloride on the absorption spectra of **8c** in chloroform.

and equilibrium mixtures of monomers and aggregate were included in the solution.

In summary, we have synthesized a new type of tetrapyrazinoporphyrazinato copper complex equipped with polyphenylene dendrons from 2,3-dicyanopyrazines. Tetrapyrazinoporphyrazinato copper complexes (**8**) with long alkyl groups dramatically changed its absorption spectra by molecular aggregation depending on the polarity of solvent. Molecular aggregations and their functionality as non linear optical (NLO) materials will be reported elsewhere.

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- 7c**: ¹H-NMR (300 MHz, CDCl₃) δ 0.88 (t, 3H, J 6.9, CH₃), 1.28-1.33 (br. s, 18H, CH₂), 1.88 (m, 2H, CH₂), 3.63 (s, 3H, OCH₃), 3.67 (s, 3H, OCH₃), 3.99 (t, 2H, J 6.9, OCH₂), 6.44 (d, 2H, J 8.9, ArH), 6.50 (d, 2H, J 8.9, ArH), 6.66 (d, 2H, J 8.6, ArH), 6.73 (d, 2H, J 8.6, ArH), 6.79-6.82 (m, 4H, ArH), 6.96 (m, 2H, ArH), 7.14-7.18 (m, 8H, ArH), 7.38 (d, 2H, J 8.5, ArH), 7.46 (d, 2H, J 8.9, ArH), 7.53 (s, 1H, ArH); Calcd.: for C₆₂H₅₈N₄O₃: C, 82.09; H, 6.44; N, 6.18. Found: C, 82.01; H, 6.51; N, 6.11.
- Typical procedure to synthesize tetrapyrazinoporphyrazinato copper complexes (**8b**): The mixture of compound **7b** (1 mmole) and CuCl (1 mmole) was refluxed in 1,2-dichlorobenzene (5 mL) in the presence of hexaammonium heptamolybdate tetrahydrate as catalyst. After refluxing for 8 h, the solvent was removed partially *in vacuo*. The crude product was purified by column chromatography in silica gel, eluting with chloroform: ¹H-NMR (300 MHz, CDCl₃) δ 0.90 (br. s, 12H, CH₃), 1.31-1.46 (br. s, 56H, CH₂), 1.87 (br. s, 8H, CH₂), 3.70 (br. m, 24H, OCH₃), 3.99 (br. s, 8H, OCH₃), 6.47-7.23 (br. m, 108H, ArH); Calcd.: for C₂₁₀H₁₂₁₆N₁₆O₁₂Cu: C, 80.52; H, 6.08; N, 6.26. Found: C, 81.01; H, 6.20; N, 6.13; MALDI-TOF-mass-spectrum: *m/z*: 3578.63 (100%, M⁺, calcd., 3579.93).