

Spectra and stabilities of α -substituted phthalocyaninatoirons

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Abstract

Three aryloxy (alkoxy) α -substituted phthalocyaninatoirons (FePcs) were prepared and their UV–vis spectra in air or by adding of peroxide showed a new band at the red side of the Q band which can be assigned to a complexes of phthalocyaninatoirons with oxygen or peroxide. The appearance of this band related to the instability of these FePcs so their decomposition was also studied, by the benzoylperoxide oxidation.

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1. Introduction

Phthalocyanines, especially those containing redox-active central metal ions such as phthalocyaninatoirons, are excellent catalysts of oxidative desulfurisation of hydrocarbons [1]. In recent years, these compounds have also been examined as biologically simulated oxidative metalloenzymes [2]. Generally, unsubstituted phthalocyanines have poor solubility and a high tendency of aggregation in solvents [3], which considerably limits the scope of the investigations. Substituents such as alkyl and alkoxy groups have often been introduced to the periphery of the phthalocyanine macrocycle to improve their solubility. But the stability decreasing of substituted phthalocyanines in the oxidizing media has also been found, even under very mild conditions [4]. A few investigations on the stability of phthalocyanines have been reported to date [4,5]. Here we report some experimental results of the decompositions of three aryloxy (alkoxy) α -substituted phthalocyaninatoirons with benzoylperoxide oxidation, and related changes of their spectra.

2. Experimental

2.1. Materials

The substituted phthalonitriles [3-phenoxyphthalonitrile, 3-(2',4'-ditertbutylphenoxy)phthalonitrile, and 3-(2',2',4'-

trimethyl-3'-pentoxy)phthalonitrile] were synthesized as described in literature [6]. All other reagents and solvents were of reagent grade and used without further purification. All synthetic reactions were performed under nitrogen atmosphere.

2.2. Measurements

The infrared spectra were recorded in the range of 400–4000 cm^{-1} by use of a Perkin–Elmer FT-IR spectrophotometer. Elemental analyses were carried out on a Vario EL III elemental analyses instrument. And UV–vis spectra were recorded on PE-Lambda9 UV–vis spectrophotometer using 1 cm path length cuvettes at room temperature.

2.3. General process of the synthesis of lithium and metal-free phthalocyanines **1a–1c**

Compounds **1a–1c** were obtained by the procedure similar to the literature [7]. Under nitrogen atmosphere, 40 mmol of phthalonitrile and 40 mmol of Li were heated at 120 °C for 4 h in 10 mL of *n*-pentanol. After cooling down to room temperature, 10 mL of methanol and 5 mL of hydrochloric acid were added with vigorous stirring for 10 min. The residue was immediately passed through a silica gel column (using CHCl_3 as eluant), and the obtained green eluate was evaporated, to give desired compounds.

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2.4. Tetrakis(2,2,4-trimethyl-3-pentoxy)phthalocyanine (**1a**)

Yield: 0.932 g (9.1%). C₆₄H₈₂N₈O₄ (1023.43): calc., C, 74.82; H, 8.07; N, 10.91; found, C, 74.82; H, 8.04; N, 10.78; mass: *m/z*: 1023 (*M*⁺); IR (KBr): 1585.1 (ν_{C=C}), 1480.7 cm⁻¹ (ν_{C=N}), 1241.1, 1108.8 cm⁻¹ (ν_{Ar-O-C}), 2955.6, 2868.9 cm⁻¹ (ν_{CH₃}).

2.5. Tetrakis(2',4'-ditertbutylphenoxy)phthalocyanine (**1b**)

Yield: 2.31 g (17.4%). C₈₈H₉₈N₈O₄ (1330.7): calc., C, 79.36; H, 7.42; N, 8.41; found, C, 79.51; H, 7.60; N, 7.77; mass: *m/z*: 1032.0 (*M*⁺); IR (KBr): 1585.8 (ν_{C=C}), 1484.9 cm⁻¹ (ν_{C=N}), 1250.9, 1086.1 cm⁻¹ (ν_{Ar-O-Ar}), 2958.8, 2867.9 cm⁻¹ (ν_{CH₃}).

2.6. Tetrakisphenoxyphthalocyaninato lithium (**1c**)

Yield: 2.24 g (25.5%). C₅₆H₃₃N₈O₄Li (888.28): calc., C, 75.76; H, 3.36; N, 12.62; found, C, 75.22; H, 3.59; N, 12.22; mass: *m/z*: 889.4 (*M*⁺); IR (KBr): 1582.6 (ν_{C=C}), 1488.8 cm⁻¹ (ν_{C=N}), 1245.9, 1180.5 cm⁻¹ (ν_{Ar-O-Ar}).

2.7. General process of the synthesis of phthalocyaninatoiron **2a–2c**

Compounds **2a–2c** were obtained by the procedure similar to the literature [8]. Under nitrogen atmosphere, 0.45 mmol of precursors **1a–2c** and 7.9 mmol of FeCl₃ were heated at 115 °C for 2 h in 10 mL of pyridine. The reaction mixture was immediately passed through a short alumina column (20:1, v/v of toluene:pyridine as eluant) to remove unreacted metal salt. Then the obtained green eluate was evaporated to give desired compounds.

2.8. Tetrakis(2,2,4-trimethyl-3-pentoxy)-phthalocyaninatoiron (**2a**)

Yield: 0.34 g (70%). C₆₄H₈₀N₈O₄Fe (1080.57): calc., C, 71.09; H, 7.46; N, 10.36; found, C, 70.80; H, 7.38; N, 9.40; mass: *m/z*: 1080 (*M*⁺); IR (KBr): 1587.4, 1485.6 cm⁻¹ (ν_{C=N}), 1244.3, 1114.7 cm⁻¹ (ν_{Ar-O-C}), 1587.4 cm⁻¹ (ν_{C=C}), 2956.1, 2869.9 cm⁻¹ (ν_{CH₃}), 742.47 (ν_{M-N}).

2.9. Tetrakis(2',4'-ditertbutylphenoxy)phthalocyaninatoiron (**2b**)

Yield: 0.594 g (95.4%). C₈₈H₉₆N₈O₄Fe (1384.69): calc., C, 76.28; H, 6.98; N, 8.09; found, C, 76.32; H, 6.90; N, 8.42; mass: *m/z*: 1384 (*M*⁺); IR (KBr): 1585.8, 1481.2 cm⁻¹ (ν_{C=N}), 1384, 1082.0 cm⁻¹ (ν_{Ar-O-Ar}), 1585.8 cm⁻¹ (ν_{C=C}), 2953.7, 2849.1 cm⁻¹ (ν_{CH₃}), 741.01 (ν_{M-N}).

2.10. Tetrakisphenoxyphthalocyaninatoiron (**2c**)

Yield: 0.402 g (95.5%). C₅₆H₃₂N₈O₄Fe (936.19): calc., C, 71.80; H, 3.44; N, 11.96; found, C, 72.22; H, 4.30; N, 11.61; mass: *m/z*: 936 (*M*⁺); IR (KBr): 1581.9 (ν_{C=C}), 1488.9 cm⁻¹ (ν_{C=N}), 1246.2, 1205.7 cm⁻¹ (ν_{Ar-O-Ar}), 748.76 (ν_{M-N}).

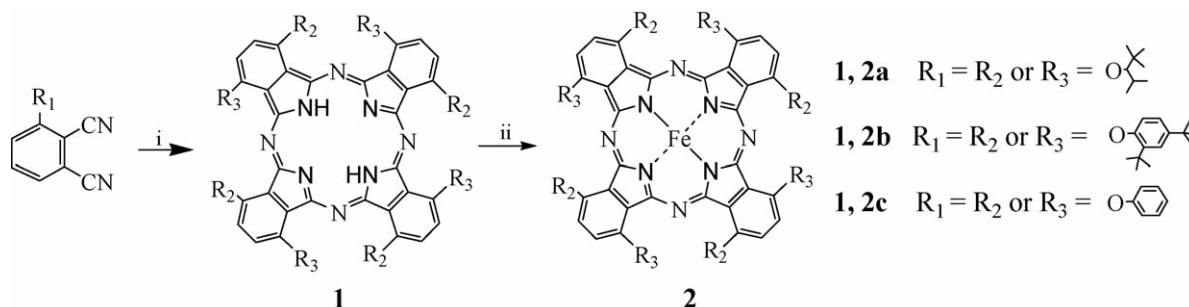
3. Results and discussion

3.1. Synthesis of substituted phthalocyaninatoirons

As shown in the Scheme 1, instead of commonly used method of condensation of precursor and metal salt, the title phthalocyaninatoirons are synthesized from corresponding metal-free phthalocyanines so as to simplify the process of purification because of the easy decomposition of these substituted phthalocyanines, even though the yields of metal-free phthalocyanines were lower. Another result was that with smaller substituents, the protonation of LiPc by acid was uneasy and resulted with a half protonated LiHPC, as **1c**, which was used in the next reaction without further treatment.

3.2. The UV-vis spectroscopy studies of substituted phthalocyaninatoirons in atmosphere

The alkoxy complex **2a** showed a typical Q₀₋₀ and Soret bands of Pc ring at 683, 618 and 347 nm in pyridine at atmosphere, but in the toluene, a new band (753 nm, named as L bands) was found at the longer wavelength side of the Q band, and its intensities increase accompanied by the intensity decreasing of the Q band, while standing the solution at room temperature in air, as shown in Fig. 1. This L bands were also observed in acetone and acetonitrile solutions, but not observed in polar solvents, DMF, dimethyl sulfoxide, and pyridine. In case of **2b**



Scheme 1. Reagents and conditions: (i) pentanol, Li, 120 °C, 4 h, and then con. HCl; (ii) FeCl₃, DMF, 150 °C, 4 h.

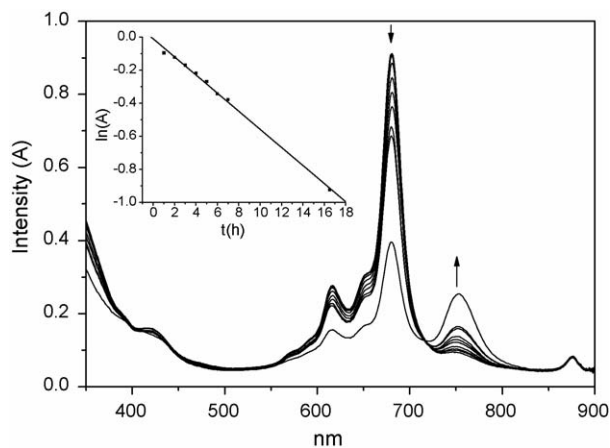


Fig. 1. Electronic absorption spectral changes of the toluene solution containing compound **2a** with time ($[2a]_0 = 1 \times 10^{-5} \text{ mol L}^{-1}$), and the inset is the correction between $\ln(A)$ and time.

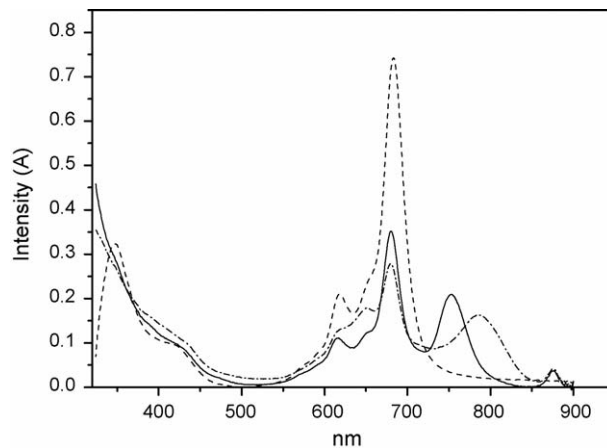


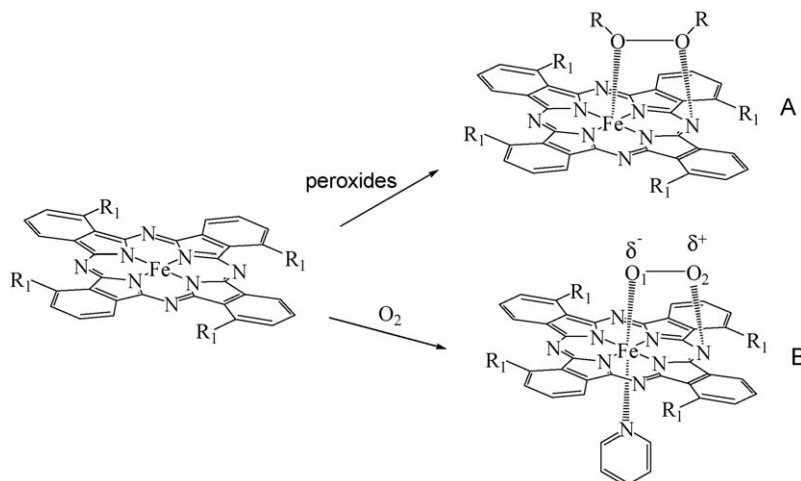
Fig. 2. Absorption spectra of **2a** ($1 \times 10^{-5} \text{ mol L}^{-1}$) in toluene (solid line), pyridine (dashed line) and toluene containing 0.1 mol L^{-1} phenol (dot line).

and **2c**, the L bands also appeared but with weak intensities than that of **2a**.

For the origin of this L band, we checked if it is whatever reported. It is known that the Q bands of MPCs are shifted to the longer wavelength region by formation of the slipped face-to-face dimer [9]. And the red shift of the Q bands was also reported for the zeolite encapsulated MPCs, of which pc rings are considered to be distorted so as to reside in the narrow cavities of the zeolite. Furthermore, it is also reported that the electronic absorption of μ -oxo dimeric PcFe complex in non-coordinating solvents, the Q and B bands always bathochromic shift. However, these reasons could not give us some accessible explain for the L band. The structure of PcCo with the same substituents as compound **2a** showed that their ring skeleton maintained the planar conformation and the distance of the two neighboring rings is 7.5 \AA [10]. And the bond distance of Fe–O–Fe is 3.42 \AA in μ -oxo PcFe dimer [11]. These results ruled out the possibility of the slipped face-to-face dimer, ring distortion or μ -oxo PcFe dimer as the L bands origin. It can be further confirmed by the fact that the vibrations of Fe–O–Fe at 852 and 824 cm^{-1} [12] were not found in the IR spectra of com-

pound **2a**. Recently, Kobayashi and co-workers reported that one phthalocyaninatoiron substituted with eight phenyl groups at α position shows absorption bands that may be assigned to metal-to-ligand charge transfer (MLCT) transitions, in the near-IR region beyond the Q band in pyridine, due to lowering of molecular symmetry from D_{4h} to D_{2d} [8]. But for compound **2a**, this MLCT band was not found in pyridine. In addition, the oxidation of the pc ring also gives rise to a new band at the longer wavelength side of the Q band. But in this case, a relatively strong band should be accompanied in the wavelength range from 500 to 600 nm [13]. However, such a band was not observed for the present complex. In Fig. 2, we can also find a band at 785 nm for the protonated **2a** by phenol in toluene, so the L bands at 753 nm cannot also be assigned to the protonation.

In checking the origin of this L band, we found that this L band disappeared immediately after adding a small amount of acid, such as acetic acid or phenol, or decreased by adding of pyridine to the solution. These facts led to a conjecture that the L band at 753 nm was related to the center Fe and meso-nitrogen atoms. Another clue was that a peak was found out in the mass spectra for one pyridine coordination and an additional small group



Scheme 2. The schematic diagram of the complexes of title compounds with oxygen and oxidants in some solvents.

with mass 32. Also considered a model reported by Kaliya et al. for PcFe catalysts interact with oxidants (dioxygen, peroxides, hydroperoxides and peracids) [14], as shown in Scheme 2A, we surmised a model for the origin of this L band as showed in Scheme 2B, in which electrons of O1 and O2 are attracted to Fe atom and the O2 atom with somewhat lacking of electron interact with meso-nitrogen atoms. And the coordinated pyridine at one side of the center Fe could enhance the coordination of the O₂ on the other side, as well known for the analog porphyrins. In these complexes, the O₂ ligand can be replaced by the stronger coordinate pyridine at Fe and stronger protonate H at meso N, so the L band can be disappeared by acid or decreased by pyridine. No appearance of the L bands in analogous metal-free, Zn, Co, Cu, Pd derivatives [15] or the PcFe with small bulk substituents [16] is perhaps mainly attributed to their weak coordination abilities of center atoms or short distances of two neighboring Pc rings.

In order to further prove out our assumption, the benzoyl peroxide (BPO) was added to the toluene solution of compound **2a**. As expected, there was a new band at 746 nm that was also found (Fig. 3).

3.3. The decomposition by benzoylperoxide oxidation

It was observed that when this L band appeared, the substituted FePcs slowly decomposed, as shown in Fig. 1. The decomposition also occurred when protonated by adding acid but not by adding pyridine. When standing the sample solution in air, the decomposition rate was not clearly recorded because the air diffusion into the sample was difficult to be controlled.

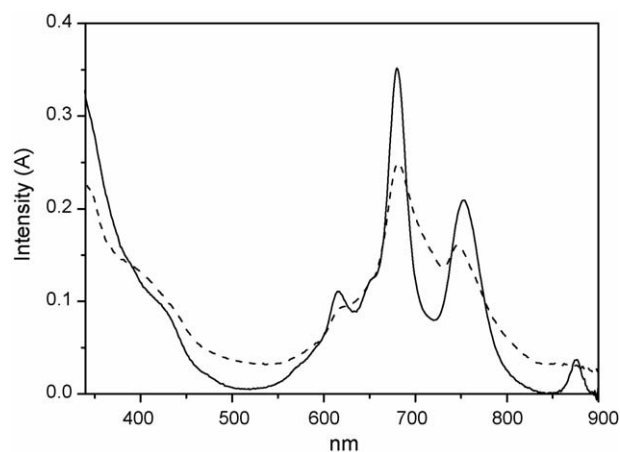


Fig. 3. The absorption spectra of **2a** ($1 \times 10^{-5} \text{ mol L}^{-1}$) in toluene (solid line) and in toluene containing BPO ($5 \times 10^{-3} \text{ mol L}^{-1}$) (dash line, after 26 min).

The decomposition of title compounds by the oxidation of BPO was relatively fast where the effect of air was ignored. The decomposition with BPO in toluene or pyridine is shown in Fig. 4. It was found that the order of their decomposition rate is **2a** > **2b** > **2c** and in good agreement with the order of their maximum absorption wavelengths. As foregoing mentioned model, the key step is to form the intermediate as shown in Scheme 2. Firstly, the donor substituents at α position lead to some increase of the electronic densities of meso-nitrogen atom and the rise of C=N bond length, and the corresponding red shift of the Q band indicated the level of this effect. So the introduction of the donor substituents at α position will increase the electron of meso N atom what is beneficial for the forming of intermediate, and the

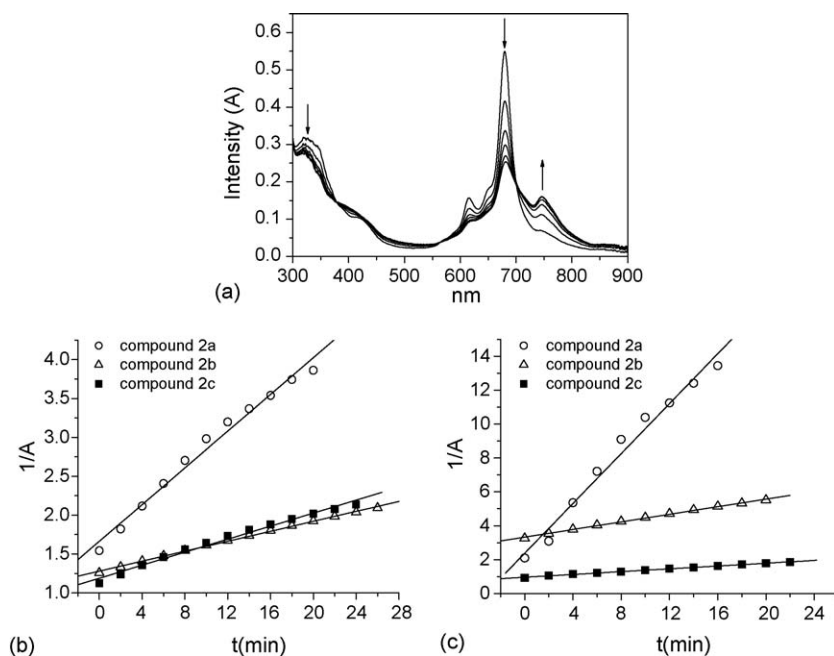


Fig. 4. Electronic absorption spectral changes of the toluene solution containing compound **2a** and BPO with time ($[\mathbf{2a}]_0 = 1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{BPO}]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$) (a); the correction between $1/A$ and time in toluene/BPO solution (b) where $[\mathbf{2a-2c}]_0 = 1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{BPO}]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$) and in pyridine/BPO solution (c) where $[\mathbf{2a-2c}]_0 = 1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{BPO}]_0 = 0.1 \text{ mol L}^{-1}$).

C=N bond lengthen also lowered the stability of Pc. Secondly, and perhaps more importantly, the bulk of the substituents affect the ease of interaction between the PcFe and oxidant. Finally, the fact that the decomposition in the pyridine needs a high concentration of oxidant may suggest the coordination of the solvent to the axial position compete with the coordination of oxidant to the Fe ion.

The decomposition reaction order was 2, extracted from the maximum absorption of the original Q band, indicated the formation of intermediate from Pc and oxidant is a second-order reaction and the L band is a “new Q band” of the intermediate. Where the decomposition in air was a first-order reaction belongs to the constant O₂ concentration in solution come by the diffusion of O₂ from air. As a band of intermediate, the strength of L band was held constant within the decomposition and disappeared slowly at last when the most of phthalocyanine decomposed. In addition, the decomposition of BPO itself in this condition is very slow [17].

4. Conclusion

The formation of the complexes of phthalocyaninatoirons with oxygen and oxidant BPO leads to a new band (named as L band) at the longer wavelength side of Q band. This L band belongs to an oxygen or peroxidant-coordinated intermediate which leads to the decomposition of the phthalocyaninatoirons. The donor substituents at α position can enhance the decomposition so as to reduce the chemical stability of phthalocyaninatoirons, and the steric congestion of substituent further enhances the decomposition.

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References

- [1] (a) K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, vol. 19, Academic Press, New York, 2003; (b) C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines, Properties and Applications*, vols. I–IV, VCH, New York, 1989–1996; (c) A.L. Thomas, *Phthalocyanine Research and Applications*, CRC Press, Boston, 1990.
- [2] (a) M. Sono, M.P. Roach, E.D. Coulter, J.H. Dawson, *Chem. Rev.* 96 (1996) 2841; (b) S. Ferguson-Miller, G.T. Babcock, *Chem. Rev.* 96 (1996) 2889; (c) V.N. Nemykin, I.N. Tert'yakova, S.V. Volkov, V.D. Li, N.G. Mekhryakova, O.L. Kaliya, E.A. Luk'yanets, *Russ. Chem. Rev.* 69 (4) (2000) 325.
- [3] A.W. Snow, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, vol. 17, Academic Press, New York, 2003, pp. 130–176 (Chapter 109).
- [4] N. d'Alessandro, L. Tonucci, M. Bressan, L.K. Dragani, A. Morvillo, *Eur. J. Inorg. Chem.* (2003) 1807–1814.
- [5] (a) N. Grootboom, T. Nyokong, *J. Mol. Catal. A.* 179 (2002) 113–123; (b) W. Pasiuk-Bronikowska, M. Krajewska, I. Flis-Kabluska, *Polyhedron* 18 (1998) 561–569.
- [6] W. Xie, H. Xu, C. Gan, Z. Pan, T. Yan, B. Peng, *Chin. J. Chem. Phys.* 16 (6) (2003) 491–498.
- [7] K. Kasuga, M. Kawashima, K. Asano, T. Sugimori, K. Abe, T. Kikkawa, T. Fujiwara, *Chem. Lett.* (1996) 867–868.
- [8] T. Fukuda, S. Homma, N. Kobayashi, *Chem. Commun.* (2003) 1574–1575.
- [9] K. Kasuga, N. Matsuura, K. Inoue, M. Handa, T. Sugimori, K. Isa, M. Nakata, *Chem. Lett.* 31 (3) (2002) 352–353.
- [10] J.D. Wang, J.L. Huang, X.Z. Xu, J.W. Cai, N.S. Chen, *Chinese J. Struct. Chem.* 5 (2004) 516–519.
- [11] M.J. Lin, J.D. Wang, N.S. Chen, J.L. Huang, *Inorg. Chem. Commun.* 8 (2005) 900–902.
- [12] V.N. Nemykin, I.N. Tert'yakova, S.V. Volkov, V.D. Li, N.G. Mekhryakova, O.L. Kaliya, E.A. Luk'yanets, *Russ. Chem. Rev.* 69 (4) (2002) 325–346.
- [13] E.A. Ough, M.J. Stillman, *Inorg. Chem.* 34 (1995) 4317–4325.
- [14] O.L. Kaliya, E.A. Lukyanets, G.N. Vorozhtsov, *J. Porphyrins Phthalocyanines* 3 (1999) 592–610.
- [15] M.J. Lin, Master's Degree Thesis, University of Fuzhou, 2003.
- [16] G. Schmid, E. Witke, U. Schlick, S. Knecht, M. Hanack, *J. Mater. Chem.* 5 (6) (1995) 855–859.
- [17] W.E. Cass, *J. Am. Chem. Soc.* 68 (10) (1946) 1976–1982.