Chinese Chemical Letters Vol. 10, No. 6, pp. 459–462, 1999

A New Binuclear Bisphthalocyanine: Tetrahydroxo(hexa-tetradecanobisphthalocyaninato) Disilicium

Dai Hua TANG*, Xiao Bing WANG, Zhen ZHEN, Feng Qi WANG, Xin Hou LIU

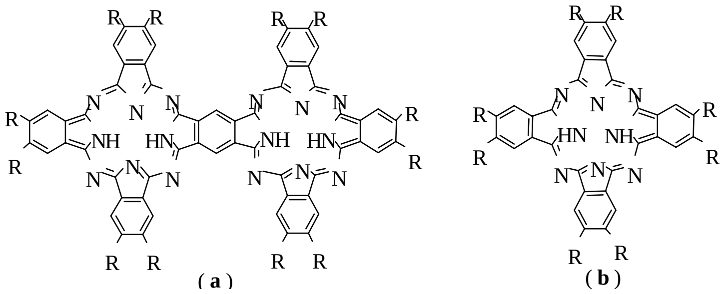
Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101

Abstract: A new binuclear bisphthalocyanine — tetrahydroxo(hexa-tetradecanobisphthalocyaninato) disilicium is synthesized and characterized, and one of its important applications is introduced.

Keywords: Binuclear bisphthalocyanine, synthesis, double-axial linear phthalocyanine.

The first synthesis of planar binuclear phthalocyanines and porphyrins sharing a benzene was achieved ten years ago[1,2]. Up to now, many dimeric complexes with similar structures have been synthesized , and their properties have been studied[3–9]. These dimers, with rigid cofacial configuration, often show spectroscopic and electrochemical properties which differ significantly from the parent monomers. They are becoming of increasing importance in the domain of molecular materials[5,8]. According to their electronic absorption spectra, they could be divided into two types. One is general binuclear bisphthalocyanine: its maximum absorption wavelength is red-shifted compared with that of mononuclear phthalocyanine. Most of bisphthalocyanines belong to this type. The other one is " atypical" binuclear bisphthalocyanines: π-electrons can not delocalize well in the two phthalocyanine rings. Its maximum absorption wavelength is not red-shifted compared with that of mononuclear phthalocyanine. This kind of binuclear bisphthalocyanine is seldom found[3, 8, 9].

Scheme 1.

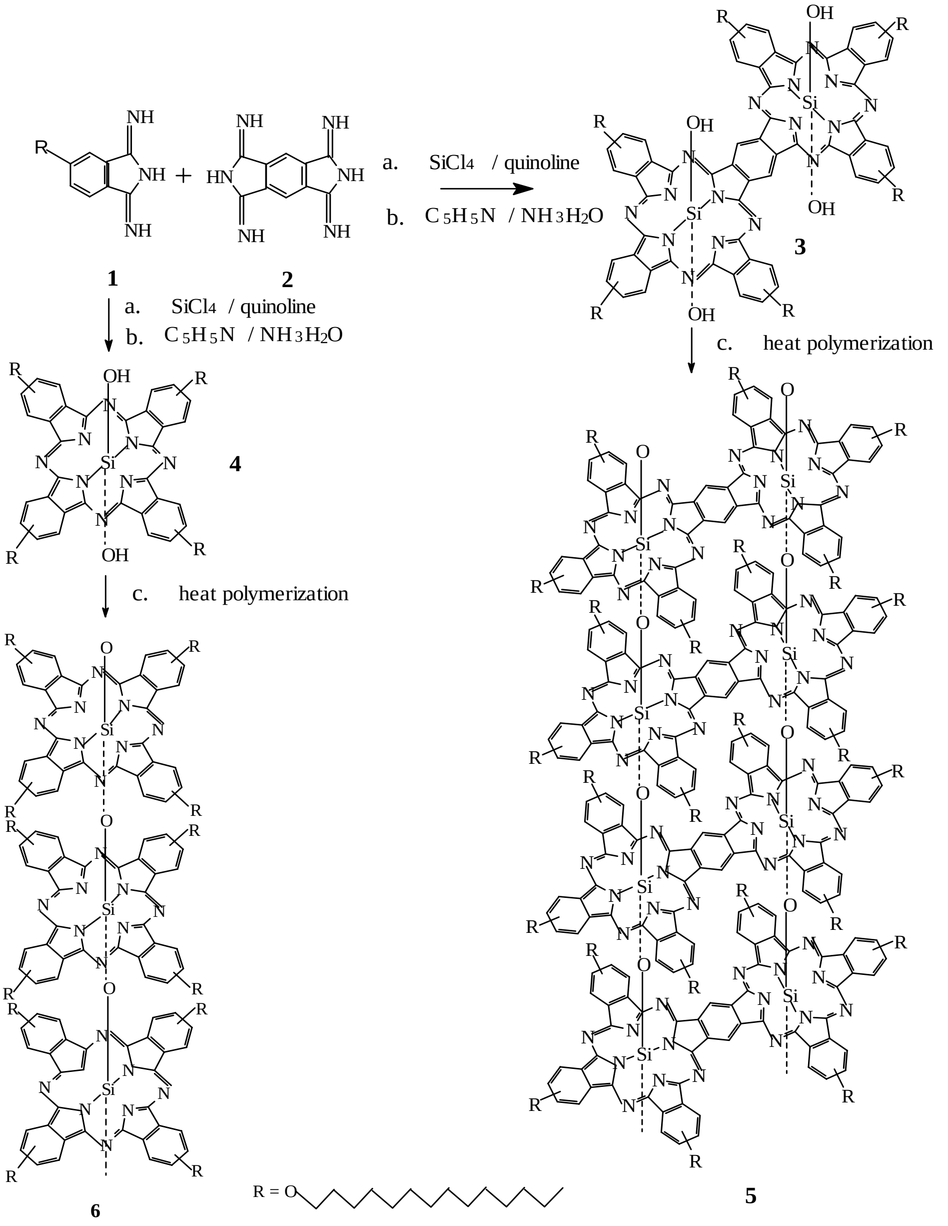


R= H.alkyl.alkoxy.*etc.*

It is particularly mentioned that there were inconsistent reports for the maximum absorption wavelength of metal-free bisphthalocyanine (a) compared with that of metal-free phthalocyanine (b) (see **Scheme 1)**[3, 4, 6, 8].

Here we report a new binuclear bisphthalocyanine — tetrahydroxo(hexa-tetradecanobisphthalocyaninato) disilicium. Its synthetic method is summarized in **scheme 2**.

Scheme 2.

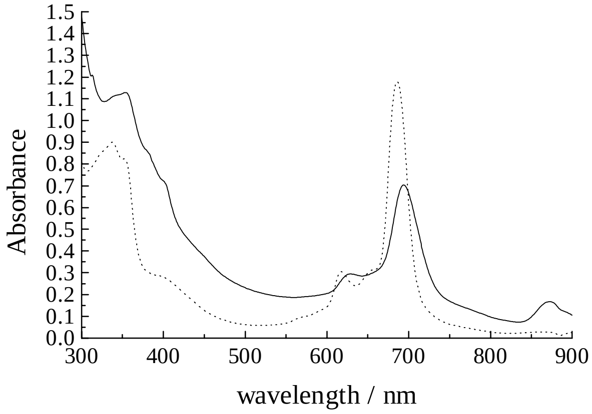


The starting reactants, 5-tetradecanoxy-1,3-diiminoisoindoline **1** and benzene bisdiiminoisoindole derivative **2**, were prepared according to the literatures[3, 8, 9]. The mixture of 1112 mg (3.11 mmol) of **1**, 22 mg (0.104 mmol) of **2** and 5 mL of $SiCl_4$ was heated in 15 mL of anhydrous quinoline at 230°C for 30 min. After cooling, 20 mL of hydrochloric acid was added. The mixture solution was stirred at 60 °C for 1 h and filtered. The residue was washed with hydrochloric acid and water, then mixed with 100 mL of pyridine / ammonia solution (v / v = 1 / 1). The mixture was stirred at 80 °C for 72 h, and filtered. The residue was dried at room temperature under vacuum and separated by column chromatography (silica gel; dichloromethane, chloroform, methanol and methylcyclohexane as eluents in turn). The fraction eluant from methylcyclohexane was separated on silica gel columns twice. The product **3** was obtained as a dark green powder in 12% yield.

A similar procedure could be used to prepare compound **4** in 55% yield.

Using MALDI — TOF (matrix assistant laser deposition ionization — time of flight) technique, the molecular ion peaks were at 2345 for compound **3** and at 1424 for compound **4**; The infrared spectrum ($\nu_{O\text{–}H}$, characteristic peak): 3200cm^{-1}.

Figure 1. The electronic absorption spectra of compound **3** (solid line) and compound **4** (dot line) in chloroform at room temperature



The electronic absorption spectrum (**Figure 1)** showed the maximum absorption wavelength of compound **3** was red-shifted to 880 nm compared with that of compound **4**. This result verified that the π-electrons of molecule **3** can delocalize well in the two phthalocyanine rings, and that molecule **3** is planar. The lack of fluorescence is another characteristic of compound **3**.

Compound **3** and its similar compounds are important intermediates which can be used to synthesize soluble double-axial one-dimensional μ –oxo (bisphthalocyaninato) disilicium polymer **5** by polymerization (see **Scheme 2**). Compared with the single-axial one-dimensional μ -oxo (phthalocyaninato) silicium polymer **6**[10－16], the double-axial one-dimensional μ –oxo (bisphthalocyaninato) disilicium polymer **5** should improve axis-directional one-dimensional photo-electronic conductivity, ions transportation efficiency and other properties because of their structural advantages. Our work is in progress and details will be published later.

Acknowledgment

This project (No.29584003) is financially supported by the National Natural Science Foundation of China.

References

1. C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, and A. B. P. Lever, *J. Chem. Soc., Chem. Commun.*, **1987**, 699.
2. M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, **1987**, 39.
3. J. Yang and M. R. V. D. Mark, *Tetrahedron Letters*, **1993**, *34* (33), 5223.
4. N. Kobayashi, Y. Higashi, and T. Osa, *J. Chem. Soc., Chem. Commun.*, **1994**, 1785.
5. M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, **1991**, 1569.
6. D. Lelievre, O. Damette, and J. Simon, *J. Chem. Soc., Chem. Commun.*, **1993**, 939.
7. B. Hauschel, D. Ruff, and M. Hanack, *J. Chem. Soc., Chem. Commun.*, **1995**, 2449.
8. N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, and H. Shirai, *J. Am. Chem. Soc.*, **1994**, *116*, 879.
9. D. Lelievre, L. Bosio, J. Simon, J. J. Andre, and F. Bensebaa, *J. Am. Chem. Soc.*, **1992**, *114*, 447.
10. C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, **1983**, *105*, 1539.
11. B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, **1983**, *105*, 1551.
12. J. Metz, G. Pawlowski, and M. Hanack, *Z. Naturforsch*, **1983**, *38b*, 378.
13. N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, **1987**, *109*, 7433.
14. O. E. Sielcken, L. A. V. D. Kuil, W. Drenth, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, **1988**, 1232.
15. O. E. Sielcken, M. M. V. Tilborg, M. F. M. Roks, R. Hendriks, W. Drenth, and R. J. M. Nolte, *J. Am. Chem. Soc.*, **1987**, *109*, 4261.
16. O. E. Sielcken, L. A. V. D. Kuil, W. Drenth, J. Schoonman, and R. J. Nolte, *J. Am. Chem. Soc.*, **1990**, *112*, 3086.

Received 26 November 1998