ELSEVIER

Dyes and Pigments 41 (1999) 193–198

DYES and PIGMENTS

Synthesis, spectral and aggregation properties of a novel water-soluble tetracarboxynaphthalocyaninatozinc

Xiaobing Wang *, Daihua Tang, Zhen Zhen, Jiancheng Zhang, Xinhou Liu

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, People's Republic of China

Received 28 September 1998; accepted 21 October 1998

Abstract

A water-soluble tetracarboxynaphthalocyaninatozinc was prepared by hydrolysis of a novel tetracyano naphthalocyaninatozinc for the first time. Some factors affecting the kinds and yields of product are discussed and solvent effects affecting their visible absorption spectra are also reported. The compound showed a great tendency to form aggregate in NaOH solution. However, CTAB dissociated the aggregates to form cationic micelles. In DMSO, the degree of aggregation was different, and the aggregates were demonstrated to be dimers.

Keywords: Naphthalocyaninatozinc; Water-soluble; Synthesis; Cationic micelle; Visible absorption spectra; Aggregation

1. Introduction

Phthalocyanine compounds are a very important class of organic materials. They often show high thermal and chemical stability. Over the past decades, they have been found to be promising functional materials as semiconductors, photocatalysts, gas-sensors and in electrochromism, non-linear optical materials and photodynamic therapy (PDT) for cancer [1,2].

The PDT process in clinical use employs one of several dyes that are injected and selectively absorbed by cancer cells. The cancerous tissue interacts with the dye to form a toxin under the influence of lasers, and the toxin kills the cancer cells. A valuable dye should absorb light at wavelength longer than about 600 nm to avoid competitive absorption from blood, should show a good selectivity towards tumour cell uptake, and should have low general toxicity to healthy tissues.

It has been reported that phthalocyanines, particular the aluminum and zinc derivatives, show excellent PDT characteristics and low toxicity [3]. Their maxima absorption wavelengths are over 600 nm due to their 18π-electron ring-conjugation systems. These properties make these species potential candidates for use in PDT.

Naphthalocyanine derivatives (Nc) are similar in structure to phthalocyanines (Pc), but the additional benzo-substituents give rise to light absorption at longer wavelength, in the range of 780 nm, due to their extended conjugation systems. However, their notorious insolubility in organic solvents precludes their potential application. Some soluble substituted Ncs, including water-soluble tetrasulphonated naphthalocyaninatozinc

* Corresponding author.

0143-7208/99/$ - see front matter
PII: S0143-7208(98)00082-5

[4], have been prepared. Water-soluble naphthalocyanines are potentially more suitable than other Ncs in PDT, since they are compatible with biological media. This present investigation is aimed at the preparation of a novel water-soluble tetracarboxynaphthalocyaninatozinc, and an investigation of its spectral and aggregation properties, since these properties are important in its application.

2. Results and discussion

2.1. Preparation of tetracarboxynaphthalocyaninatozinc

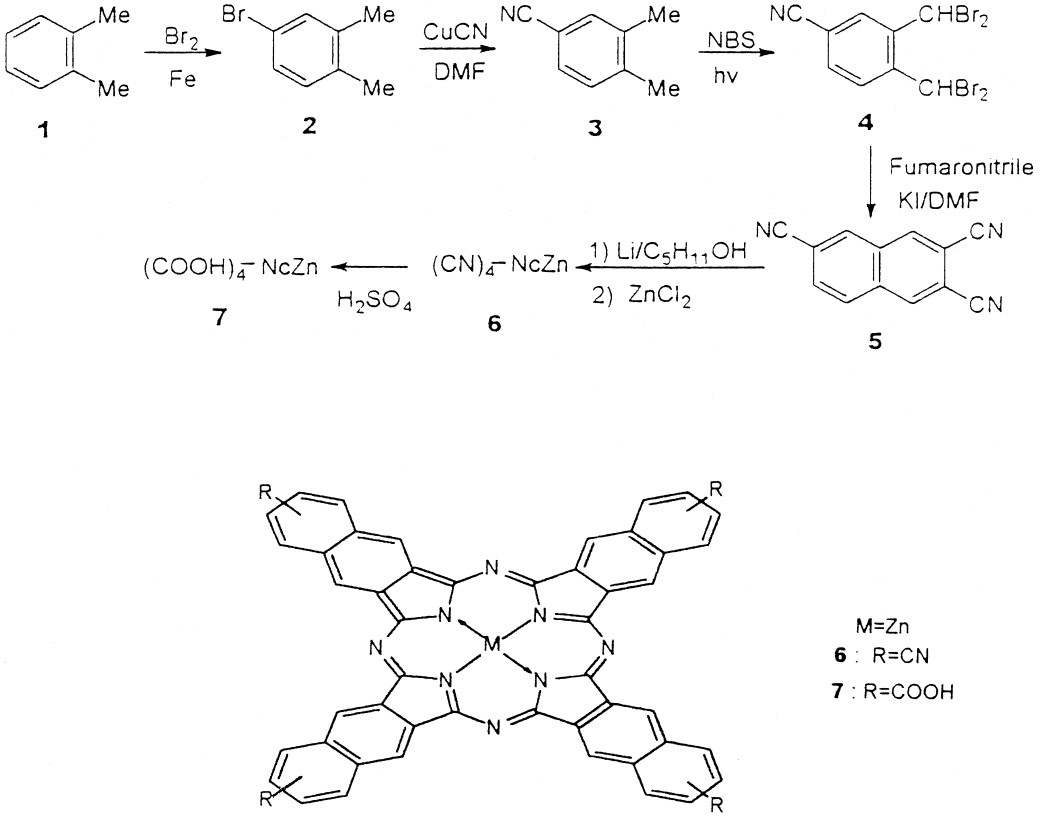
Two methods can be used to improve the solubility of Ncs [5]:

i. Introduction of substituents at the periphery of the Nc molecule;

ii. Coordination of the axial-bridged ligand with the central atom in Ncs.

The latter method is often limited by the central atom, since only a few atoms such as Si, Fe and Co, can be coordinated by some ligands. In the first method, substituents can be introduced before or after the formation of the phthalocyanines. In the latter case the number of substituents can be controlled by the reaction conditions. The situation is complicated by the numerous possibilities of positional isomerism. Water-soluble sulphonated Pcs or Ncs are typical examples [6].

In this paper, a novel water-soluble compound was prepared according to the synthetic route shown in Scheme 1. The carboxyl derivative was obtained by hydrolysis of the cyano groups which were introduced before the formation of the related naphthalocyanine. As is well known, water-soluble tetracarboxymetallophthalocyanines have



Scheme 1.

been directly prepared from carboxyphthalonitrile in mild reaction conditions. However, the difficulty in obtaining carboxynaphthalonitrile and the occurrence of decarboxylation at high temperature make the procedure unfeasible to be used to prepare the desired product.

Compounds **2–5**, were prepared by literature methods [7,8]. Compound **6**, a new tetracyano naphthalocyaninatozinc, was prepared from compound **5** in two steps in about 60% yield. Compound **6** was insoluble in many organic solvents such as ether, alcohol and chloroform.

Using compound **6** as a starting material, the desired water-soluble product was prepared by hydrolysis under acidic conditions. However, the acid concentration, the reaction time and temperature were the main factors which affected the yield of **7**. With respect to the acid concentration, 50% sulfuric acid was appropriate for the hydrolysis reaction, a higher concentration of acid readily giving rise to decomposition of compound **7**. The experimental work indicated that if aq HCl was used instead of sulfuric acid, compound **7** could not be obtained. Temperatures higher than 60°C were inappropriate; at 80–90°C, more than 5 h were necessary for the hydrolysis, otherwise mixtures containing partially-hydrolyzed products would be obtained. The yield was about 45%.

Product **7** was identified by elemental analysis, MALDI-TOF-MS (matrix assistant laser desorption ionization-time of flight-MS), IR and UV/Vis spectra. MALDI-TOF-MS is a recently developed technique, one of the advantages of which is the laser power can be varied so as to provide a range of ionization conditions. Low power laser ionization promotes parent ion formation rather than extensive fragmentation. It has been found that this technique is efficient to be used to identify Pcs on Ncs which are insensitive to light. The MS result demonstrated that no demetalization of the central atom occurred in the hydrolysis reaction.

2.2. Visible absorption spectra

The visible spectra of compounds **6** and **7** are shown in Figs. 1 and 2, respectively. In Fig. 1, compound **6** shows an intense peak at 756 nm, and a smaller peak at 704 nm in DMF. The peak at

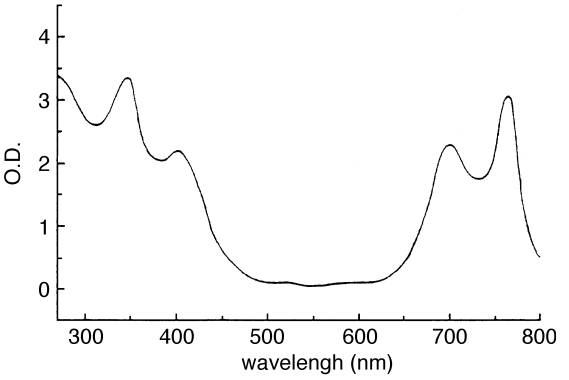


Fig. 1. Electronic absorption spectrum of compound **6** in DMF.

756 nm corresponds to the Q-band of the monomer, and the other peak at 704 nm is due to its aggregates. Fig. 2 shows the solvent effect on the spectrum of compound **7**. In dilute aq. sodium hydroxide, only one peak in the visible region was observed, at 699 nm ($\varepsilon = 4.51 \times 10^4$) (Fig. 2a). After the addition of CTAB (hexadecyltrimethylammonium bromide), the peak was split into two, one at the original wavelength and the other one at 766 nm (Fig. 2b). The peak at 766 nm was due to the monomer, which had an extinction coefficient of 1.26×10^5, which was greater than that of the aggregate. With increase of concentration of CTAB, the peak at 699 nm decreased and finally disappeared, whilst the peak at 766 nm increased to its maximum value. The effect of CTAB is the formation of cationic micelles, which can dissociate the aggregates. Fig. 2c shows two peaks at 769 and 711 nm in DMSO. The peak at 769 nm is the Q-band of the monomer and 711 nm is due to its aggregates. In DMF two peaks were obtained at 764 nm (Q-band) and 714 nm (Fig. 2d). Above all, whether the substituents are cyano- or carboxyl- groups, the maxima absorption wavelengths are over 750 nm since the main chromophore is their large π-conjugation systems.

2.3. Study of aggregation

It is well known that phthalocyanines tend to form molecular aggregates. The aggregated states have quite different characteristics when compared with the monomers. The water-soluble compound

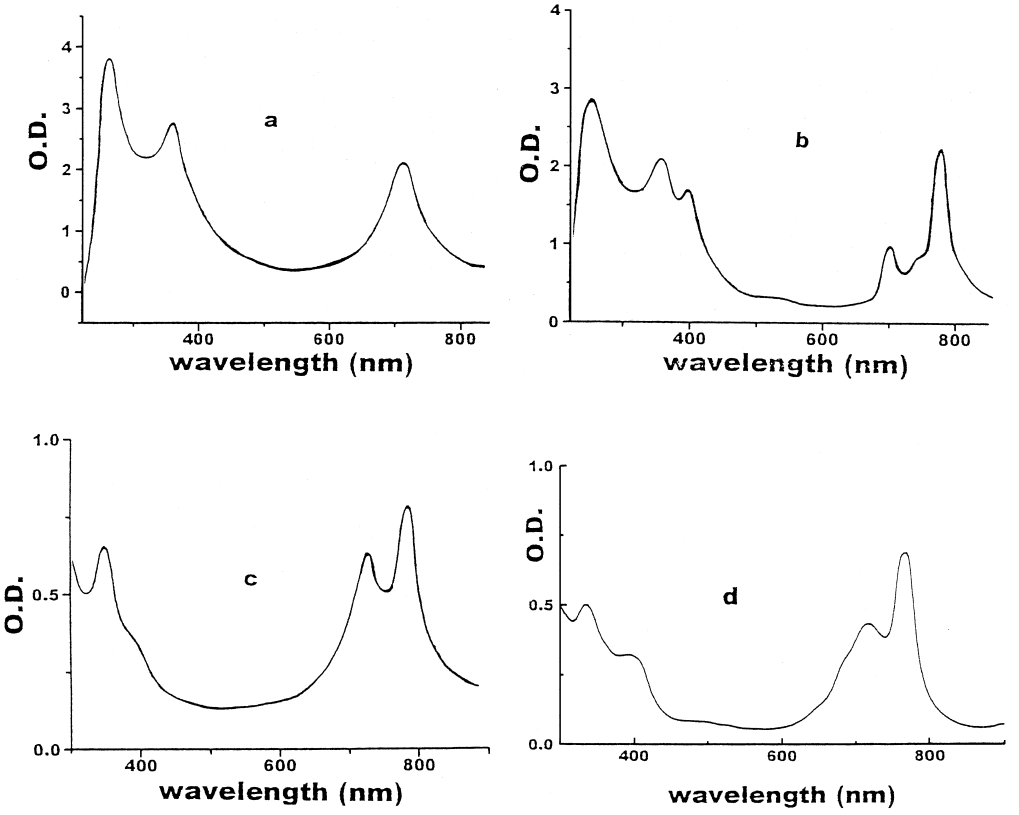


Fig. 2. Electronic absorption spectrum of compound **7**: (a) in 0.1 mol/dm^3 NaOH solution; (b) in the presence of CTAB; (c) in DMSO; (d) in DMF.

7 has a great tendency to form aggregate. In this paper a literature method [9] was used to determine the aggregation number. Assuming a one-step equilibrium between naphthalocyanine monomer (M) and its aggregates (An), the equilibrium is denoted by Eq. (1), where k is the aggregation constant and n is the aggregation number.

$$n\mathrm{M} \overset{k}{\rightleftharpoons} \mathrm{An} \tag{1}$$

k is given by Eq. (2), where x represents the ratio of monomer concentration to the total concentration, C_t. The observed extinction coefficient (ε) at a specific wavelength (λ) is represented by Eq. (3), where ε_m and ε_n are the extinction coefficients for pure monomer and the aggregate at λ, respectively.

$$K = x/[n\cdot C_t^{n-1}\cdot(1-x)^n] \tag{2}$$

$$\varepsilon = x\cdot\varepsilon_n/n + (1-x)\cdot\varepsilon_m \tag{3}$$

From Eqs. (2) and (3), Eq. (4) is obtained, where $C = n^n/(n-\varepsilon/\varepsilon_m)^{n-1}$. If the extinction coefficients of n-aggregates (ε_n) is very small at the maxima absorption wavelength of the monomer; Eq. (4) pertains:

$$\begin{aligned}&\log[C_t\cdot(1-\varepsilon/\varepsilon_m)]\\ &=\log(C\cdot k) + n\cdot\log[C_t\{\varepsilon/\varepsilon_m - \varepsilon_n/(n\cdot\varepsilon_m)\}]\end{aligned} \tag{4}$$

and this can be simplified to Eq. (5) at the maxima absorption wavelength by assuming $\varepsilon/\varepsilon_m >> \varepsilon_n/(n\cdot\varepsilon_m)$ and $n >> \varepsilon_n/\varepsilon_m$.

$$\log[C_t\cdot(1-\varepsilon/\varepsilon_m)] = \log(n\cdot k) + n\cdot\log[C\cdot(\varepsilon/\varepsilon_m)] \quad (5)$$

From Eq. (5), the slope of the plot of $\log[C_t\cdot(1-\varepsilon/\varepsilon_m)]$ vs $\log[C_t\cdot(\varepsilon/\varepsilon_m)]$ gives the aggregation number.

In NaOH solution, Beer's law was strictly obeyed for the band at 699 nm up to a concentration of 1×10^{-4} mol/dm^3 (Fig. 3a). The excellent linearity indicated that over wide ranges of concentration in NaOH solution, it had a very strong aggregation and the aggregates existed only in one form, though the peak at 699 nm was somewhat broad. In the presence of CTAB, the strong aggregates were dissociated. Fig. 3b shows the effect of CTAB on the aggregation in NaOH solution. The relationship between the concentration of CTAB and the aggregation degree is represented by the plot of absorption value (O.D.) vs log([CTAB]/[C]), where [CTAB] is the concentration of CTAB, and [C] is the concentration of compound **7**. The result shows that when the concentration of CTAB is about 100 times that of compound **7**, the monomer absorption reaches the maximum. That implies the aggregation is almost completely prevented.

In DMSO, the condition was quite different from that in NaOH solution. Fig. 3c shows that in DMSO, Beer's law was obeyed for the band at 769 nm up to a concentration of 4×10^{-5} mol/dm^3, above which the results show considerable deviation from linearity due to the apparent formation of aggregates.

An average extinction coefficient of the monomer at its maxima absorption wavelength was obtained from the slope of the line in Fig. 3c ($\varepsilon_m = 7.99\times10^4$). The slope of $\log[C_t\cdot(1-\varepsilon/\varepsilon_m)]$ vs $\log[C_t\cdot(\varepsilon/\varepsilon_m)]$ showed a good linearity as depicted in Fig. 3d. From the slope of the line, the aggregation number was obtained, viz., 2.01; this means that aggregated dimers formed in DMSO. The aggregation form was considered to be plane-

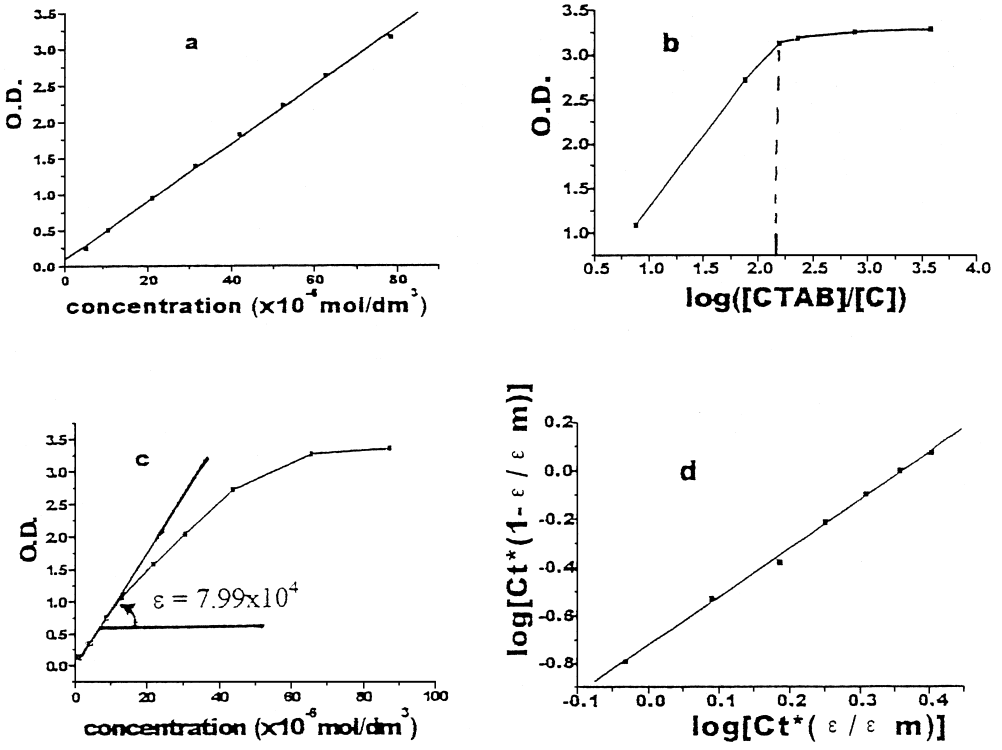


Fig. 3. (a) Aggregation of **7** in pure NaOH solution; (b) effect of CTAB in NaOH solution; (c) concentration dependence of absorption maxima of the monomer **7**; (d) plot of $\log[C_t\cdot(1-\varepsilon/\varepsilon_m)]$ vs $\mathrm{Log}[C_t\cdot(\varepsilon/\varepsilon_m)]$ in DMSO.

to-plane, due to the blue-shift of the maxima absorption peak of the aggregate, according to the theory of molecular exciton [10]. This present work also demonstrated that similar aggregation occurred in DMF.

3. Conclusions

Water-soluble tetracarboxynaphthalocyaninatozinc was prepared by hydrolysis of a novel tetracyano naphthalocyaninatozinc. Some factors which affected the product and its yield in the reaction are discussed. When the product was dissolved in NaOH solution, it showed a very great tendency to aggregate, so that no monomer was observed. In the presence of CTAB, the strong aggregates can be dissociated to form cationic micelles, and when the concentration of CTAB was about 100 times than that of compound **7**, aggregation was almost prevented. In DMSO or DMF, the degree of aggregation was quite different, and the aggregates in DMSO were demonstrated to be plane-to-plane dimers.

4. Experimental

Elemental analysis was measured by the ST-02.G.L. method, MALDI-TOF-MS was obtained on a Biflex III, IR on a Perkin–Elmer 983G, and electronic spectra on a Hewlett Packard 8451A. All solvents employed were of CP grade and were used without further purification.

4.1. Synthesis of tetracyano naphthalocyaninatozinc (**6**)

To the solution of lithium in *n*-pentanol was added 1.0 g of 2,3,6-tricyanonaphthalene under reflux. After 2 h, 1.5 g of $ZnCl_2$ was added, and refluxing was continued while stirring for 10 h; acetic acid was then used to decompose the mixture. After removal of the solvents under reduced pressure, the blue residue was extracted with methanol and chloroform, respectively. The resulting solid was washed with water and dried; yield 60% (0.65 g).

Elem. analy. ($C_{52}H_{20}N_{12}Zn$) calc: C71.15, H2.28, N19.16; found: C70.98, H2.57, N19.81; selected IR data (KBr pellets, cm^{-1}): 2222(s), 1644(m), 1351(s), 1086(m-s), 1027(m).

4.2. Synthesis of tetracarboxynaphthalocyaninatozinc (**7**)

Compound **6** obtained as above was hydrolyzed in 50% sulfuric acid at 80–90°C for 5–6 h. The resulting mixture was diluted with water and filtered. The solid was dissolved in NaOH solution. After removal of insoluble solid by suction-filter, the product was precipitated from the solution when acid solution was added. The precipitate was washed with water and dried. The yield was 45% (0.32 g).

Elem. analy. ($C_{52}H_{24}N_8O_8Zn$) calc: C65.48, H2.52, N11.75; found: C66.02, H2.73, N12.11, MALDI-TOF-MS: 952 (m/z); selected IR data (KBr pellets, cm^{-1}): 1709(vs), 1611(m), 1354(s), 1334(s), 1146(m), 1080(m).

Acknowledgements

This work was supported by National Natural Science Foundation of China (Project no. 29584003). The authors also wish to express their gratitude to the research group in the Institute of Chemistry for provision of element analysis and mass spectrometry services.

References

[1] Snow AW, Barger WR. In: Lexoff CC, Lever ABP, editors. Phthalocyanines: properties and applications vol. 1. New York:VCH, 1989. p. 121–73.
[2] Griffiths J, Schofield J, Wainwright M, Brown SB. Dyes and Pigments 1997;33(1):65–78.
[3] Rosenthal I. Photochem. Photobiol. 1991;53:859.
[4] McCubbin I, Phillips D. J Photochem 1986;34:187–95.
[5] Hanack M, Kang YG. Synthetic Metals 1992;48:79–90.
[6] Linstead RP, Weiss FT. J Chem Soc 1950;5:2975.
[7] Friedman L, Schechter H. J Org Chem 1961;26:2522.
[8] Kovshev EI, Puchnova VA, Luk'yanets EA. Zh Org Khim 1971;7:369–70.
[9] Tai S, Hayashi N. J Chem Soc Perkin Trans 2 1991;1275.
[10] Bartolo BD. Spectroscopy of the excited state. New York: Plenum Press, 1976. p. 337.