

Dendritic metallophthalocyanines: synthesis and characterization of a zinc(II) phthalocyanine[8]³-arborol

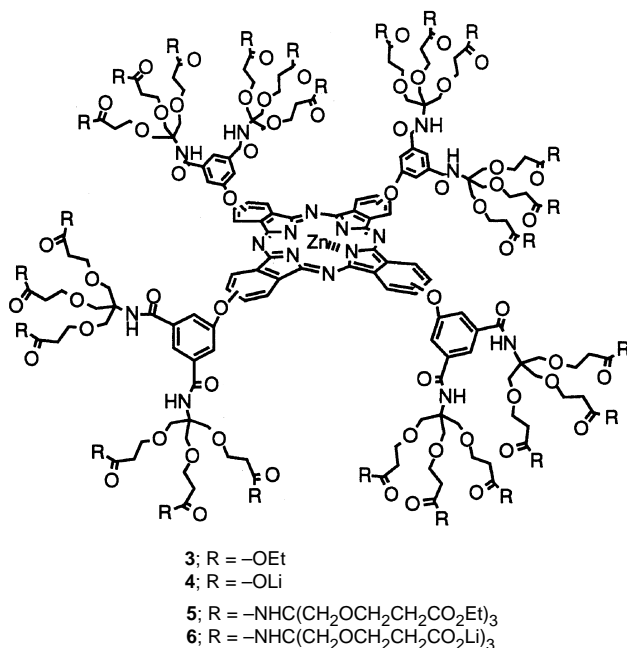
Mutsumi Kimura,^{*a} Kazuaki Nakada,^a Yuji Yamaguchi,^a Kenji Hanabusa^a Hirofusa Shirai^a and Nagao Kobayashi^b

^a Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan

^b Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

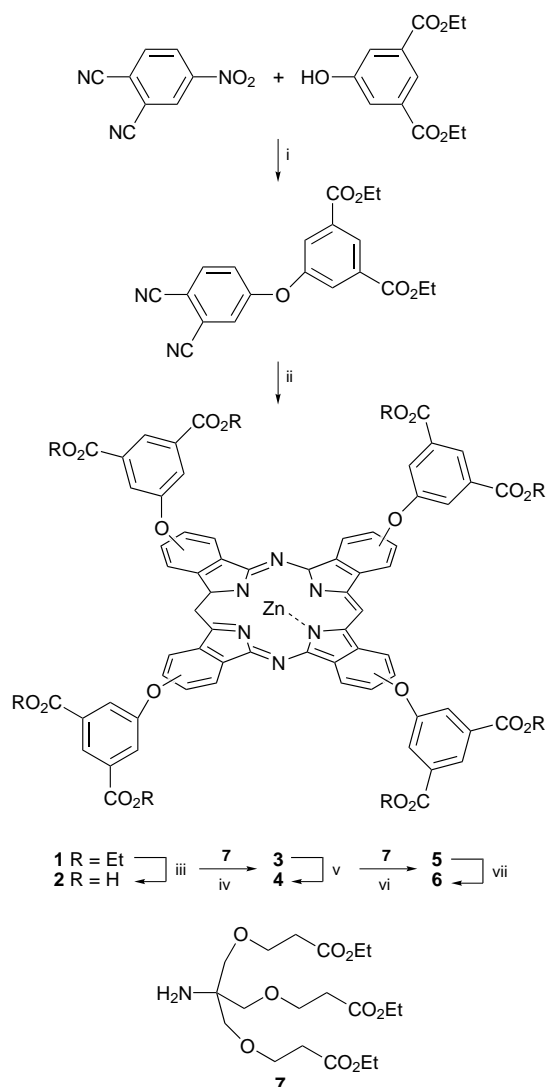
New dendritic metallophthalocyanines are prepared on the basis of Newkome's divergent-growth approach; the number of generations within the dendrimer is found to affect the aggregation behaviour of the zinc(II) phthalocyanine moiety which forms the interior core of the dendrimers.

The synthesis of dendrimers has recently attracted much interest. Dendrimers have a well defined globular structure with uniform molecular mass.¹ Functional dendrimers have been prepared by the introduction of functional compounds such as metal complexes, fullerenes and biomaterials to the exterior surface and the interior cores of dendrimers.² Highly branched dendrimers have provided a unique environment for these functional compounds, giving rise to a variety of new and modified properties.³ Constructing a dendrimer around a phthalocyanine core could control the aggregation of the complex in aqueous media and modify its photoreactivity. Here, we report the synthesis of the first dendritic zinc(II) phthalocyanines 3–6 using cascade polymer methodology. The environment of photoactive zinc phthalocyanine can be controlled through encapsulation in dendrimers.



The polyether–amide dendrimers containing zinc(II) phthalocyanine derivatives were prepared by the method of Newkome *et al.*⁴ according to Scheme 1.⁴ The starting point for the synthesis of the dendrimers 3–6 was the octacarboxylic acid 2 prepared from ester 1. Reaction of acid 2 with amine 7, dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) in THF at 5 °C affords the first generation dendrimer 3 in 75% yield which was purified by gel permeation chromatog-

raphy (Biorad Biobeads SX-3, ethyl acetate). The hydrolysis of 3 with LiOH in MeOH–H₂O afforded the first-generation dendrimer 4 bearing 24 carboxylic acid groups. A repeat of this reaction gave the second-generation dendrimers 5 and 6. Dialysis of the reaction mixture for 2 d after hydrolysis of 3 and 5 in water, followed by freeze-drying, gave the water-soluble dendrimers 4 and 6. The structures of these compounds were confirmed by ¹H and ¹³C NMR spectroscopies, FTIR, UV–VIS



Scheme 1 Synthesis of dendrimers 3–6. Reagents and conditions: i, K₂CO₃, DMF, room temp., 72%; ii, DBU, ZnCl₂, *n*-pentanol, reflux, 24 h, 42%; iii, NaOH, H₂O–THF, 48 h, 96%; iv, DCC, HOBt, THF, 5 °C, 72 h, 75%; v, LiOH, MeOH–H₂O (1 : 1), 20 °C, 48 h, 96%; vi, DCC, HOBt, THF, 5 °C, 72 h, 70%; vii, LiOH, MeOH–H₂O, 48 h, 81%.

and mass spectrometric analysis. Compounds **1**, **3** and **5** were soluble in organic solvents (*e.g.* chloroform, benzene, THF, DMF, acetonitrile) while **2**, **4** and **6** were water-soluble. GPC chromatograms of esters **3** and **5** show a single sharp peak for each dendrimer. These results indicate that the dendrimers are monodispersed. Dendrimer **6** (0.5 mM aqueous solution) was negatively stained, dried and examined using transmission electron microscopy (Fig. 1). The aggregates of small spheres (*ca.* 20 nm diameter) appear as light areas against a darker background. CPK models of **6** predict a highly branched,

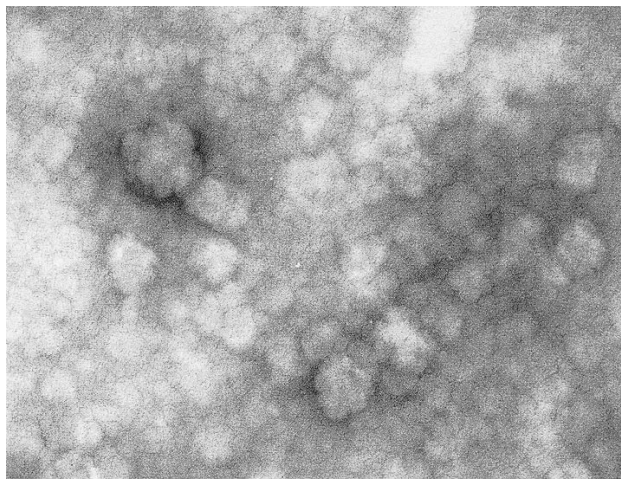


Fig. 1 Transition electron micrograph of **6**, negatively stained with 2% phosphotungstic acid. Bar = 100 nm; 120 000 × magnification.

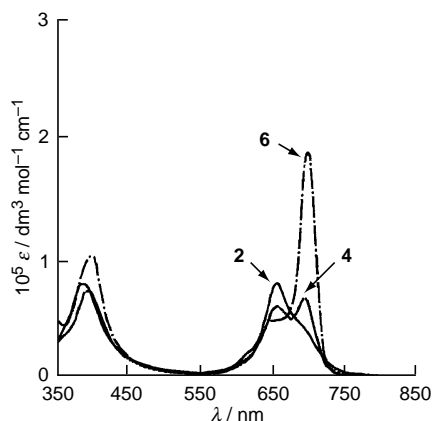


Fig. 2 UV-VIS spectra of dendritic phthalocyanines **2**, **4** and **6** in aqueous phosphate buffer at pH 7.1

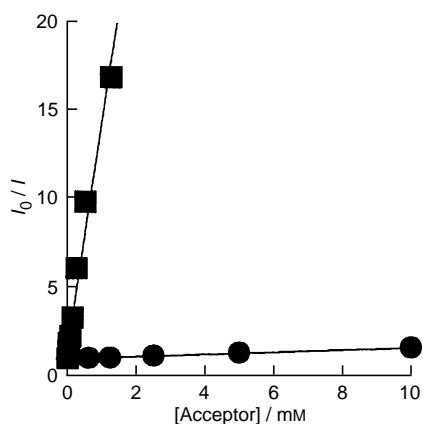


Fig. 3 Steady-state fluorescence titration of MV^{2+} (■) and SPV (●) into **6** (1.2 μM), excitation 370 nm, emission 674 nm in aqueous phosphate buffer at pH 7.1

globular structure, approximately 5 nm in diameter. From the dimensions of **6** *ca.* 30 molecules of the dendrimer per aggregate is estimated.

The UV-VIS spectra indicate the inner environment of zinc phthalocyanine located within the interior core of the dendrimers. The spectra of **3** and **5** showed a sharp peak at 678.0 nm [$\log(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) = 5.47$] with a shoulder at 621.0 nm in CHCl_3 , and were not influenced by the number of the generations. In aqueous media, the UV-VIS spectra of **2**, **4** and **6** were quite different, reflecting the number of generations. Dendrimer **6** showed a Q band at 687.0 nm which is typical of non-aggregated Zn phthalocyanines (Fig. 2). However, a sharp peak was not observed for **2** and **4**. The spectra of **2**, **4** and **6** were little affected upon increasing the pH from 7.1 to 10.5. The broad peak at 622.0 nm, attributed to the aggregation of Zn phthalocyanine, indicates that the complexes interacted hydrophobically in aqueous media.⁵ With increasing dendrimer generation, the shielding effect of the dendrimer is enhanced owing to the increased size of the molecular cage. Zinc phthalocyanine exhibits a strong fluorescence peak at 674 nm upon excitation at 370 nm, which is quenched by the addition of methyl viologen (MV^{2+}) and propylviologen sulfonate (SPV). Dendrimer **6** displays a strong fluorescence peak in aqueous media, however, **2** and **4** did not fluoresce because of aggregation of zinc phthalocyanine units. Stern-Volmer plots differ using MV^{2+} or SPV as electron-transfer quenching agents (Fig. 3). Addition of a small amount of positively charged MV^{2+} to an aqueous solution of **6** led to efficient fluorescence quenching. On the other hand, only little fluorescence quenching occurred upon addition of zwitterionic SPV. Addition of NaCl drastically diminished the fluorescence quenching by MV^{2+} . This behaviour can be explained by a decrease in the local concentration of MV^{2+} adjacent to the dendrimer surface. This efficient quenching of the phthalocyanine fluorescence occurs *via* accumulation of MV^{2+} on the negatively charged dendrimer surface. The fluorescence quenching results suggest an electron-transfer reaction between the zinc phthalocyanine and MV^{2+} through the dendrimer framework. The electron-transfer quenching agents were reduced by **6** under light irradiation in the presence of triethanolamine as a sacrificial donor.

In conclusion, the number of generations affected the aggregation behaviour of the zinc phthalocyanine located in the centre of the dendrimer. The molecular cage inhibited aggregation of the zinc phthalocyanines in aqueous media, and electron transfer was observed through the dendrimer architecture from the zinc phthalocyanine core to MV^{2+} accumulated on the surface of the dendrimer.

Footnote

* E-mail: mkimura@giptc.shinshu-u.ac.jp

References

- 1 D. A. Tomalia and H. D. Durst, *Top. Curr. Chem.*, 1993, **165**, 193; J. M. J. Fréchet, *Science*, 1994, **263**, 1710.
- 2 S. Achar and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1994, 1895; C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1994, 925; G. R. Newkome, X. Lin and C. D. Weis, *Tetrahedron: Asymmetry*, 1991, **2**, 957; K. Aoi, K. Itoh and M. Okada, *Macromolecules*, 1995, **28**, 5391.
- 3 R.-H. Jin, T. Aida and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1993, 1260; R. Sadamoto, N. Tomioka and T. Aida, *J. Am. Chem. Soc.*, 1996, **118**, 3978; P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and M. E. Sanford, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1739.
- 4 G. R. Newkome and X. Lin, *Macromolecules*, 1991, **24**, 1443.
- 5 A. Louati, M. E. I. Meray, J. J. Andre, J. Simon, K. M. Kadish, M. Gross and A. Giraudeau, *Inorg. Chem.*, 1985, **24**, 1175; J. R. Darwent, I. MacCubbin and G. Porter, *J. Chem. Soc.*, 1982, **78**, 903.

Received in Cambridge, UK, 24th February 1997; Com. 7/01263B