Pergamon

Tetrahedron Letters 44 (2003) 5163–5165

TETRAHEDRON
LETTERS

Soluble precursors convertible to tetrabenzoporphyrins below room temperature

Hidemitsu Uno,[a,]* Takayuki Ishikawa,[a,b] Toru Hoshi[a] and Noboru Ono[c]

[a]*Division of Synthesis and Analysis, Department of Molecular Science, Integrated Center for Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan*
[b]*i Material Development Center, Canon Inc., 16-1 Shimonoge 3-chome, Takatsu-ku, Kawasaki 213-8512, Japan*
[c]*Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan*

Received 1 May 2003; revised 19 May 2003; accepted 22 May 2003

Abstract—Porphyrins fused with dihydroxylated bicyclo[2.2.2]octadiene at β-positions were quantitatively converted to the corresponding tetrabenzoporphyrins either by treatment with NaH in DMF at 0°C or on boehmite at room temperature. © 2003 Published by Elsevier Science Ltd.

Highly π-extended compounds attract great attention in various fields. Among them, phthalocyanines and their isoelectronic compounds such as tetrabenzoporphyrins (TBPs) are of considerable interest not only as common, easily-accessible, and well-known colorants but also due to their wide applicability for non-linear optical materials,[1] optical memories,[2] and opt-electronic materials.[3] For the application of these compounds, one of the biggest problem associated with such pigments is the low solubility in common solvents, which hampers the reliable preparation of their derivatives and requires several manipulations of a high vacuum sublimation technique for purification. In the final stage of device preparation, too, the vapor deposition technique under high vacuum is the only applicable method, although the precious compounds are considerably lost during the manipulation. In order to circumvent the problem, we explored the preparation of TBPs from the readily-soluble, bicyclo[2.2.2]octadiene-fused porphyrin precursors based on the retro Diels–Alder reaction.[4] This method opens new usage of TBPs as pigment for spin-coating. In the retro Diels–Alder reaction, however, rather high temperature (>170°C) was required. The high temperature may become a problem when the materials and their derivatives are applied for organic thin film transistors (OTFT).[5] This problem has been solved by introduction of hydroxyl groups on the leaving ethylene moieties. In this communication, we will demonstrate our strategy for the conversion of soluble precursors to TBPs below room temperature.

Our strategy is based on the qualitative consideration of HOMO–LUMO interaction of TBPs and the leaving ethylene moiety.[6] Both strongly electron-donating and electron-withdrawing groups on the leaving ethylene unit will facilitate both the Diels–Alder and the retro Diels–Alder reactions.[7] Among them, a hydroxy group is thought to be superior, because the group makes the retro Diels–Alder reaction irreversible and can be converted to one of the strongest electron-donating group, alkoxide, under alkaline conditions. In addition, the precursor porphyrin would become soluble in environment-friendly protic solvents such as alcohols. Therefore, we planned to synthesize the TBP precursors **5**.

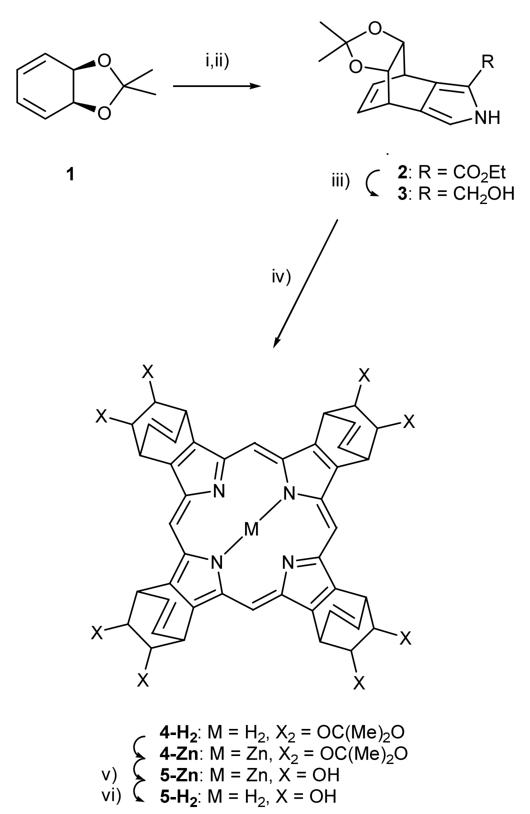
Preparation of the TBP precursors **5** is summarized in Scheme 1. The known acetonide-protected diene **1**[8] was converted to bicyclo[2.2.2]octadiene-fused pyrrole **2** in 48% yield by the Diels–Alder reactions with 2-nitro-1-(phenylsulfonyl)ethylene followed by the Barton–Zard reaction.[9] Reduction of the ester group with $LiAlH_4$ at 0°C followed by the acidic cyclotetramerization gave a diastereomeric mixture of porphyrin **4-H$_2$**, which was purified by column chromatography on silica gel after conversion to zinc porphyrin **4-Zn** (38% yield). Deprotection of the acetonide group with diluted HCl (0.5 M in H_2O/THF = 1/1) gave the zinc TBP precursor **5-Zn**†

---

* Corresponding author. Tel.: +81-89-927-9660; fax: +81-89-927-9670; e-mail: uno@dpc.ehime-u.ac.jp

† Spectroscopic data for **5-Zn**: diastereomeric mixture, red powder, R_f 0.05 (EtOAc/$CHCl_3$); δ_H ($CDCl_3$) 10.6–10.3 (4H, m), 7.18 (8H, br-m), 5.85 (8H, m), 4.34 (8H, m) and 1.27 (8H, br, OH); ν_{max} 3359, 2937 and 1035 cm^{-1}; λ_{max} 405, 533 and 567 nm. Calcd for **5-Zn**·$2.5H_2O$, $C_{44}H_{41}N_4O_{10.5}Zn$: C, 61.51; H, 4.81; 6.52. Found: C, 61.52; H, 4.55; N, 6.41%.

0040-4039/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4039(03)01265-6



Scheme 1. *Reagents, conditions, and yields*: (i) $PhSO_2CH{=}CHNO_2$, toluene, 60°C, 4 h, 49%; (ii) $CNCH_2CO_2Et$, DBU, THF, rt, 12 h, 98%; (iii) $LiAlH_4$, THF, rt, 1 h, quant; (iv) *p*TSA, $CHCl_3$, rt, 24 h; chloranil, $CHCl_3$, rt, 24 h; $Zn(OAc)_2$, $CHCl_3$, MeOH, rt, 4 h, overall 38%; (v) 1 M HCl/THF = 1/1, rt, 4 h, 84%; (vi) TFA, rt, quant.

in 84% yield. This TBP precursor was a mixture of four diastereomers according to the relative position of 1,2-dihydroxyethano and etheno bridges. Demetallation of **5-Zn** was achieved by treatment with TFA and **5-H$_2$** was obtained in quantitative yield. The precursors **5** were readily soluble in alcoholic solvents. The solubility of **5-Zn** in *i*-PrOH, MeOH, and *i*-PrOH/H_2O (1/9) was 2.56, 1.40, and 0.77 g/100 g, respectively. The UV–vis spectrum of **5-Zn** is shown in Figure 1 and is very similar to that of octaethylporphyrin–Zn.

The thermal behavior of **5** was examined and **5** was heated at a rate of 15°C/min to 250°C by DSC. Very complex peaks corresponding to the conversion to TBPs were observed above 170°C, and the residue was first treated with deuterium oxide and then with pyridine-d_5. The NMR analysis of both extracts revealed clean conversion of the precursors **5** to TBPs and hydroxyacetaldehyde, the latter of which was detected as cyclic dimers and polymeric species in the D_2O extract. Formation of hydroxyacetaldehyde was unambiguously determined by comparison of TG-GC/MS data with the EPA/NIH MS data base.[10] The conversion temperature was similar to those when ethylene molecules were evolved.[4] Contrary to the neutral decomposition of **5-Zn** in solid, the TBP formation from **5-Zn** was remarkably facilitated when **5-Zn** was treated with NaH in DMF.[11] Even at 0°C, **5-Zn** was completely transformed into TBP–Zn within 1 h.

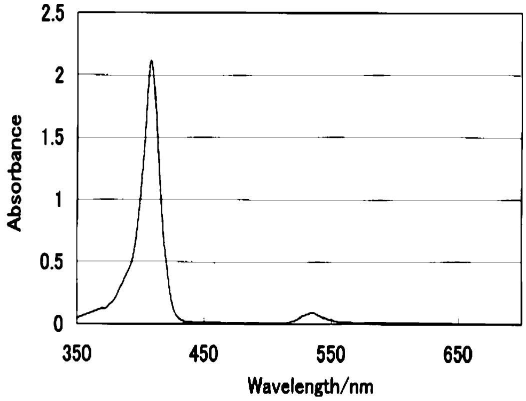


Figure 1. UV–vis spectrum of the zinc TBP precursor **5-Zn**.

In order to extend the utility of precursors **5**, we next searched for solid catalysts for TBP formation. A solution of **5-Zn** in *i*-PrOH was treated with some adsorbents such as neutral alumina, silica gel, Florisil, and Celite at room temperature, but no change was observed except in the case of alumina. When the red solution of **5-Zn** was treated with neutral alumina for chromatography, surface of the alumina gradually colored to green, which indicated the formation of TBP on alumina, as the red color of the solution faded. Finally, the red color of the solution completely disappeared and the solution became colorless after 1 day. Thorough extraction of the green alumina with pyridine gave almost quantitative amounts of TBP–Zn. More efficient conversion was observed in the case of boehmite, $Al_2O_x(OH)_{3-x}$, which is used as an additive in some specially high quality papers for ink-jet printers. In this case, the conversion completed within 1 h and the *i*-PrOH solution became colorless. In order to check whether intermediary mono-, di-, and tri-benzoporphyrins existed on the boehmite during the retro-Diels–Alder reaction of **5-Zn** to TBP–Zn, UV–vis spectra of

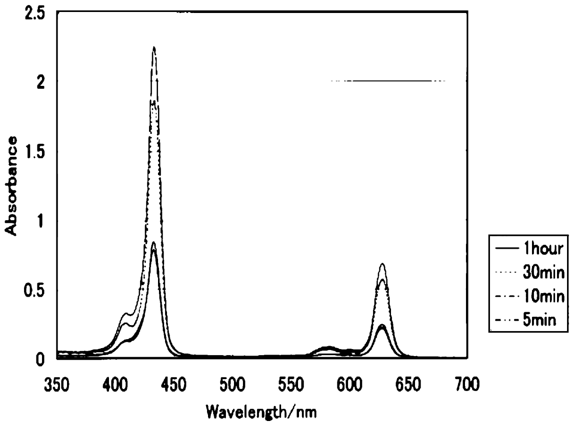


Figure 2. Time-dependent UV–vis spectra in the conversion of **5-Zn** to TBP–Zn on boehmite

the adsorbed colorants were measured by thorough extraction of the boehmite with pyridine after the indicated time (Fig. 2).[‡] In all cases, the boemite became almost colorless after extraction with pyridine; all colored materials on the boemite were extracted with pyridine. In any case, no other Soret band corresponding to mono- and di-benzoporphyrins[12] was observed. Therefore, we deduced that the four successive retro-Diels–Alder reactions giving TBP–Zn proceeded very smoothly on the adsorbent. This conversion was, of course, observed on the papers for ink-jet printers within several hours, although the conversion speed were rather slower.

In conclusion, we lowered the conversion temperatures of readily-soluble precursors to TBPs. The conversion was also demonstrated on the adsorbents such as alumina and boehmite. In the latter cases, conversion to TBPs was almost instantaneously, when the precursors were adsorbed. This type of precursors is very useful for patterning of insoluble pigments such as TBPs by the ink-jet printing technique.

Acknowledgements

We appreciate the partial financial support of Canon Inc. T.I. thanks Canon Inc. for permission of researching at Ehime University.

References

1. (a) Nalwa, H. S.; Kakuta, A.; Mukoh, A. *J. Phys. Chem.* **1993**, *97*, 1097; (b) Cho, Z. Z.; Ju, C. Y.; Hetherrington III, W. M. *J. Appl. Phys.* **1987**, *62*, 716.
2. Jankowiak, R.; Small, G. J. *Chem. Rev.* **1993**, *93*, 1471.
3. (a) Saito, T.; Sisk, W.; Kobayashi, T.; Sasaki, S.; Iwayanagi, T. *J. Phys. Chem.* **1993**, *97*, 8026; (b) Okada, K.; Okada, O.; Nukade, K. *Jpn. J. Appl. Phys.* **1992**, *31*, 2181; (c) Fujimaki, Y.; Tadokoro, H.; Oda, Y.; Yoshida, Y.; Homma, T.; Morigucgi, H.; Watanabe, K.; Kinoshita, A.; Hirose, N.; Itami, A.; Ikeuchi, S. *J. Imaging Technol.* **1991**, *17*, 202; (d) Stanbery, B. J.; Gouterman, M.; Burgess, R. M. *J. Chem. Phys.* **1987**, *89*, 4950; (e) Yokura, Y.; Koda, T.; Iyechika, Y.; Kuroda, H. *Chem. Phys. Lett.* **1986**, *102*, 174; (f) Loutfy, R. O.; Sharp, J. H. *J. Chem. Phys.* **1978**, *71*, 1211.
4. Ito, S.; Murashima, T.; Uno, H.; Ono, N. *Chem. Commun.* **1998**, 1661.
5. Dimitrakopoulas, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
6. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: London, 1976.
7. (a) Rickborn, B. The Retro-Diels–Alder Reaction. Part I. C–C Dienophiles in Organic Reactions. In *Organic Reactions* **1998**, *52*, Chapter 1; (b) Rickborn, B. The Retro-Diels–Alder Reaction. Part II. Dienophiles with One or More Heteroatoms. In *Organic Reactions* **1998**, *53*, Chapter 2.
8. (a) Gillard, J. R.; Burnell, D. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1439; (b) Cotteril, I. C.; Roberts, S. M.; Williams, J. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1628.
9. (a) Uno, H.; Ito, S.; Wada, M.; Watanabe, H.; Nagai, M.; Hayashi, A.; Murashima, T.; Ono, N. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4347; (b) Ito, S.; Murashima, T.; Ono, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1316.
10. Heller, S. H.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*, National Bureau of Standards, Washington, DC, US Department of Commerce, National Technical Information Service, 1978, Vol. 1.
11. Rajanbabu, T. V.; Eaton, D. F.; Fukunaga, T. *J. Org. Chem.* **1983**, *48*, 652.
12. Ito, S.; Nakamoto, K.; Uno, H.; Murashima, T.; Ono, N. *Heterocycles* **2002**, *52*, 399.

[‡] The time-dependent UV–vis spectra were obtained as follows. A solution of **5-Zn** (5 mg) in *i*-PrOH (50 mL) was stirred with boehmite powder (1 g). After the indicated time, an aliquot of the suspension was filtered. The filtered green boehmite was thoroughly extracted with pyridine until the boehmite became colorless, and the pyridine extract was concentrated. All amounts of the residue was dissolved in spectroscopic-grade pyridine and the UV–vis spectra were measured.