HETEROCYCLES, Vol. 77, No. 2, 2009, pp. 755 - 758. © The Japan Institute of Heterocyclic Chemistry
Received, 28th July, 2008, Accepted, 26th September, 2008, Published online, 29th September, 2008
DOI: 10.3987/COM-08-S(F)63

PREPARATION OF UNSYMMETRIC PHTHALOCYANINES WITH BENZYLCHALCOGENO AND BUTOXY GROUPS

Takeshi Kimura,* Takeru Obonai, and Toshiharu Namauo

Center for Instrumental Analysis, Iwate University, Morioka, Iwate 020-8551, Japan
E-mail: kimura@iwate-u.ac.jp

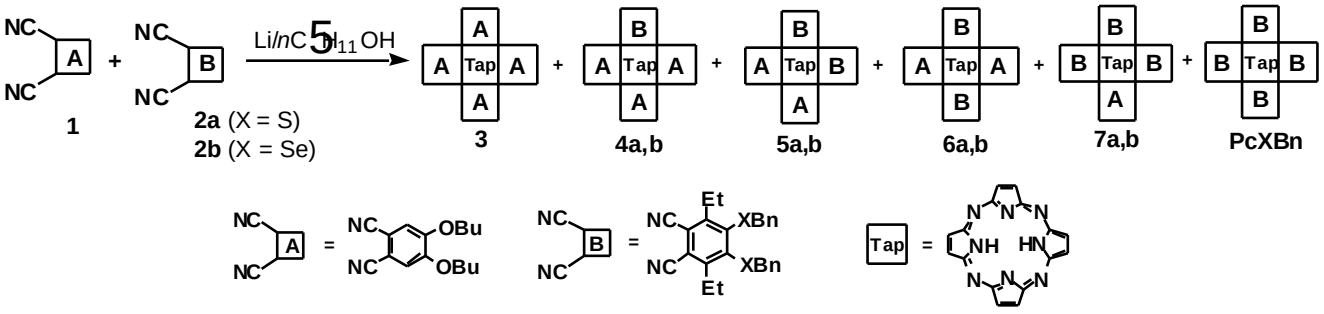
Dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

Abstract – A mixture of 4,5-dibenzylchalcogeno-3,6-diethylphthalonitrile and 4,5-dibutoxyphthalonitrile was treated with lithium in *n*-pentanol at 110 °C to give unsymmetric phthalocyanines. Optical and electrochemical properties of them were examined by UV-vis spectroscopy and cyclic voltammetry.

Phthalocyanines have a variety of actual and/or potential applications as catalysts, optical disks, charge-generating materials, and sensitizers for photodynamic therapy.[1] Although there are many procedures for preparing phthalocyanines, three approaches have been used to obtain unsymmetric ones.[2-4] We recently reported the preparation of octakis(benzylchalcogeno)phthalocyanines [**PcSBn** and **PcSeBn**] and their related compounds.[5a] In the UV-vis spectra of **PcSBn** and **PcSeBn**, the difference of their wavelengths of the Q-band absorption is small ($\Delta \lambda_{max}$ = 2 nm) although the peripheral chalcogen atoms are different each other. It is likely that the π-electronic system of symmetric phthalocyanines is not strongly affected by the peripheral benzylthio and benzylseleno groups. To estimate the influence of different chalcogen atoms, phthalocyanines with the butoxy, benzylthio, and benzylseleno groups at the β-positions were prepared, and their absorption spectra and electrochemical properties were examined by UV-vis spectroscopy and cyclic voltammetry.

Typically, phthalonitriles (**1**) and (**2a**) were mixed in a 1:1 ratio and treated with lithium in *n*-pentanol at 110 °C for 1 h (Scheme 1 and Table 1).[5] The blue-green precipitate was purified by column chromatography to produce six phthalocyanines; **3** (16%), **4a** (20%), **5a** (12%), **6a** (trace), **7a** (trace), and **PcSBn** (5%). Compounds (**4a**), (**5a**), and (**7a**) easily dissolved in $CHCl_3$, respectively, while the solubility of **6a** was low in the solvent. By the similar reaction at 100 °C, the products were obtained in the following distribution; **3** (21%), **4a** (17%), **5a** (12%), **6a** (8%), and **7a** (14%). When the reaction

was performed at 110 °C (**1**:**2a** = 5:1), **3** (27%) was obtained together with **4a** (17%), **5a** (17%), **6a** (2%), and **7a** (trace), and **PcSBn** could not be determined in the reaction mixture.



Scheme 1

Table 1.

A : B	X	Temp.	Time [min]	Yield (%)					
				3	**4a**	**5a**	**6a**	**7a**	**PcSBn**
5:1	S	120	55	63	-	2	-	-	-
5:1	S	110	60	27	17	17	2	trace	-
1:1	S	110	60	16	20	12	trace	trace	5
1:1	S	100	60	21	17	12	8	14	-
				3	**4b**	**5b**	**6b**	**7b**	**PcSeBn**
6:1	Se	110	120	38	11	1	trace	-	-

In the ^{1}H NMR spectrum of **4a**, the integral ratio of CH_3 was 3:1 for the butyl and the ethyl groups.[6] In contrast, the ratio of CH_3 of **7a** was observed as 1:3 for the butyl and the ethyl groups. The results suggest that **4a** has three A units and one B unit while **7a** has one A unit and three B units. The ^{1}H NMR spectrum of **5a** showed two triplet signals for CH_2 linked to the oxygen atom and two singlet peaks for CH_2 connected to the sulfur atom in which the integral ratio of two types of CH_2 was 1:1. To observe the signal of **6a** with ^{1}H NMR spectroscopy, the sample was measured in $CDCl_3$ at 55 °C. In the spectrum, two types of CH_2, which are bonded to the oxygen and sulfur atoms, were observed as one triplet and one singlet peak, respectively, in a 1:1 ratio. The results reveal that **5a** is the *cis* isomer and **6a** is the *trans* isomer. FABMS showed the molecular ion peaks of **4a**, **5a**, and **7a** while the structure of **6a** was determined with ESIMS.[6] As shown in Figure 1, UV-vis spectra of the products were measured in $CHCl_3$ ($c = 1.0 \times 10^{-5}$ mol/L). The Q-bands of **3** and **5a** were observed as split signals while the wavelength of the absorption of **5a** (λ_{max} = 724 nm) was longer than that of **3** (λ_{max} = 704 nm). The split and broad absorption of **4a** was found at 621, 654, 683, 702, and 721 nm, which may show the both characters of the absorption spectra of **3** and **5a**. The absorption of **6a** was observed as a sharp signal at 703 nm together with a weak signal at λ_{max} = 741 nm. It seems that the Q-band absorptions of these phthalocyanines are shifted to longer wavelength when the number of the B unit is increasing. Although the λ_{max} value of **7a** was found at 715 nm, the wide Q-band should contain the absorption peak lying at around 740 nm.

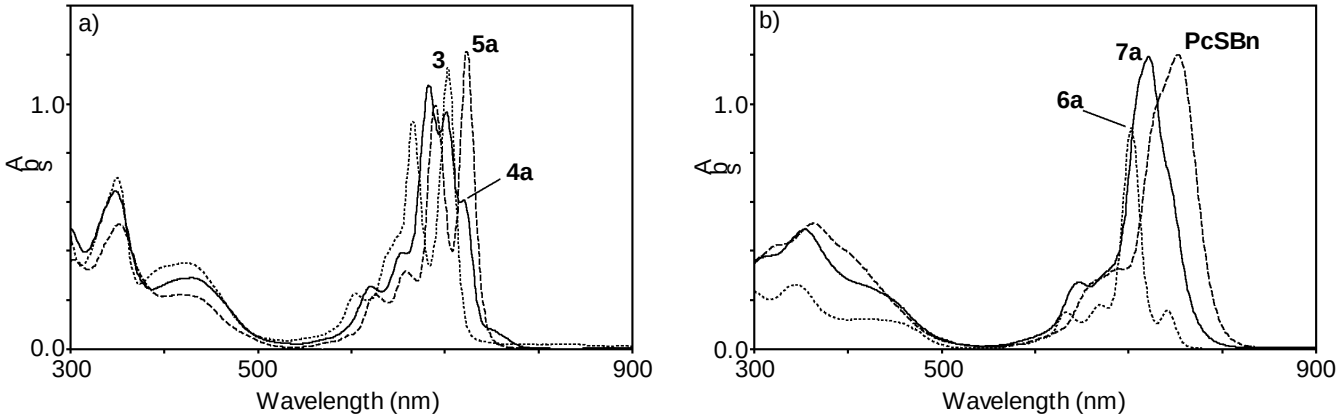


Figure 1. UV-vis spectra of phthalocyanines measured in $CHCl_3$: a) **3**, **4a**, and **5a** and b) **6a**, **7a**, and **PcSBn**.

Table 2. Redox potentials (V)

Pc	2nd redn	1st redn	1st oxid	2nd oxid	3rd oxid	Pc	2nd redn	1st redn	1st oxid	2nd oxid
4a	-1.11	-0.84	0.66	1.02[b]	1.24[a]	**PcSBn**	-1.31	-1.02	0.49	0.72
5a	-1.62	-1.32	0.24	0.51[b]	0.62[a]	**4b**	-1.49[a]	-1.20	0.32	0.72
7a	-0.97	-0.69	0.86	1.06	-	**PcSeBn**	-1.32	-1.03	0.46	0.74[b]

When the scan rate was fast, the differences between cathodic and anodic peaks for the oxidation potential were large. So the oxidation potential was measured at 20 mV/s as the scan rate except for **PcSBn** and **PcSeBn**. In contrast, reversibility of the reduction potentials was not good when the scan late was slow. Therefore, the scan rate was 200 mV/s for the reduction potential measurement; [a]Quasi reversible, [b]Irreversible (Ep /V).

To prepare phthalocyanines with two benzylseleno groups predominantly, **1** and **2b** were mixed in a 6:1 ratio, which was reacted with lithium in *n*-pentanol at 110 °C for 2 h (Scheme 1). After purification, phthalocyanines (**4b**), (**5b**), and (**6b**) were obtained in low yields together with **3** (Table 1). ^{1}H NMR of **4b**, **5b**, and **6b** are similar to those of **4a**, **5a**, and **6a**, respectively.[7] UV-vis spectrum of **4b** shows a similar absorption pattern to that of **4a**. In the ^{77}Se NMR spectrum, the signal of **4b** was observed at δ = 326.2 ppm, which is a value shifted upperfield from that of **PcSeBn** (δ = 356.0 ppm).[5a]

Meanwhile, **4a** was treated with lithium in THF/NH_3 at –78 °C and then with elemental sulfur at room temperature.[5a] However, the phthalocyanine skeleton was decomposed under the reaction condition and 2,5-diethyl-3,4-trithiolophthalimide (**8**) was obtained in low yield.[8]

The redox potentials of **4a**, **5a**, **7a**, and **4b** were measured by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode; solvent: CH_2Cl_2 (Table 2). However, the electrochemical property of **6a** could not be determined for its low solubility. The voltammogram of **4a** showed one reversible, one irreversible, and one quasi-reversible peak for the oxidation potential while two reversible couples were observed for the reduction potential. Compound (**7a**) exhibited two reversible oxidation and two reversible reduction potentials. One reversible and one irreversible peak were observed for the oxidation potential of **4b** while the reduction potential of **4b** was found as one reversible and one quasi-reversible couple. It appeared that the oxidation potential of **5a** is extremely lower than those of **4a**, **7a**, **PcSBn**, **4b**, and **PcSeBn**. In addition, although the first oxidation potential of **4a** is higher than that of **PcSBn**, the selenium derivatives (**4b**) and **PcSeBn** show the opposite results.[5a]

REFERENCES

1. "The Porphyrin Handbook," Vols. 15-20, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 2003; "Phthalocyanines: Properties and Applications," Vols. 1-4, ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989-1996.
2. H. Kliesch, A. Weitemeyer, S. Müller, and D. Wöhrle, *Liebigs Ann.*, 1995, 1269; U. Michelsen, H. Kliesch, G. Schnurpfeil, A. K. Sobbi, and D. Wöhrle, *Photochem. Photobiol.*, 1996, **64**, 694.
3. N. Kobayashi, R. Kondo, S. Nakajima, and T. Osa, *J. Am. Chem. Soc.*, 1990, **112**, 9640; N. Kobayashi, T. Ishizaki, K. Ishii, and H. Konami, *J. Am. Chem. Soc.*, 1999, **121**, 9096.
4. D. Wöhrle and G. Krawczyk, *Polymer Bull.*, 1986, **15**, 193; C. C. Leznoff, P. I. Svirskaya, B. Khouw, R. L. Cerny, P. Seymour, and A. B. P. Lever, *J. Org. Chem.*, 1991, **56**, 82.
5. Compounds (**1**) and (**2**) were prepared by the methods described in the literature; a) T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, and T. Akasaka, *J. Org. Chem.*, 2004, **69**, 4716; b) M. Kohn, *J. Am. Chem. Soc.*, 1951, **73**, 480.
6. **4a**: mp 240-242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ –3.72 (s, 2H, NH), 1.20-1.26 (m, 18H, CH_3), 1.78 (t, J = 7.3 Hz, 6H, CH_3), 1.81-1.92 (m, 12H, CH_2), 2.12-2.24 (m, 12H, CH_2), 4.42-4.56 (m, 12H, OCH_2), 4.45-4.52 (m, 4H, CH_2), 4.63 (s, 4H, SCH_2), 7.29-7.64 (m, 10H, ArH), 8.15 (s, 2H, ArH), 8.20 (s, 2H, ArH), 8.21 (s, 2H, ArH); FAB MS (m/z) 1247.6 (MH^+); **5a**: mp 224-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ –2.66 (s, 2H, NH), 1.09-1.21 (m, 12H, CH_3), 1.70-1.84 (m, 8H, CH_2), 1,93 (t, J=7.1 Hz, 12H, CH_3), 2.08-2.22 (m, 8H, CH_2), 4.47 (t, J = 6.6 Hz, 4H, OCH_2), 4.54 (t, J = 6.5 Hz, 4H, OCH_2), 4.65 (s, 4H, SCH_2), 4.67 (s, 4H, SCH_2), 4.78-4.93 (m, 8H, CH_2), 7.20-7.61 (m, 20H, ArH), 8.30 (s, 2H, ArH), 8.55 (s, 2H, ArH); FAB MS (m/z) 1403.6 (MH^+); **6a**: mp 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ –2.02 (s, 2H, NH), 1.18 (t, J = 7.4 Hz, 12H, CH_3), 1.74-1.83 (m, 8H, CH_2), 1.86 (t, J = 7.3 Hz, 12H, CH_3), 2.10-2.19 (m, 8H, CH_2), 4.53 (s, 8H, SCH_2), 4.57 (t, J = 6.5 Hz, 8H, OCH_2), 4.71-4.79 (m, 8H, CH_2), 7.16-7.39 (m, 12H, Ar), 7.46 (d, J = 7.2 Hz, 8H, Ar), 8.67 (s, 4H, Ar), ESIMS (m/z) 1403.68 (MH^+); **7a**: mp 212-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.41 (s, 2H, NH), 1.17 (t, J = 7.4 Hz, 6H, CH_3), 1.57 (t, J = 7.4 Hz, 12H, CH_3), 1.78 (sext, J = 7.4 Hz, 4H, CH_2), 1.94 (t, J = 7.3 Hz, 6H, CH_3), 2.11-2.19 (m, 4H, CH_2), 4.47 (s, 4H, SCH_2), 4.50 (s, 8H, SCH_2), 4.59 (t, J = 6.6 Hz, 4H, OCH_2), 4.62-4.86 (m, 4H, CH_2), 7.14-7.43 (m, 30H, ArH), 8.79 (s, 2H, Ar); FABMS (m/z) 1559.6 (MH^+).
7. **4b**: mp 228-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.33 (br, 2H, NH), 1.18-1.30 (m, 18H, CH_3), 1.76 (t, J = 7.1 Hz, 6H, CH_3), 1.79-1.94 (m, 12H, CH_2), 2.11-2.26 (m, 12H, CH_2), 4.41-4.63 (m, 16H, OCH_2, $ArCH_2$), 4.64 (s, 4H, SCH_2), 7.21-7.28 (m, 2H, ArH), 7.32 (t, J = 7.2 Hz, 4H, ArH), 7.52 (d, J = 7.2 Hz, 4H, ArH), 8.24 (s, 2H, ArH), 8.28 (s, 2H, ArH), 8.31 (s, 2H, ArH); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 236.2; FAB MS (m/z) 1342.57 (MH^+); UV-vis ($CHCl_3$) λ_{max} = 621, 654, 683, 702, and 721 nm.
8. **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.5 Hz, 6H), 3.14 (t, *J* = 7.5 Hz, 4H), 7.49 (br, 1H); HRMS Calcd for $C_{12}H_{11}NO_2S_3$, 296.9952. Found, (m/z) 296.9958 (M^+).