Crystal and Electronic Structure of Metal-Free Porphyrin: A New Material for Organic FET

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Abstract

Porphyrin compounds are widely known to play an important role in biological systems. We have recently found that tetrabenzoporphyrin (*i.e.* metal-free porphyrin: BP) exhibits an excellent FET characteristic. BP is usually synthesized via metal salts such as Zn and Cd. Because of this, FET characteristics are rather limited due to incur-porated metallic impurities. However, FET performance is greatly improved when BP is directly prepared by thermal decomposition from its precursor (CP) that is free from metals. The present paper deals with crystal structure of both BP and CP as well as their electronic characterization. Special attention has been focused on the comparison in electronic structure between BP and metal-free phthalocyanine (H_2Pc). Both compounds are quite similar in molecular conformation and arrangement. Nevertheless, the crystallographic parameters are quite different. Furthermore, their polarized reflection spectra measured on single crystals are also significantly different.

1. Introduction

Organic field effect transistors (FET) are advantageous to lower fabrication costs and large area devices as compared with inorganic FETs, although the performance of the latter is still much better than the former. We have recently found that tetrabenzoporphyrin (BP shown in Fig. 1), commonly known as metal-free porphyrin, exhibits an excellent FET characteristic.[1] However, the FET characteristics are still limited because BP includes inevitably a trace of metal impurities such as Zn and Cd owing to the synthetic route via metal salts.[2] On the other hand, the FET performance is greatly improved when BP is directly prepared by thermal decomposition from its metal-free precursor (CP; Fig. 1).[1]

The purpose of the present investigation is to study the crystal and electronic structure of both BP and CP, since electronic characterization is considered most basic to an understanding of the high performance FET characteristics. Special attention has been focused on the comparison in electronic structure between BP and BP-analogue of phthalocyanine (*i.e.* metal-free phthalocyanine; H_2Pc).

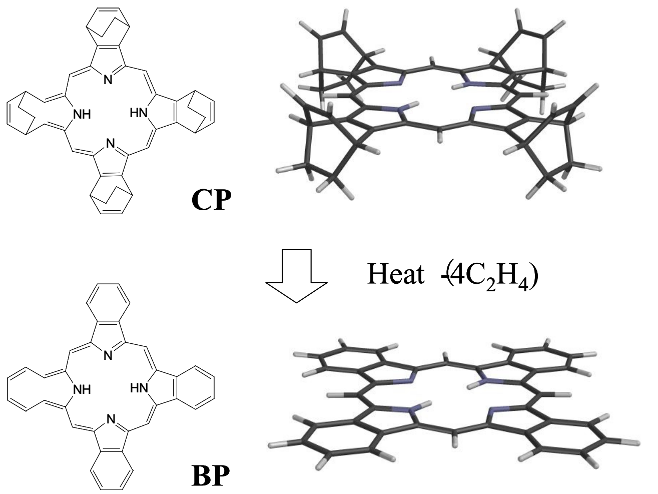

Figure 1. Molecular conformation of 1,4:8,11:15,18:22,25-tetraethano-29H,31H-tetrabenzo[b,g,l,q]porphine (CP) and 29H, 31H-tetrabenzo[b,g,l,q]porphine (BP).

2. FET Device and its Characteristics

Figure 2 shows the schematic illustration of the FET structure composed of source and drain Au-electrodes prepared on a highly-doped *n*-type Si substrate. On top, a 0.7 wt% CP solution in chloroform was spin-coated, followed by thermal decomposition of CP into BP at 210°C for 5 minutes. The FET performance is shown in Fig. 3. A high mobility of 1.7×10^{-2} cm^2/Vs and an on/off ratio of about 1×10^5 were obtained.

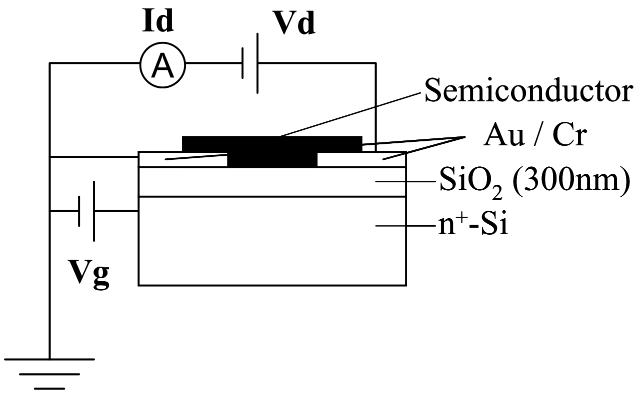

Figure 2. Schematic illustration of the FET device.

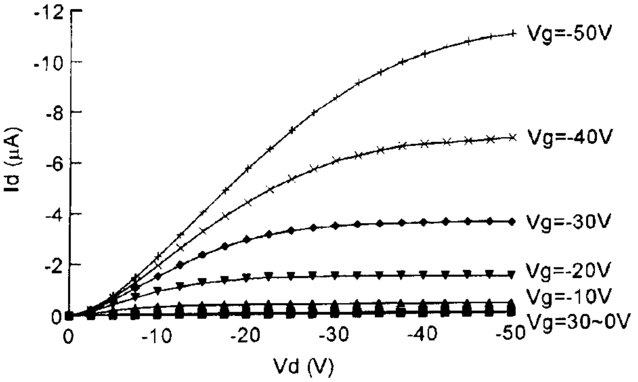

Figure 3. FET characteristics of the FET device based on BP.

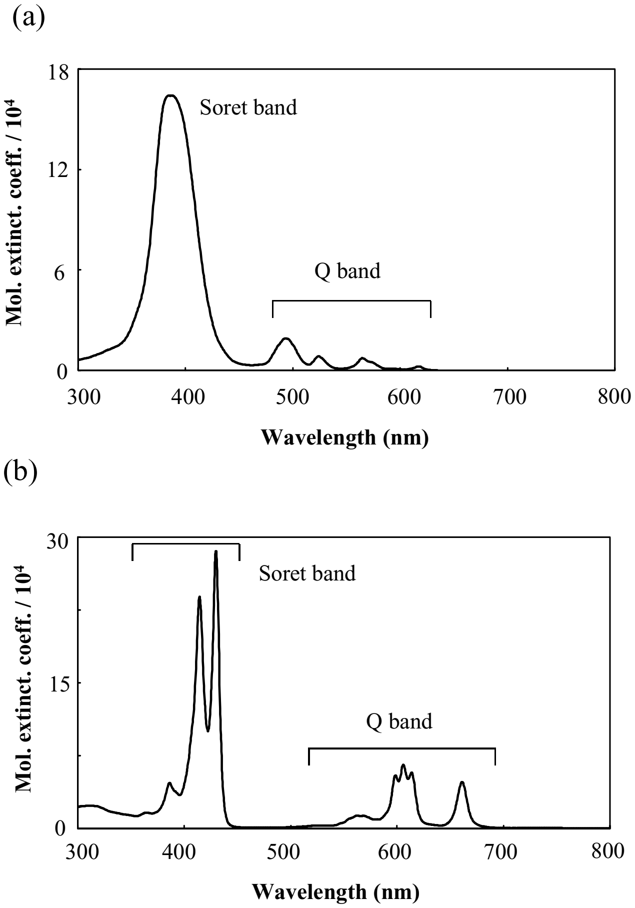

Figure 4. Solution spectra : (a) CP and (b) BP.

3. Results and Discussion

3.1 Solution Spectra of CP and BP

Figures 4(a) and 4(b) show the solution spectra of CP in toluene and of BP in DMSO (dimethylsulfoxide), respectively. As typical of porphyrin compounds, the broad shorter-wavelength band in CP is assigned to the Soret band while the Q band composed of four small bands appears at longer-wavelengths and are assigned as shown. The solution spectrum of BP is more structured than that of CP, but the similar spectroscopic behavior is observed.

3.2 Thermal Transformation from CP to BP

Figure 5 shows the TGA/DTA curves (Thermo-grapvimetric Analysis; Differential Thermal Analysis, respectively) of powdered CP. The weight-loss begins at about 130°C and completes around 200°C. The weight-loss amounts to about 18% which exactly corresponds to the transformation from CP to BP. On the other hand, there observed two DTA peaks around 180 and 200°C, indicating that that the thermal decomposition proceeds in two steps.

3.3 Absorption Spectra of Evaporated BP

Thermally-transformed BP was evaporated onto glass substrate, followed by vapor or heat treatment. Figure 6 shows the absorption spectra of evaporated BP with vapor or heat-treatment. Vapor treatment means that the evaporated films were exposed to acetone vapor for one hour to bring about spectral changes. Acetone vapor loosens the crystal lattice, thus allowing the molecules to slide and/or rotate to find energetically more stable sites. Vapor treatment brings about a spectral shift toward longer wavelengths. On the other hand, heat treatment gives a similar result, but the bathochromic shift is still larger. Although the absorption bands are bathochromically displaced, the one-to-one correspondence between absorption bands in solution and in the solid state is still possible, indicating that the molecular nature is well preserved ever in the solid state.

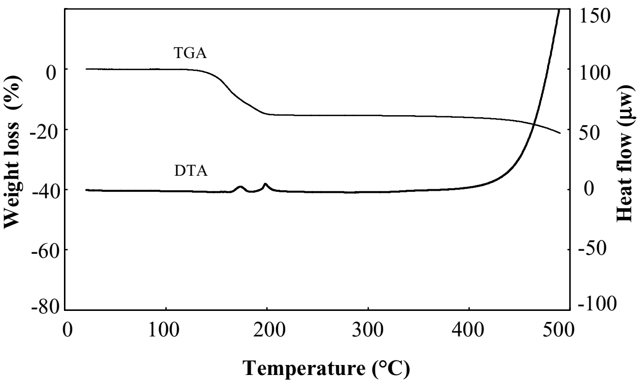

Figure 5. TGA/DTA curves measured on powdered CP.

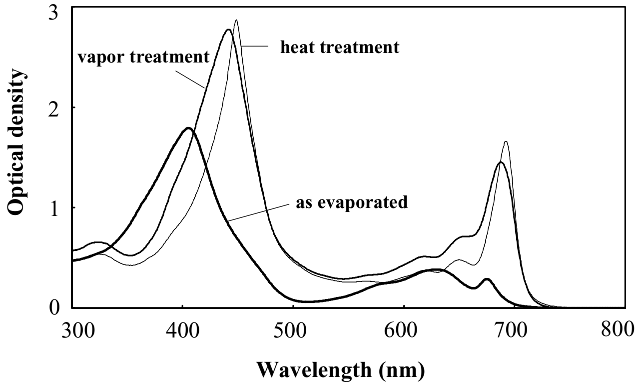

Figure 6. Spectral changes of evaporated BP due to vapor or heat treatment.

3.4 X-ray Diffraction Diagrams of Evaporated Films

Figure 7 shows the changes in X-ray diffraction diagrams of evaporated BP with vapor or heat treatment. The broad band around 2θ = 27° is due to the glass substrate used. As evaporated, two prominent diffraction peaks appear around 2θ = 6.7 and 13.5°. However, no assignment is possible on the basis of the BP structure analysis as described below. On the other hand, these diffraction peaks disappear completely due to vapor treatment. Instead, two peaks appear newly around 2θ = 8.4 and 14.4°. These peaks are attributed to the (10-1) and (200) reflections, respectively, according to the structure analysis. Heat treatment gives a similar result to that of vapor treatment. Two initial peaks disappear and then only one diffraction peak appears around 2θ = 14.4° attributed to the (200) plane.

3.5 Preparation of Single Crystals of CP and BP

CP was prepared by a method described in Refs. 3 and 4. Single crystals of CP were grown by recrystallization from solution in toluene. A number of dark red crystals were obtained in a tetragonal form. On the other hand, single crystals of BP were grown from the vapor phase by thermal decomposition of CP in a closed sublimation tube at about 250°C. After 24 h, dark blue acicular crystals were obtained. Collection of reflection data was made at –180°C, using a Rigaku Diffractometer of RAPID F. Both structures were solved by direct methods using Shelxs-86 and refined by full matrix least squares method in teXsan program package.

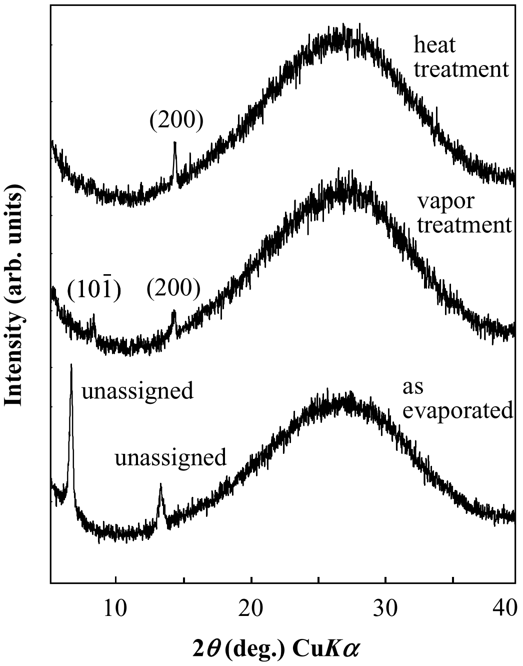

Figure 7. X-ray diffraction diagrams measured on evaporated BP with vapor or heat treatment.

3.6 Crystal Structure of CP and BP

Table 1 details the crystallographic parameters for CP and BP. CP is found to include two solvent molecules.

Figures 8(a) and 8(b) show the ORTEP plot and the molecular arrangement of CP onto the (*b,c*) plane.

Table 1. Crystallographic Parameters for Solvated CP and BP.

	CP	BP
Formula	$C_{44}H_{38}N_4 \cdot 2(C_7H_8)$	$C_{36}H_{22}N_4$
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/n$
Molecular symmetry	C_i	C_i
Z	1	2
a (Å)	90990(3)	12.405(7)
b (Å)	11.630(3)	6.5910(7)
c (Å)	12.203(3)	14.927(1)
α(°)	117.15(2)	-
β(°)	103.64(2)	101.445(8)
γ(°)	95.52(3)	-

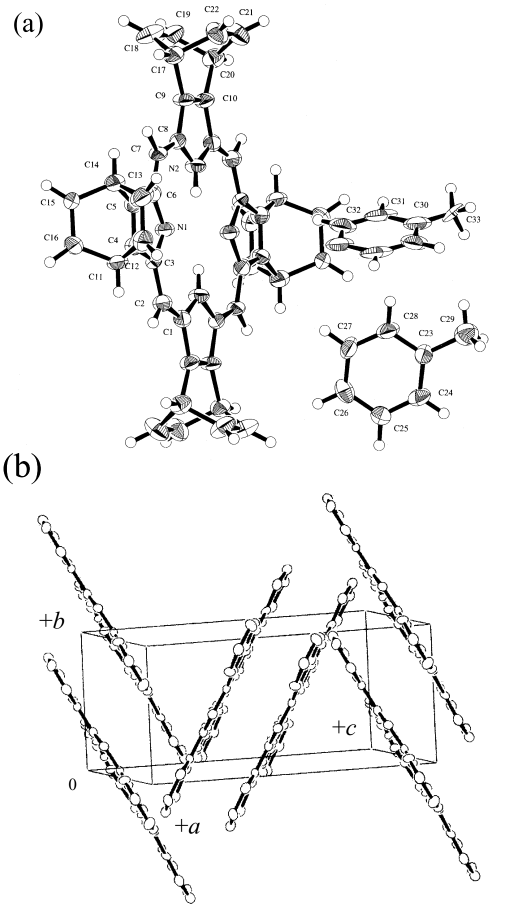

Figure 8(a) and 8(b). ORTEP plot and molecular arrangement of CP.

The ORTEP plot of BP is shown in Fig. 9(a). The molecule has an inversion center, but the molecular symmetry is not D_{2h} but C_i because the molecule is not entirely flat as shown below. The angles between the plane of the four central nitrogen atoms ($N1/N1^{i}/N2/N2^{i}$)) and the plane of each phenyl ring at the corner amount to ± 6.96(1)° for the plane (C2/C3/C4/C5/C6/C7) and its symmetry related plane, respectively; whereas the angles are ± 6.42(1)° for the plane (C11/C12/C13/C14/C15/C16) and its symmetry-related plane, respectively. The molecules are arranged in a fashion "herringbone" as shown in Fig. 9(b).

3.7 Comparison of the Crystal Structure Between BP and H_2Pc

As is well known, BP and H_2Pc are quite similar in molecular structure. If four aza N atoms in BP are replaced by C atoms, then it gives H_2Pc. In fact, the bond parameters of H_2Pc[5] are found to be quite similar to those of BP. However, the lattice parameters are appreciably different from each other as shown in Table 2 where the unit cell of BP has been transformed from $P2_1/n$ to $P2_1/a$ for comparison with H_2Pc. Nevertheless, both molecules are stacked in the same way along the *b*-axis in a fashion "herringbone" as shown in Fig. 9(b). H_2Pc exhibits a lower FET performance by two orders of magnitude at the moment as compared with that of BP.

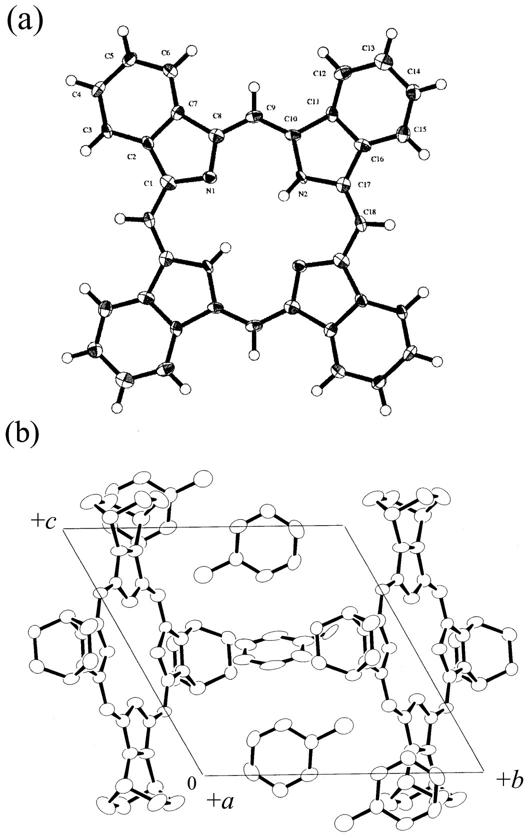

Figure 9(a) and 9(b). ORTEP plot and molecular arrangement of BP.

Table 2. Comparison of the Lattice Parameters Between BP and H_2Pc.

	BP*	H_2Pc
Formula	$C_{36}H_{22}N_4$	$C_{32}H_{18}N_8$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/a$
Molecular symmetry	C_i	C_i
Z	2	2
a (Å)	17.413(1)	19.8707(7)
b (Å)	6.5910(7)	4.731(7)
c (Å)	12.405(1)	12.198(4)
α(°)	-	-
β(°)	122.841(7)	121.98(4)
γ(°)	-	-

* The unit cell has been transformed for comparison with H_2Pc.

3.8. Polarized Reflection Spectra Measured on Single Crystals of BP

Figure 10(a) shows the polarized reflection spectra of BP single crystals measured on the *(a,b)* plane and the projection onto the *(a,b)* plane is given in Fig.10(b). The direction of the transition dipoles for the Soret and Q bands are deduced from MO calculations on the basis of the X-ray coordinates using the INDO/S Hamiltonian. The results are shown in Fig. 11 together with calculated absorption maxima. Since no significant difference in the direction of the transition dipoles is recognized between the Soret and Q bands (Fig. 11), both polarizations for parallel and perpendicular to the *b*-axis excite both absorption bands at the same time. In addition, the molecules are inclined by about 45° with respect to the *b*-axis and arranged in a zigzag fashion along the *a*-axis (Fig. 10(b)), both polarizations give approximately the same amount of reflectivity (Fig. 10(a)). The fine structure of the Soret and Q bands is better for polarization parallel to the *b*-axis than perpendicular to the *b*-axis. The reason is not clear at the moment.

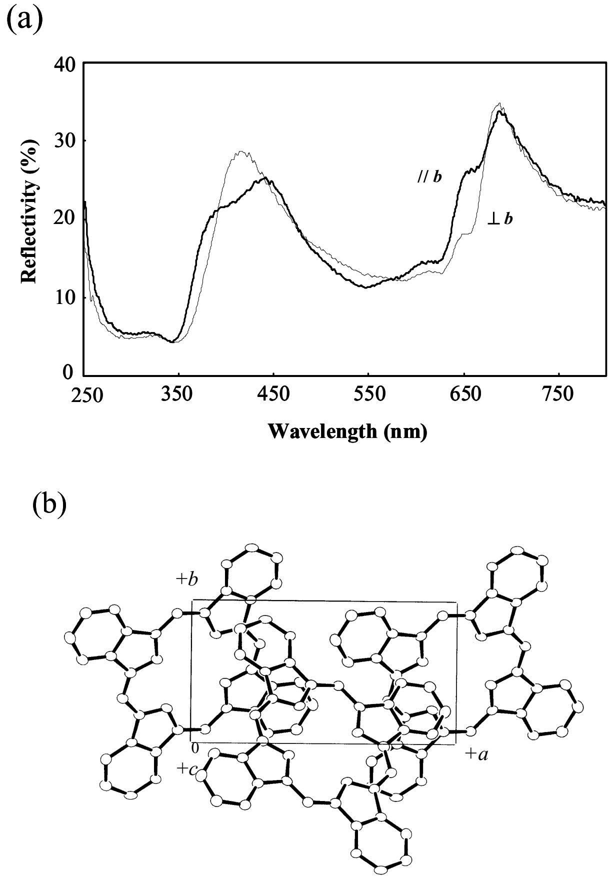

Figure 10. (a) Polarized reflection spectra BP single crystals measured on the (a,b) plane of BP single crystals and (b) projection onto the (a,b) plane.

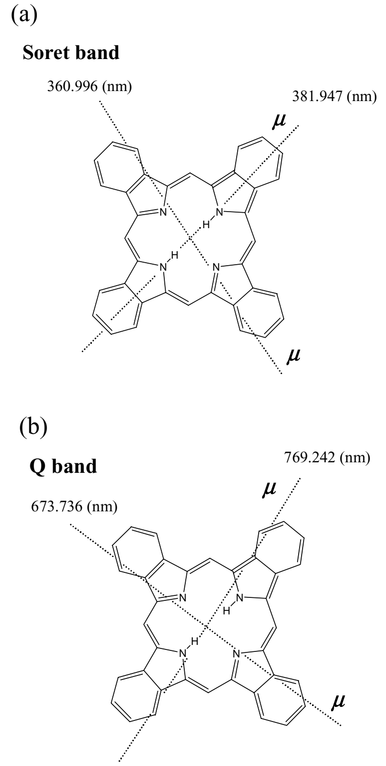

Figure 11. Direction of the transition dipoles for the Soret and Q bands as deduced from MO calculations on the basis of the X-ray coordinates using the INDO/S Hamiltonian.

The polarized reflection spectra are similar to those of absorption spectra of evaporated BP with vapor or heat treatment (Fig. 6), but are slightly different, especially in spectral shape and absorption wavelengths. This difference can presumably be attributed to the poor crystallinity of evaporated BP as shown in Fig. 7.

4. Conclusions

1. The crystal structure of BP and its precursor (CP) has been determined. The crystal structure and its space group of BP are monoclinic and *P*21/*n*, respectively.
2. BP and BP-analogue in phthalocyanine (*i.e.* H_2Pc) are similar in molecular conformation and arrangement, but still different in lattice parameters.
3. H_2Pc exhibits a lower FET performance at the moment by two orders of magnitude as compared with that of BP.

References

1. S. Aramaki and Y. Sakai: Appl, Phys. Lett., 84, 2085 (2004).
2. S. Aramaki and J. Mizuguchi: Acta Crystallogr. E **59**, o1556 (2003).
3. S. Ito, N. Ochi, T. Murashima, H. Uno and N. Ono: Chem. Commun. (Cambridge) **1998**, 1661.

4. S. Ito, N. Ochi, T. Murashima, H. Uno and N. Ono: Heterocycles **52**, 399 (2000).
5. S. Matsumoto, K. Matsuhama and J. Mizuguchi: Acta Cryst. C**55**, 131 (1999).
6. J. Mizuguchi and S. Matsumoto: J. Phys. Chem. A, **103**, 614 (1999).

Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi ("Habilitation") from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science. His current interest is centered on the electronic characterization of organic pigments and their applications.

Appendix

- Solution and solid state spectra of H_2Pc -

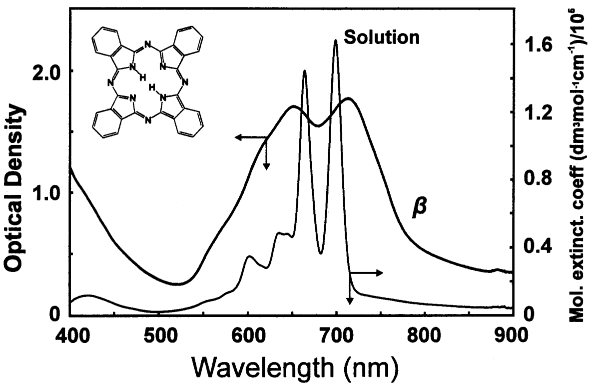

Figure 12. Solution spectrum in DMSO and solid-state spectrum in evaporated films of β H2Pc.

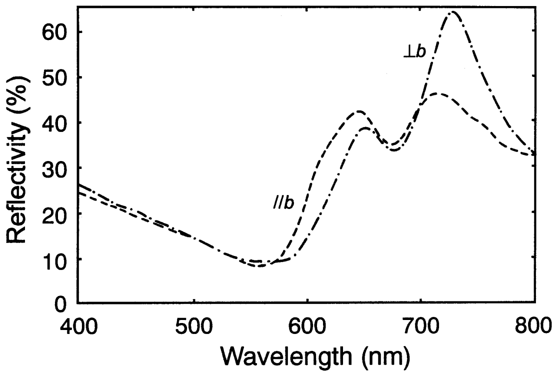

Figure 13. Polarized reflection spectra measured on the (a,b) plane of β H_2Pc.