

Complexation of phosphorus(III) with a novel tetrapyrrolic phthalocyanine-like macrocyclic compound

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Abstract

This contribution reports a detailed study of the complex formed by a novel phthalocyanine-like compound (2,9,16,23-tetraisopropoxy tetrabenzotriazacorrole) with phosphorus(III). The structure of this new tetrapyrrolic macrocycle ($H[TBC(O'Pr)_4P(OH)]$) was identified by elemental analysis, conventional spectral measurements (FAB-MS, UV-Vis, IR, 1H NMR, ^{13}C NMR, and ^{31}P NMR), as well as its chemical reactivities. The Q band in the electronic transition spectra of the complex lies at a wavelength of around 660 nm, which is slightly shorter than in the mother phthalocyanine. The ϵ of the Q band is approximately one half of the value of the sharp Soret band which exists at 450 nm. The unusual electronic transition spectra are interpreted as the molecular symmetry of the novel complex being reduced to C_1 or lower two-fold symmetry. Three chemically different species formed by protonation or/and deprotonation of the compound with acid and base were characterized and identified. In addition, the previously reported phosphorus(III) phthalocyanine $[PcP^{III}]^+$ is proposed to be $H[TBCP(OH)]$ when compared with $H[TBC(O'Pr)_4P(OH)]$ in detail.

Keywords: Tetrabenzotriazacorrole; Phthalocyanine; Phosphorus complex; UV-Vis spectra

1. Introduction

Phthalocyanine complex chemistry is one of the subjects of recent interest because of the current and potential applications in many fields including photodynamic therapy (cancer treatment) [1], photoconductors [2], catalysts [3], electrodes [4], non-linear optical materials [5], optical recording media [6], molecular electronic devices [7], heme and chlorophyll biosystem models [8], LB films as conductometric sensors [9], and new selective NMR shift reagents [10], etc. Over the past years considerable research has been carried out on the preparation of phthalocyanine complexes with various metals. Until now phthalocyanine complexes were known with nearly all the metals in the periodic table, together with several complexes containing semimetals and non-metals of Groups IVA and VA [11]. The latter type of complexes are of particular interest chemically and spectroscopically because at least two different valence states (II and IV or III and V) are accessible to the central atom and phthalocyanines containing metalloids can provide low-dimensional molecular solids [12].

Gouterman and coworkers [13,14] have reviewed the preparation and electronic spectra of phthalocyanines containing lower valent metalloids of Groups IVA and VA and

have compared them with their corresponding higher valent equivalents. In their reviews, they pointed out the fact that $[PcP^{III}]^+$ exhibits unusual electronic absorption in contrast to the normal spectrum of PcP^V . The Q band and B band of $[PcP^{III}]^+$ are markedly blue-shifted and red-shifted respectively, as well as changes occurring in absorption intensity. They proposed that in $[PcP^{III}]^+$ a new filled orbital $a_{2u}(3p_z)$ is introduced into the Fermi energy region, where $3p_z$ is an orbital on phosphorus. The unusual spectrum of $[PcP^{III}]^+$ can be attributed to the porphyrin-like four-orbital electronic transition $a_{1u}(\pi), a_{2u}(3p_z) \rightarrow e_g(\pi^*)$, resulting from a closing between a_{1u} and a_{2u} . However, a lot of doubts about the structure of $[PcP^{III}]^+$ remain to be clarified; one reason may be its poor solubility and tedious route of preparation. Therefore, the confusions and suspenses in the literature are reasonable.

In order to clarify the origin of its unusual electronic absorption and to overcome the difficulties cited, 2,9,16,23-tetraisopropoxy phthalocyanine ($H_2Pc(O'Pr)_4$) was chosen instead of H_2Pc to complexate P(III) since the former is quite similar to H_2Pc and is soluble in most organic solvents [15,16]. Our study showed that the species formed by $H_2Pc(O'Pr)_4$ and trivalent phosphorus reagent has the same unusual electronic absorption as that of $[PcP^{III}]^+$, it is not a

simple complex formed by phosphorus(III) and 2,9,16,23-tetraisopropoxy phthalocyanine but rather a hydrogen hydroxy-phosphorus(III)-2,9,16,23-tetraisopropoxy tetrabenzotriazacorrole ($H[TBC(O^iPr)_4P(OH)]$), which was formed by a ring-contractive reaction. Furthermore, by detailed comparison between $H[TBC(O^iPr)_4P(OH)]$ and $[PcP^{III}]^+$, we found that the structural skeleton of $[PcP^{III}]^+$ should be reasonably similar to $H[TBCP(OH)]$.

2. Experimental details

2.1. Instruments and methods

Ultraviolet-Visible (UV-Vis) and second differential UV-Vis absorption spectra were recorded by a HP8452A diode-array spectrophotometer. Infrared (IR) absorption spectra were obtained on a PE-1600 FT-IR spectrophotometer. Fast atom bombardment mass (FAB-MS) spectra were obtained on a ZAB-HS mass spectrometer. All nuclear resonance (1H NMR, ^{13}C NMR and ^{31}P NMR) spectra were recorded by a JEOL FX-90G NMR spectrometer (FT, 90 MHz). Elemental analysis for C, H, N and Br was performed at Beijing Institute of Chemistry, Academia Sinica.

Fluorescence measurements were carried out with a PE LS50B luminescence spectrometer. Fluorescence quantum yields (Φ_f) were determined by a comparative calibration method using unsubstituted ZnPc as standard ($\Phi_f=0.3$) with an excitation wavelength at 610 nm and excitation and emission slit widths of 5.0 nm. Singlet excited-state lifetimes (τ_f) were measured by phase-modulation method on a SLM48000-TMS multiple frequency lifetime spectrofluorometer with a precision of ± 20 ps. Sample solutions for fluorescence measurement were purged with argon before measurement. All the solvents for measurement were spectrograde.

2.2. Synthesis

2.2.1. 2,9,16,23-tetraisopropoxy phthalocyanine ($H_2Pc(O^iPr)_4$)

This compound was prepared and purified following the literature [16] and characterized by elemental analysis, IR, UV-Vis, MS and NMR spectroscopy. The results are as follows. IR (KBr, cm^{-1}): 3476 (NH), 1612 (aromatic C=C), 1524 (C=N), 1235 (R-O-Ar), 1111 (aromatic C-H), 1096, 1008 (NH), 962. UV-Vis ($CHCl_3$, nm): 708 (log ϵ , 4.77), 672 (4.70), 644 (4.36), 610 (4.16), 388 (4.27), 338 (4.71). MS (m/e , rel. intensity): 746 (M^+ , 100), 703 ($(M-C_3H_7)^+$, 34), 660 ($(M-C_3H_7 \times 2)^+$, 20), 617 ($(M-C_3H_7 \times 3)^+$, 14), 574 ($(M-C_3H_7 \times 4)^+$, 50). 1H NMR ($(CD_3)_2SO$, ppm): 7.5–8.6 (m, 4H, ring external H), 6.8–7.4 (m, 8H, ring internal H), 4.5–5.2 (m, 4H, CH-O), 1.0–1.8 (broad d, 24H, CH_3). ^{13}C NMR ($(CD_3)_2SO$, ppm): 161.18 (N-C=N), 159, 19 (aromatic C-O), 138.38, 136.56, 128.15, 127.93, 122.09, 118.62, 106.85, 102.50 (benzene

ring), 70.42 (CH-O), 22.58, 21.80 (CH_3). Elemental analysis for $C_{44}H_{42}N_8O_4$: found (calcd.): C, 70.67 (70.76); H, 5.59 (5.63); N, 14.82 (15.00).

Although a specific isomer is annotated here and in the following, in fact the synthesis gives a mixture of isomers with the isopropoxy groups randomly distributed (one per peripheral benzene ring) around the 4,5-positions of the phthalocyanine unit. Fortunately the electronic spectra of all these isomers are nearly identical.

2.2.2. Hydrogen hydroxyphosphorus(III)-2,9,16,23-tetraisopropoxy tetrabenzotriazacorrole ($H[TBC(O^iPr)_4P^{III}(OH)]$)

A mixture of 1.0 g $H_2Pc(O^iPr)_4$ (1.34 mmol) and 60 ml of dry pyridine was placed in a 100 ml three-neck round-bottom flask, equipped with magnetic stirrer, reflux condenser and gas inlet tube. Approximately 3.8 ml of PBr_3 (40.4 mmol) were gradually added under argon protection. The mixture was heated at 90–100 °C with stirring for 2–3 h under argon bubbling until the solution changed from green to dark blue-green. After cooling to room temperature, the mixture was diluted with water and the green-colored residue was collected by filtration under vacuum and washed thoroughly with water. The crude product was then purified by column chromatography on neutral alumina with chloroform and pyridine as eluants. The chloroform eluted a faint green fraction ($H_2Pc(O^iPr)_4$), and the dark blue-green fraction from pyridine contained the bulk of the product. The solution was evaporated to dryness and then dried at 100 °C under vacuum. 0.65g of dark blue-purple shining solid of $H[TBC(O^iPr)_4P(OH)]$ as a mixture of isomers was obtained in a 62% yield. IR (KBr, cm^{-1}): 3455 (PO-H), 1615 (C=C), 1521 (C=N), 1358, 1237 (R-O-Ar), 1104, 980 (P-OH), 825. UV-Vis (pyridine, nm) 658 (log ϵ , 4.62), 634 (4.39), 602 (4.04), 450 (4.95), 420 (4.49), 330 (4.47). FAB-MS (m/z , rel. intensity): 779 (M^+ , 90), 778 ($(M-H)^+$, 100), 735 ($(M-H-C_3H_7)^+$, 50), 692 ($(M-H-C_3H_7 \times 2)^+$, 25), 649 ($(M-H-C_3H_7 \times 3)^+$, 15), 606 ($(M-H-C_3H_7 \times 4)^+$, 15), 558 ($(M-H-C_3H_7 \times 4-P-OH)^+$, 72). 1H NMR ($(CD_3)_2SO$, ppm): 8.5–9.6 (m, 4H, ring external H), 7.2–7.9 (m, 8H, ring internal H), 3.9–5.4 (m, 4H, CH-O), 3.3 (s, 2H, PO-H and counter proton), 1.3–1.7 (broad d, 24H, CH_3). ^{13}C NMR ($(CD_3)_2SO$, ppm): 169.35 (C=C), 161.11 (N-C=N), 158.68 (aromatic C-O), 138.75, 119.42, 112.92, 102.2 (benzene ring), 70.88, 70.44 (CH-O), 22.08, 21.65 (CH_3). ^{31}P NMR ($(CD_3)_2SO$, ppm) –202.83. Analysis: Calcd. for $C_{44}H_{42}N_7O_5P$: C, 67.78; H, 5.39; N, 12.60; Br, 0. Found: C, 68.00; H, 4.94; N, 12.76; Br, <0.2.

3. Results and discussion

3.1. Recognizing $H[TBC(O^iPr)_4P^{III}(OH)]$

Fig. 1 illustrates the structure of the TBC derivative, which has been confirmed by means of NMR, EA, MS and UV-

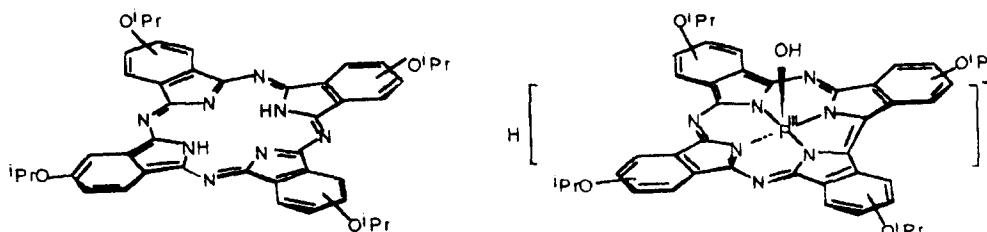


Fig. 1. Chemical structure of (left) H₂Pc(OⁱPr)₄ and (right) H[TBC(OⁱPr)₄P(OH)].

Vis. The observed mass peaks are in good agreement with the fragments expected. The corresponding vibrational bands of PO–H and P–OH are found in the IR spectrum. The emergence of a new peak at 169 ppm in the ¹³C NMR spectrum indicates a new C=C bond formed between two pyrrolic rings in the macrocycle. Furthermore, the signs of PO–H and counter-ion H stand together at 3.3 ppm as a single peak in the ¹H NMR spectrum. Especially, the δ value of ³¹P NMR is typical for a six-coordinated phosphorus complex, while the lone-pair electrons on P(III) is considered as another axial ligand counter to (–OH) in the TBC derivative. The formal charge on TBC and P are 3– and 3+ respectively, and H[TBC(OⁱPr)₄P^{III}(OH)] should be H⁺[TBC^{3–}(OⁱPr)₄P³⁺(OH)[–]]. The TBC ring is formed through the ring-contractive reaction of the Pc ring, and it has been confirmed as the phthalocyanine complex with Ge^{II} [17]. The fact that the extremely stable Pc ring easily loses a bridging N is quite unusual, however the exact mechanism of this novelty is still not clear. To our knowledge, there have been no synthetic reports on metal-free TBC macrocycles until now.

H[TBC(OⁱPr)₄P(OH)] at room temperature is slightly to moderately soluble in the sequence of benzene < trichloromethane \approx dichloromethane < ethanol. In pyridine, *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), its solubility becomes higher.

Although many metallophthalocyanines can be demetalled with cold concentrated H₂SO₄, H[TBC(OⁱPr)₄P(OH)] shows its unique stability. While in cold concentrated H₂SO₄ the absorption of H[TBC(OⁱPr)₄P(OH)] shows a red shift (Q bands at 696 nm and B bands at 498 nm) and exists as

several structureless broad bands without splitting. All these spectroscopic changes can be reversed when it is diluted with excess DMF and pyridine. The H₂SO₄ solution remains unchanged over several days in the dark. However, the decomposition of the macrocycle can be induced when a drop of 30% H₂O₂ is added to 5 ml solution of H[TBC(OⁱPr)₄P(OH)] in pyridine, as a result the solution turns from green to bright yellow in several minutes.

3.2. Spectral assignments for H[TBC(OⁱPr)₄P^{III}(OH)]

The UV–Vis and second differential UV–Vis spectra of H[TBC(OⁱPr)₄P^{III}(OH)] have been shown in Fig. 2 and Table 1. In order to study the difference between the TBC ring and the Pc ring, the spectrum of [Pc(OⁱPr)₄P^V(OH)₂]OH is also listed. [Pc(OⁱPr)₄P^V(OH)₂]OH was prepared following a known method and identified by comparing its spectrum with that of [PcP^V(OH)₂]⁺ reported in the literature [13]. The demetallization of [Pc(OⁱPr)₄P^V(OH)₂]OH in air is easy, one of the conceivable reasons may be the uncomplementarity between the small radius of the P^V atom and the large cavity of the Pc ring.

It can be seen from Fig. 2 that [Pc(OⁱPr)₄P^V(OH)₂]OH possesses a degenerated and intense Q(0'–0'') band at 685 nm, which is assigned to the allowed transition ($e_g \leftarrow a_{1u}$), and additional weak vibrational bands Q(0'–1'') and Q(0'–2''). It also has the broad and intense B bands (Soret bands), which are assigned to the allowed transition ($e_g \leftarrow a_{2u}$). These electronic absorption spectra are expected for molecules with the D_{4h} symmetry [18,19].

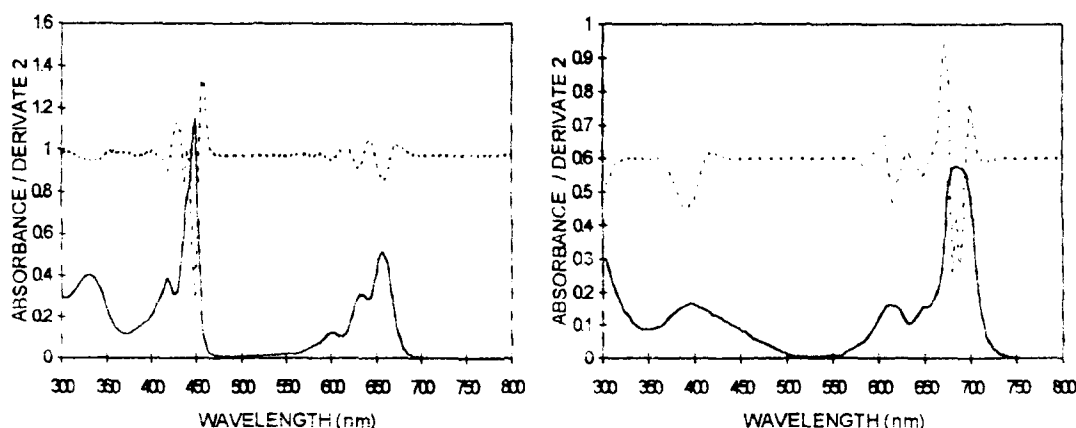


Fig. 2. UV–Vis (solid line) and second differential UV–Vis (broken line) spectra of (left) H[TBC(OⁱPr)₄P(OH)] in DMF and (right) [Pc(OⁱPr)₄P(OH)₂]OH in pyridine.

Table 1
Electronic absorption parameters and partial assignments in $H_2Pc(O^iPr)_4$, $H[TBC(O^iPr)_4P(OH)]$ and $[Pc(O^iPr)_4P(OH)_2]OH$

Compound	Solvent	E^a (cm^{-1})	Assignment	$\log \epsilon^b$	f^c
$H_2Pc(O^iPr)_4$ (D_{2h})	DMF	14200	$Q_x(0'-0'')$	4.72	0.34
		14900	$Q_y(0'-0'')$	4.74	
		15500	$Q_x(0'-1'')$	4.31	
		16300	$Q_y(0'-1'')$	4.17	
		25500	$B_1(0'-0'')$	4.23	
		29600	$B_2(0'-0'')$	4.67	
$H[TBC(O^iPr)_4P(OH)]$ (C_1)	DMF	15200	$Q_1(0'-0'')$	4.64	0.21
		15800	$Q_2(0'-0'')$	4.42	
		16700	$Q(0'-1'')$	4.03	
		22300	$B_1(0'-0'')$	4.98	
		22800	$B_2(0'-0'')$	4.62	
		23900	$B(0'-1'')$	4.52	
$[Pc(O^iPr)_4P(OH)_2]OH$ (D_{4h})	Pyridine	14600	$Q(0'-0'')$		0.84
		25400	$B(0'-0'')$		
			$(e_g \leftarrow a_{1u})$		
			$(e_g \leftarrow a_{2u})$		

^a E is the electronic transition energy.

^b ϵ is the molar absorption coefficient.

^c f is the oscillator strength.

On the other hand, although $H[TBC(O^iPr)_4P^{III}(OH)]$ has two characteristic Q and B bands at ca. 450 nm and 660 nm, from the second differential UV-Vis spectrum both $Q(0'-0'')$ and $B(0'-0'')$ bands are different from those of $[Pc(O^iPr)_4P^V(OH)_2]OH$ since the symmetry of the TBC ring is reduced at least from D_{4h} to C_{2v} , supposing the TBC ring is located in the plane and disregarding its axial ligand as well as its peripheral substitutions. Such splitting of the electronic spectrum arises from the splitting of the degenerated LUMO (e_g) of Pc with D_{4h} symmetry, such as $H_2Pc(O^iPr)_4$ with D_{2h} symmetry [18,19]. Since the counter proton of $H[TBC(O^iPr)_4P^{III}(OH)]$ should reside on the peripheral bridging (also called meso) N atom in the TBC ring with lone pair electrons (see Section 3.3), the symmetry of the molecule will be C_{2v} or C_1 depending on the site of the protonated N. For the lowest possible symmetry C_1 , there are only two $Q(0'-0'')$ or $B(0'-0'')$ bands so that one of the three Q bands or B bands in the spectrum should be a vibrational satellite.

The oscillator strengths of the Q bands and B bands of $H[TBC(O^iPr)_4P(OH)]$ are about two thirds of the corre-

sponding bands for $H_2Pc(O^iPr)_4$ (see Table 1), which means the planarity in the $H[TBC(O^iPr)_4P(OH)]$ structure may be distorted to a certain extent.

In contrast to $[Pc(O^iPr)_4P^V(OH)_2]OH$, $H[TBC(O^iPr)_4P^{III}(OH)]$ is a strong fluorescent compound. A possible explanation for this is since the radius of the P^V atom is much smaller than the cavity of the Pc ring, it may leave the cavity easily under excitation. And the coupling of shape change to optical transition will enhance the radiationless decay of the S_1 state of $[Pc(O^iPr)_4P^V(OH)_2]OH$. On the other hand, the P^{III} atom is buried deeper in the TBC ring, which is in consistent with the observed chemical stability. Hence, there is no P-atom movement coupled to the optical transition. In addition, the heavy-atom effect of phosphorous on intersystem crossing is rather weak for it is not heavy enough.

3.3. Protonation and deprotonation of $H[TBC(O^iPr)_4P(OH)]$

$H[TBC(O^iPr)_4P(OH)]$ shows spectral changes at acidic or basic pH. Small amount of hydrochloric acid in the DMF solution of $H[TBC(O^iPr)_4P(OH)]$ may induce a visible spectroscopic shift, and it is reversible through the addition of pyridine. On the other hand, on addition of strong bases (e.g. tetramethylammonium hydroxide) to the DMF solution, the spectral peaks occur at 656, 618, 592 nm, and the peaks of B bands split into doublets, and it acts in the reverse direction by adding HCl. In Fig. 3 the spectral changes are shown in the two pH ranges where the isosbestic points are located, the limiting spectra can be observed as more acid or base is added. These may serve as evidence for the existence of at least three chemically different species.

Table 2
Emission data for $H_2Pc(O^iPr)_4$ and $H[TBC(O^iPr)_4P(OH)]$

Compound	Solvent	λ_{em} (nm)	Φ_f	τ_f^a (ns)
$H_2Pc(O^iPr)_4$	DMF	710	0.28	4.8 ^b
$H[TBC(O^iPr)_4P(OH)]$	DMF	663	0.80	3.1 ^c
	DMSO	672		3.0 ^d

^a These times are fit by convoluting a double exponential decay $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where $(\tau_1, \tau_2)^b = (4.8, 20)$, $A_1/A_2^b = 8$, $(\tau_1, \tau_2)^c = (3.1, 26)$, $A_1/A_2^c = 24$, $(\tau_1, \tau_2)^d = (3.0, 42)$, $A_1/A_2^d = 34$. However, τ_2 may be artificial, so τ_f is referred to τ_1 .

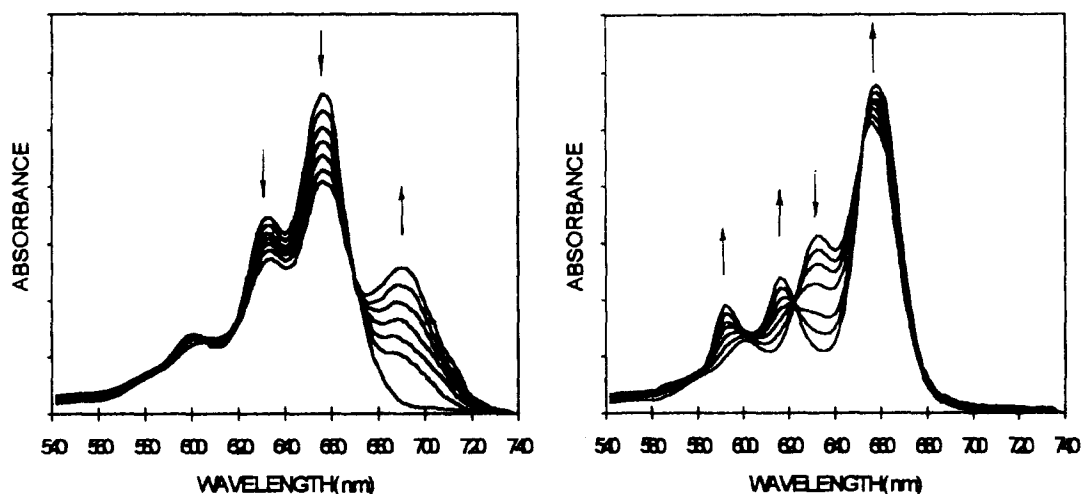


Fig. 3. Vis absorption spectral change of $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]$ in DMF upon step addition of (left) aqueous HCl and (right) aqueous $[\text{N}(\text{CH}_3)_4]^+\text{OH}^-$ until the limiting spectra. The final concentration of acid or base is $6 \times 10^{-2} \text{ mol}^{-1}$ or $6 \times 10^{-4} \text{ mol}^{-1}$ respectively, versus $6 \times 10^{-6} \text{ mol}^{-1}$ of $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]$ in solutions.

These spectral changes suggest that the ring itself is undergoing modification, which may be interpreted in terms of the protonation and deprotonation of $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]$ [20]. In $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]=\text{X}$, we can assume that the counter proton is bonded to one meso N atom by intramolecular protonation. Although there is no a priori reason to suppose that the extra proton is on the ring but not on the P–OH (to form P–OH₂), in our experimental observations this does seem to be the situation for X. Since the effect caused by the change from P–OH₂ to P–OH is rather weak on the Q band, only the removal of the proton from the protonated ring can lead to such manifest spectral change as the medium is turned alkaline by the addition of strong bases. As to X, the addition of acid will lead to successive protonation of the other two meso N atoms, which results in a stepwise change in the Q band absorption. Unfortunately, the protonation steps of the residual two meso N atoms cannot be discriminated on the spectra. The species formed with acid may be $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})] \cdot n\text{H}^+=\text{Y}$ ($n=1, 2$). The protonated species can be deprotonated to recover the original with pyridine or base as mentioned above. Pyridine is able to deprotonate Y to X, strong base can even eliminate the intramolecular protonated H in X to form $[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]^- = \text{Z}$. The spectral difference among X, Y and Z may be attributed to the change of the molecular symmetry. Even

the symmetry of three species is not known exactly, it is reasonable to predict that the symmetry grade of Y and Z is higher than X.

It is found that the fluorescence intensity of Y and Z is lower than X with the same emission wavelength λ_{em} .

The acid and base effect on $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]$ can also be found from the ³¹P NMR spectra (Table 3) which also indicates the change of the TBC ring attached to the center P(III) atom, and they are reversible by adding pyridine or acid as expected.

4. Conclusions

A complex formed by phosphorus(III) and 2,9,16,23-tetraisopropoxy phthalocyanine has been synthesized and identified as hydrogen hydroxyphosphorus(III)-2,9,16,23-tetraisopropoxy tetrabenzotriazacorrole by elemental analysis (C, H, N), FAB-MS, UV-Vis (normal and second differential), IR, NMR and its chemical reactivities. The excited state of this novel macrocyclic compound, and its structural changes under protonation or deprotonation, have also been studied. Up to three separate protonation steps have been readily observed.

From this study, we can reasonably confirm that the $[\text{PcP}^{\text{III}}]^+$ reported by Gouterman should be hydrogen hydroxyphosphorus(III)-tetrabenzotriazacorrole $\text{H}[\text{TBCP}(\text{OH})]$. The bases of our deduction are: (i) the route of synthesis, (ii) the optical spectrum and its changes with acid and base, and (iii) the chemical behaviours of the compound with H₂SO₄ and H₂O₂ as reported before are exactly the same as those of $\text{H}[\text{TBC}(\text{O}^i\text{Pr})_4\text{P}(\text{OH})]$.

The formation of TBC derivatives through the ring-contractive reaction is a challenge to the extraordinary stability of phthalocyanines. As a new member in the family of phthalocyanine analogues, TBC derivatives have many elec-

Table 3
Character of X, Y and Z

Compound	Solvent	λ_{ab} (nm)	$\delta-^{31}\text{P}$ (ppm)
X	DMF	418 448 600 632 656	-202.6
	DMSO	418 450 602 634 658	-202.8
Y	DMF + H ⁺	418 448 464 606 632 656 688	-201.5
Z	DMF + OH ⁻	420 438 450 592 618 656	-191.2
	DMSO + OH ⁻	422 438 452 594 618 660	-189.4

tronic and chemical properties. The chemistry of TBC macrocycle will be useful in biological modeling, such as vitamin B₁₂ coenzyme models, or conductive materials. It can be prophesied that this new cousin will provide a fertile field both for experimental and theoretical studies.

References

- [1] E. Ben-Hur, in B.W. Henderson and T.J. Dougherty (eds.), *Photodynamic Therapy: Basic Principles and Clinical Applications*, Marcel Dekker, New York, 1992, p. 63.
- [2] Y. Kanemitsu and S. Imamura, *J. Appl. Phys.*, **67** (1990) 3728.
- [3] Y.G. Akopyants, S.A. Borisenkova, O.L. Kaliya, V.M. Derkacheva and E.A. Lukyanets, *J. Mol. Catal.*, **83** (1993) 1.
- [4] M.A.T. Gilmartin, J.P. Hart and B.J. Birch, *Analyst*, **119** (1994) 243.
- [5] P. Chollet, F. Kajzar and J. Lemoigne, *Molecular Eng.*, **1** (1991) 35.
- [6] Z.T. Wang, *Huaxue Tongbao (Ch.)*, **1** (1993) 31.
- [7] B. Simic-Glavaski, in C.C. Leznoff and A.B.P. Lever (eds.), *Phthalocyanines: Properties and Applications*, Vol. 3, VCH Publishers, New York, 1993, p. 119.
- [8] A.L. Thomas, *Phthalocyanine Research and Applications*, CRC Press, Boca Raton, FL, 1990, p. 189.
- [9] H. Perez and A. Barraud, *Synth. Met.*, **61** (1993) 23.
- [10] I.V. Komarov, V.N. Nemykin and N.B. Subbotin, *Appl. Magn. Reson.*, **4** (1993) 377.
- [11] A.B.P. Lever, *Chemtech*, **17** (1987) 506.
- [12] B. Simic-Glavaski, A.A. Tanaka and M.E. Kenny, *J. Electroanal. Chem.*, **229** (1987) 285.
- [13] M. Gouterman, P. Sayer, E. Shankland and J.P. Smith, *Inorg. Chem.*, **20** (1981) 87.
- [14] P. Sayer, M. Gouterman and C.R. Connell, *Acc. Chem. Res.*, **15** (1982) 73.
- [15] C.C. Leznoff and T.W. Hall, *Tetrahedron Lett.*, **23** (1982) 3023.
- [16] T.W. Hall, S. Greenberg, C.R. McArthur, B. Khouw and C.C. Leznoff, *Nouv. J. Chim.*, **6** (1982) 653.
- [17] M. Fujiki, H. Tabei and K. Isa, *J. Am. Chem. Soc.*, **108** (1986) 1532.
- [18] A.B.P. Lever, *Adv. Inorg. Radiochem.*, **7** (1965) 27.
- [19] R. Taube, *Pure Appl. Chem.*, **38** (1974) 427.
- [20] P.A. Bernstein and A.B.P. Lever, *Inorg. Chim. Acta*, **200** (1992) 543.