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Spectroscopy, Electrochemistry, and Spectroelectrochemistry of Tetra-*tert*-Butylated and Octaphenylated Tetraazaporphyrins

Nagao KOBAYASHI,* Shin-ichiro NAKAJIMA,† and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Aoba, Sendai 980
†R & D Center, Ricoh Corporation, Shin-ei-cho 16-1, Kohoku-ku, Yokohama 223

Several tetraazaporphyrins (TAPs) have been characterized by electronic absorption, fluorescence, and magnetic circular dichroism (MCD) spectroscopy, together with electrochemical methods. The absorption coefficients (ε) and band positions change markedly with changing TAP structure and solvent. The potential differences of the redox couples of tetra-*tert*-butylated TAP skeleton are closer to those in general porphyrins than phthalocyanines (Pcs).

More than 30 tetraazaporphyrin (TAP) structures have been reported to date, mainly by Russian researchers.1) However, their spectroscopic properties are not necessarily well elucidated compared with general porphyrins and phthalocyanines (Pcs), although the electronic absorption spectra alone are often reported. For example, no IR and redox data are available, and ESR spectra have been reported only for a copper complex.2) TAPs are structural intermediates between porphyrins and Pcs, and accordingly elucidation of their properties should lead to a better understanding of general porphyrins and Pcs. In this communication, we report spectroscopic, electrochemical, and spectroelectrochemical properties of tetra-*tert*-butyl-tetraazaporphyrins (BTAPs) and octaphenyltetraazaporphyrins (PTAPs).

BTAPs3) and PTAPs4) were synthesized according to the literature.5) CoBTAP and VOBTAP were prepared by the so-called "nitrile" method.5,6) Figures 1 A and B show absorption and magnetic circular dichroism (MCD) spectra of some of the TAPs synthesized. H_2BTAP alone shows a split Q band, and the Q_{0-0} bands of Cu, VO, and MgBTAP appear approximately midway between the split Q band of H_2BTAP. MCD spectra of the metal complexes are appropriate as porphyrins of D_{4h} symmetry7): they show Faraday *A*-terms corresponding to the main absorption peaks of the Q and Soret bands. H_2BTAP displays negative and positive MCD corresponding to the absorption peaks at 619 and 551 nm, respectively (Faraday *B*-terms). MgPTAP reveals a Faraday *A*-term at around 460 nm. The presence of this band was anticipated already in 1963,8) and is thus proved here by MCD. If we follow Gouterman's "Four-Orbital Model",9) this is the Soret band.

Of particular interest is a large shift of the spectra due to a change of TAP structure or solvent. As seen in Fig.1B, the Q_{0-0} band position of MgBTAP and MgPTAP differs by 44 nm (*ca.* 1170 cm^{-1}) and the measured absorption coefficients (εs) of both the Soret and Q bands of MgPTAP are about 4-5 times larger than those of MgBTAP. Since the reported ε value of the Q band of MgBTAP in hexane was 1260003) and our datum in pyridine is 48000, we measured the ε value of our MgBTAP sample in hexane. The value obtained was 123000. To our knowledge, such a large change of ε resulting from a change of solvent has not been reported previously

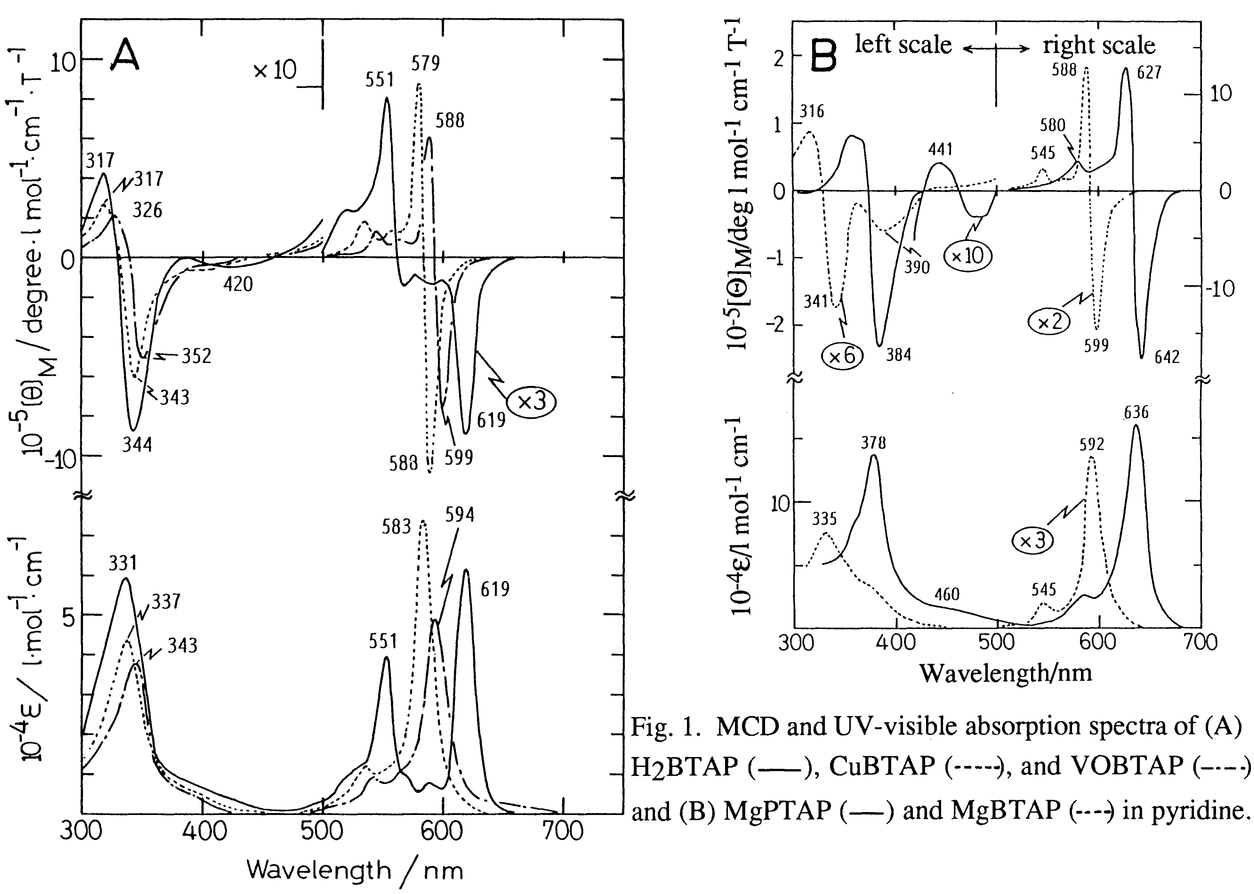

Fig. 1. MCD and UV-visible absorption spectra of (A) H_2BTAP (——), CuBTAP (-----), and VOBTAP (— - —) and (B) MgPTAP (——) and MgBTAP (- - -) in pyridine.

in either porphyrin or Pc systems. On the other hand, aside from the solvent effect, dipole lengths of the $Q_{0\text{-}0}$ bands of MtBTAP and MtPTAP in pyridine,[10] are 0.82-1.05 and 1.32-1.66 Å, respectively. Since the values for tetra-*tert*-butylated Pcs are between 1.32 and 1.47 Å,[11] the dipole length may generally be larger for Pcs than TAPs when comparison is made among compounds with the same substituent groups.

Figure 2 shows the fluorescence emission and excitation spectra of some TAPs. Fluorescence data on several TAPs have been reported previously in a few papers by Russian researchers.[12] We would just like to stress here that i) the quantum yield (Φ_F) and lifetime (τ) change significantly with varying ligand, and ii) Mg-PTAP exhibits emission not only from the S_1 state but also from the upper excited state (S_2 emission), seen for the first time in the TAP family.

Some representative cyclic (CV) and differential-pulse (DP) voltammograms are shown in Fig. 3. In the cases of Pcs and porphyrins, redox couples due to Cu and VO do not appear in the range of the potential window. Accordingly, couples discerned for VOBTAP and CuBTAP can be attributed to the redox of the ligand. The 2nd- and 1st-oxidation and 1st- and 2nd-reduction of CuBTAP are detected at 1.64, 1.27, -0.96, and -1.40 V vs. Ag/AgCl, respectively, and those of VOBTAP at 1.63, 1.36, -0.78, and -1.25 V respectively (electrochemical data on MtPTAPs could not be recorded because of their low solubility). As an average of these two compounds, the potential difference (ΔE) of the 1st-oxidation and -reduction is 2.19 V and that between the 1st- and 2nd-oxidation is 0.32 V, while that between the 1st- and 2nd-reduction is 0.46 V. In the case of general porphyrins, these values are 2.25 ± 0.15, 0.29 ± 0.05, and 0.42 ± 0.05 V, respectively,[13] while for MtPcs[14] ΔE for the 1st-oxidation and -reduction is 1.7 ± 0.2 V and that between the 1st- and 2nd-reduction is 0.41 ± 0.05 V. Accordingly, TAP may be closer to general porphyrins than Pcs in terms of the potential differences of

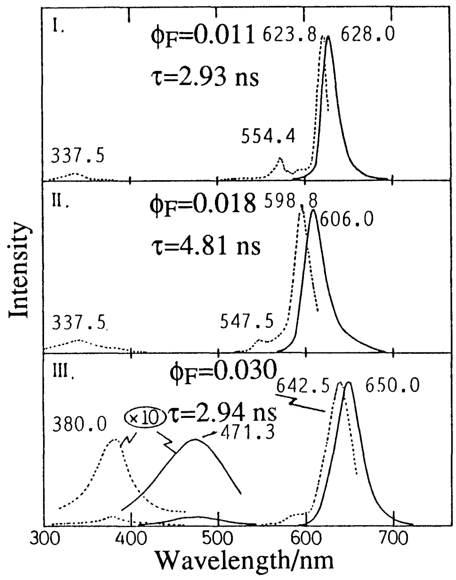

Fig. 2. Fluoresence emission (——) and excitation (.....) spectra of H_2-BTAP (top), MgBTAP (middle) and MgPTAP (bottom) in benzene. Excitation was at 335 (top and middle) and 375 (bottom) nm. Φ_F values were obtained by a comperative calibration method using the same excitation wavelength and absorbance for Mt-TAPs and zinc tetraphenylporphyrin (Φ_F=0.03 in benzene)[17] and the same emission energies. τ values were determined from the decay curves by the use of the least-squares method.

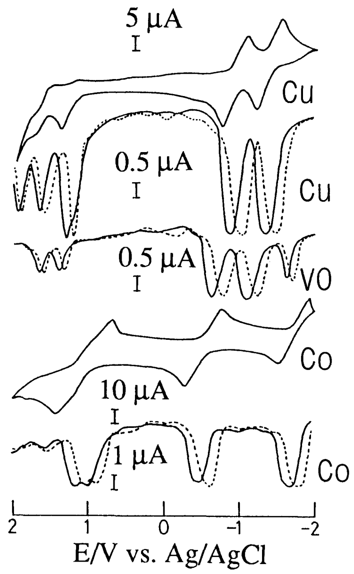

Fig. 3. CV and DP voltammograms of CuBTAP, VOBTAP, and CoBTAP in *o*-dichlorobenzene (DCB) containing 0.3 M TBAP. Sweep rate/(mV s^{-1}) = 50 for CV and 5 for DP method, electrode area/cm^2 = 0.07, and [MtBTAP] /mM = *ca.* 1.

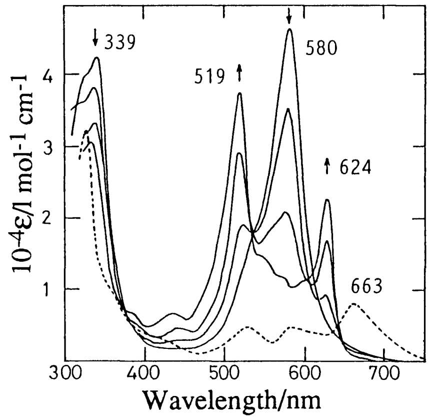

Fig. 4. Development of the electronic absorption spectra with time during the reduction of CoBTAP at -0.9 V vs. Ag/AgCl in DCB. The broken line represents the spectrum of the second reduction product.

the ligand. However, the potential *per se* of the 1st- and 2nd-reduction is very close to that of tetra-*tert*-butylPcs in the same solvent.[11]

The electrochemistry of cobalt porphyrins and Pcs differs from that of Cu, Zn, VO, and Ni complexes in that redox couples due to cobalt also appear in the potential window. Figure 3 shows the CV and DP voltammograms of CoBTAP. Redox couples are observed at 1.08, 0.92, -0.58, and -1.77 V vs. Ag/AgCl, and are assigned as $TAP^{-1/-2}$, $Co^{III/II}$, $Co^{II/I}$, and $TAP^{-2/-3}$, respectively, by comparing these data with those of cobalt neopentoxyphthalocyanine (CoTNPc) in the same solvent[15] and based upon the spectroelectrochemistry shown below. Reduction across the 1st couple of CoBTAP results in the spectroscopic changes shown in Fig. 4. As reported for CoTNPc,[15] the Q band shifts to longer wavelength with concomitant decrease in ε, while a new band which may be ascribed to charge-transfer (CT) from cobalt(I) (e_g) to TAP ring orbitals (b_{1u}, b_{2u})[16] appears between the Soret and Q bands. The 2nd-reduction between -1.5 and -2.0 V gives a pale green solution whose spectrum is shown as the broken line. Compared with the spectrum of the 1st reduction product, the Q band shifts further to the red with hypochromism. Although the intensity of the CT band seems somewhat larger than those in Co^{I}-Pcs, the above behavior is characteristic for transformation of $Co^{II}Pc^{-2}$ to $Co^{I}Pc^{-2}$ and further to $Co^{I}Pc^{-3}$.[15,16] Accordingly, we concluded that the 1st- and 2nd-reduction of CoBTAP is assigned to $Co^{II/I}BTAP^{-2}$ and $Co^{I}BTAP^{-2/-3}$ couples. On the other hand, electrolysis at 1.3 V shifted the Q band at 580 nm to 597 nm with hyperchromic effect, and subsequently further to 620 nm with hypochromic effect. Hence, the 1st- and 2nd-oxidation couples at 0.92 and 1.08 V were assigned$^{15)}$ to $Co^{III/II}BTAP^{-2}$ and $Co^{III}BTAP^{-1/-2}$, respectively.

As shown above, the position and ε of the absorption spectra of TAPs change much more markedly by varing the kind of TAP structure and solvent used for measurements than those of general porphyrins and Pcs. The potential differences of the redox couples of TAPs are closer to those in general porphyrins than Pcs. Fluorescence emission from the S_2 state was observed in a TAP for the first time.

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5) Yields and elemental analysis. Calcd for $C_{32}H_{40}N_8Mt$ for MtBTAP and $C_{64}H_{40}N_8Mt$ for MtPTAP (Mt=Mg, H_2, VO, Cu, and Co). MgBTAP, 12.8%. Found: C, 68.38; H, 7.46; N, 19.18%. Calcd: C, 68.51; H, 7.19, N, 19.97. H_2BTAP, 71.4%. Found: C, 71.25; H, 8.01; N, 20.55%. Calcd: C, 71.34; H, 7.86; N, 20.80. CuBTAP, 15.6%. Found: C, 64.26; H, 7.04; N, 18.02%. Calcd: C, 64.03; H, 6.71; N, 18.67. VOBTAP, 14.0%. Found: C, 63.74; H, 6.61; N, 18.21%. Calcd: C, 63.67; H, 6.68; N, 18.56. CoBTAP, 11.0%. Found: C, 64.47; H, 6.81; N, 18.12%. Calcd: C, 64.53; H, 6.77; N, 18.81. MgPTAP, 28.4%. Found: C, 80.91; H, 4.51; N, 11.36%. Calcd: C, 81.31; H, 4.26; N, 11.85. Cu- and CoPTAP were also synthesized but they did not give spectra typical of mononuclear species, although their analytical data were close to the theoretical ones.

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