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# Spectroscopy and Electrochemistry of a Monomer and Sandwich Dimer of Lutetium Tetra-*tert*-Butylpyrazinoporphyrazine

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A monomer and sandwich dimer (so-called "*blue form*") of lutetium tetra-*tert*-butylpyrazinoporphyrazine have been synthesized and characterized by electronic absorption and magnetic circular dichroism spectroscopy (MCD), together with cyclic- and differential-pulse-voltammetry. *A*-term MCD dispersions appear in the Q and B bands, especially corresponding in each of the split Q bands of the dimer. The potential difference between the 1st-oxidation and -reduction of the monomer is 1.98 V and that between the 1st- and 2nd-reduction is 0.72V in *o*-dichlorobenzene (DCB). The dimer shows 7 redox couples.

Tetrapyrazinoporphyrazines (PyZs) are tetraazaporphyrins containing four pyrazine rings fused to pyrrole rings, and hence can be regarded as relatives of phthalocyanines (Pcs). Although their preparation seems not necessarily difficult, their properties are not well elucidated compared with those of general porphyrins and Pcs.1) For example, concerning electrochemical data, only the 1st-reduction potentials of two compounds have been reported to date.2) In this communication, we report the preparation, spectroscopy, and electrochemistry of a monomer and sandwich dimer ("*blue form*")3) of lutetium tetra-*tert*-butylpyrazinoporphyrazine (*t*-BuPyZ).

Mononuclear Lu(*t*-BuPyZ)Cl was obtained by treating equimolar amounts of $LuCl_3$ and purified $H_2$(*t*-BuPyZ)4) in refluxing DMF, with subsequent purification using basic alumina-methylene chloride and recrystallization from DMF-ether.5) The sandwich dimer, Lu(*t*-BuPyZ)$_2$, was prepared by the "isoindoline" method.6) In the purification using basic alumina columns, chloroform, pyridine, ethyl acetate, and methanol were used as eluents, but the final fraction, which was eluted by methanol containing 0.1% of sodium methoxide, was collected and recrystallized from toluene-ether.5)

Figure 1 shows the absorption and MCD spectra of Lu(*t*-BuPyZ)Cl. The Q band lies at shorter wavelength than MtPcs (Mt; metal) by 30-50 nm indicating that the effective $\pi$-conjugation system is smaller than that of Pcs. The MCD spectrum is typical of that of metalloporphyrins and MtPcs with $D_{4h}$ symmetry: Faraday *A*-terms are observed corresponding to the main Q and B bands.7) A curvature around 360-390 nm suggests that there is a hidden band in this region which is difficult to detect by electronic absorption spectroscopy. The observed dipole strengths ($\mu$) in the B and Q bands are 18.21 and 44.59 $D^2$ (D; debye), respectively.

Spectra of Lu(*t*-BuPyZ)$_2$ are collected in Fig. 2. The absorption spectrum differs from that of Lu(Pc)$_2$s (*blue form*)8) in that the apparent molar absorption coefficient ($\varepsilon$) of the B band is more intense than that in the Q region, while the separation between the two split peaks ($Q_1$ and $Q_2$) (2750 $cm^{-1}$) is larger than that in a Lu(Pc)$_2$

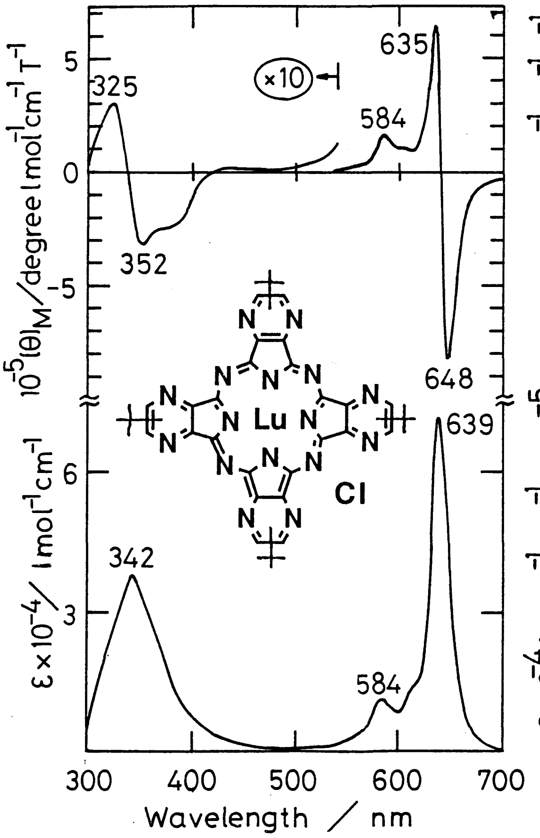

Fig. 1. Electronic absorption (bottom) and MCD (top) spectra of Lu($t$-BuPyZ)Cl in chloroform.

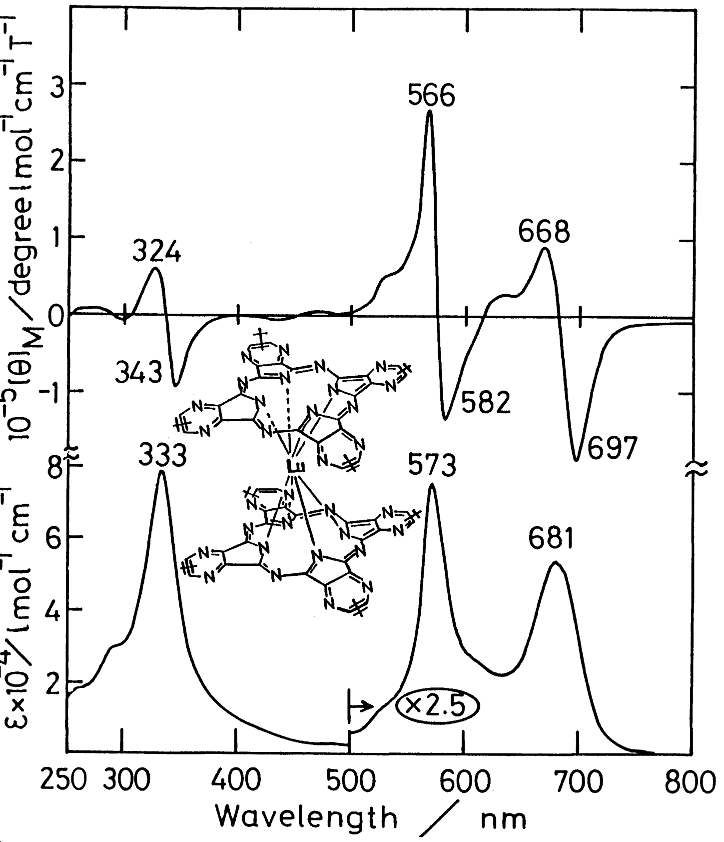

Fig. 2. Electronic absorption (bottom) and MCD (top) spectra of Lu($t$-BuPyZ)$_2$ in chloroform.

(1780 cm$^{-1}$).[8] Compared with the spectrum of Lu($t$-BuPyZ)Cl, the B band shifts to the blue by *ca.* 880 cm$^{-1}$ and increases in total intensity ($\mu_B$=87.67 D$^2$) while the Q band is weakened ($\mu_Q$=35.16 D$^2$). However, the sum $\mu_Q + \mu_B$ attributable to each $t$-BuPyZ chromophore is conserved; 61.4 and 62.8 D$^2$ for the dimer and monomer, respectively. Thus, a redistribution of transition probability between the Q and B states occurs in the dimer formation. Spectroscopic features of MCD, on the other hand, differ significantly from those of monomers in the Q band region. Its shape is more complex than in mononuclear Lu($t$-BuPyZ)Cl (Fig. 1), but band deconvolution in the Q band (Fig. 3) indicates that Faraday $A$-terms are included associated with two absorption peaks at 680 (Q$_1$) and 573 (Q$_2$) nm. This fact indicates clearly that *the two Q bands are both ascribed to transitions to the degenerated excited state* (A/D values[9] for Q$_1$ and Q$_2$ bands are 2.77 and 2.67, respectively) just as in the Q band of Lu($t$-BuPyZ)Cl (A/D=2.63). Since the Q band of several Pc dimers such as μ-oxo type SiPc dimers[10] and crown ether substituted supermolecular cofacial dimers[11] has been rationalized by a simple excitonic interaction, the above result on Lu($t$-BuPyZ)$_2$ shows an interesting contrast. In addition to the above arguments on the Faraday $A$-term, the following facts suggest that the Q band of Lu($t$-BuPyZ)$_2$ is not explained reasonably by a pure exciton mechanism due to dipole-dipole interaction.[12] i) The intensities of the Q$_1$ and Q$_2$ bands are roughly comparative. This is contrary to the prediction from the theory that the band to lower energy should be much weaker because of its forbidden character (If the Lu($t$-BuPyZ)$_2$ structure is approximated by $D_{4d}$ symmetry as in Lu(Pc)$_2$,[10] the band to lower energy (Q$_1$) is assigned to an $E_3 \leftarrow A_1$ forbidden transition while that to higher energy (Q$_2$) to an $E_1 \leftarrow A_1$ allowed transition).[13] ii) Splitting between the Q$_1$ and Q$_2$ bands (2750 cm$^{-1}$) is not necessarily larger than that in Sn(Pc)$_2$ (3100 cm$^{-1}$),[14] a SiPc dimer (*ca.* 2600 cm$^{-1}$),[10] or crown ether substitut-

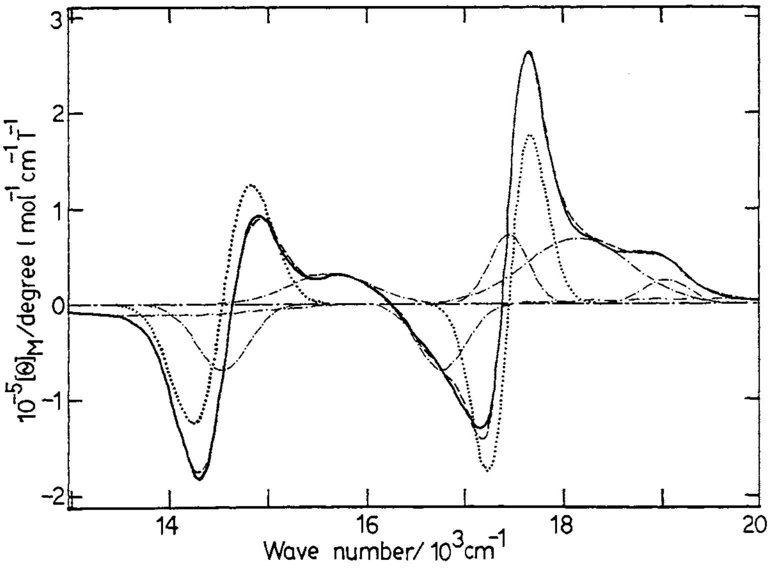

Fig. 3. Band deconvolution of the Q band MCD spectrum of Lu($t$-BuPyZ)$_2$; (———) experimental data, (– – – –) fitted data, (··········) $A$-terms, and (—·—·—) $B$-terms.

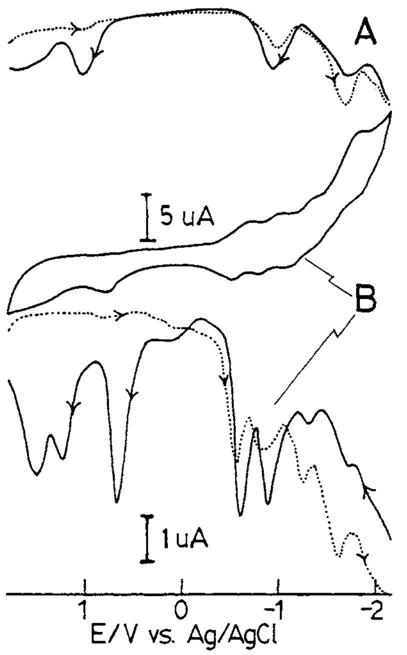

Fig. 4. Cyclic and differential-pulse voltammograms of (A) Lu($t$-BuPyZ)Cl and (B) Lu($t$-BuPyZ)$_2$ in DCB containing 0.3 M TBAP. Because of the low solubility, the concentration of the monomer is unknown. [Lu($t$-BuPyZ]$_2$/mM = $ca.$ 0.8. Sweep rate/mV s$^{-1}$ = 20 for CV and 5 for DP methods. Area of electrode/cm$^2$ = 0.07.

ed Pc dimers ($ca.$ 2000 cm$^{-1}$),11) although the expected distance of the two chromophores in Lu($t$-BuPyZ)$_2$ ($ca.$ 2.69 Å, assuming that it is nearly the same as in Lu(Pc)$_2$)15) is shorter than the latter three ($ca.$ 2.70,16) 3.3210) and 4.1 Å,11) respectively). This is also contrary to the theory that predicts a larger splitting the smaller the distance between the two chromophore. Our results on Lu($t$-BuPyZ)$_2$ are, however, in good agreement with the results of molecular orbital (MO) calculation on Lu(Pc)$_2$ by the valence effective Hamiltonian approach.17) According to these, the Q band corresponds to transitions to two pairs (separation = $ca.$ 2400 cm$^{-1}$) of nearly degenerate excited states, and has almost the same intensities. In the MO method, the Q$_1$ and Q$_2$ bands correspond to transitions from $a_2$ to $e_1$ and $b_1$ to $e_3$ orbitals, respectively, under D$_{4d}$ symmetry.

Differential-pulse (DP) and cyclic voltammograms (CV) of Lu($t$-BuPyZ)Cl and Lu($t$-BuPyZ)$_2$ are shown in Fig. 4. Low solubility of the former prevented well-resolved CV curves to be obtained. However, its DP curves show that the 1st-oxidation and 1st- and 2nd-reductions occur at $ca.$ 1.02, -0.96, and -1.68 V vs. Ag/AgCl, respectively. The potential difference (ΔE) of the 1st-oxidation and -reduction is 1.98 V and that between the 1st- and 2nd-reduction is 0.72 V. In the case of general porphyrins,18) these values are 2.25±0.15 and 0.42 ±0.05 V, respectively, and for MtPcs19) they are 1.7±0.2 and 0.41±0.05 V. Accordingly, a value of 1.98 V indicates that the size of the effective π-conjugation system is in between that of Pcs and general porphyrins. Although the potential of the 1st-reduction is close to that of $tert$-butylated Pcs in the same solvent,20) the 2nd-reduction potential lies to negative potential by about 0.3 V.

The oxidation of the Lu($t$-BuPyZ)$_2$ skeleton is irreversible as in Lu($t$-BuPyZ)Cl, and all redox couples seen in Lu($t$-BuPyZ)Cl split into two in Lu($t$-BuPyZ)$_2$. Thus, the 3rd-, 2nd-, and 1st-oxidation, and the 1st-, 2nd-, 3rd-, and 4th-reduction potentials lie at $ca.$ 1.5, 1.23, 0.67, -0.60, -0.88, -1.29, and -1.69 V, respectively. Since the 2nd- and 1st-oxidation and 1st- and 2nd-reduction of Lu(Pc)$_2$ appear at $ca.$ 0.55, 0.09, –0.99, and

$-1.35$ V, respectively in the same solvent,[21] these values are anodic by 0.4-0.7 V. Although Pc derivatives are generally $\pi$-donors, the above potentials of Lu($t$-BuPyZ)$_2$ suggest it can be a $\pi$-acceptor.

In summary, we have shown some intriguing spectroscopic and electrochemical properties of Lu($t$-BuPyZ)Cl and Lu($t$-BuPyZ)$_2$, and compared them with those of Pc analogues.

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