

Charge-Transfer Complexes of Metallated and Unmetallated meso-substituted Porphyrins

(Grad. School of Sci., Hokkaido Univ.*, Ehime Univ**.) Judy Fe F. Jose*, Yukihiro Takahashi*, Tamotsu Inabe*, Toshio Naito**

[Introduction] Wide variety of metallated and unmetallated derivatives of porphyrins had been synthesized and investigated. The application of these materials in different fields and systems had continuously increased due to their unique and modifiable properties of conductivity, magnetoresistance, optical properties and magnetic properties. These compounds are expected to function as organic donor components in charge transfer (CT) complexes. However, their CT complexes, especially in crystalline state are scarcely studied. In this report, metal-free, meso-substituted porphyrins tetramethylporphyrin, $H_2(tmp)$ and tetraphenylporphyrin $H_2(tpp)$; and, metallated $Ni(tpp)$ are combined with the molecular acceptors TCNQ and F_4TCNQ to investigate the formation of CT complexes.

[Experiment] After the synthesis of the donor $H_2(tmp)$, following the published procedures¹, crystals of the CT complex of $H_2(tmp)$ were prepared via a slow liquid diffusion method. $H_2(tpp)$ and $Ni(tpp)$ CT complexes were produced using an evaporation method varying the solvent employed. After the crystals were collected, to investigate their charge-transfer characteristics, X-ray diffraction, infrared spectroscopy and diffuse reflectance spectroscopy measurements were carried out.

[Results and Discussion] The crystal structure (**Figure 1**) of the first charge transfer complex, $[H_2(tmp)][TCNQ]$ gave almost the same crystal structure of the previously prepared metallated derivative, $[Ni(tmp)][TCNQ]^2$ both showing a mixed stack arrangement of the donor and acceptor molecules, and a stoichiometric ratio of 1:1. The overlap patterns for both complexes were also the same.

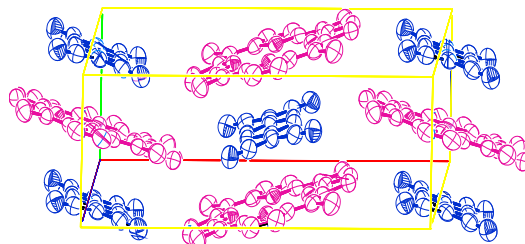


Figure 1. $[H_2(tmp)][TCNQ]$

Two kinds of CT complexes of $H_2(tpp)$ were obtained using different set of solvents. Although having the same components of donor and acceptor molecules, the two $H_2(tpp)$ complexes, $[H_2(tpp)][F_4TCNQ](CH_2Cl_2)$ in (**Figure 2**) and $[H_2(tpp)]_2[F_4TCNQ](CHCl_3)$ in (**Figure 3**) gave different crystal structures, packing, overlap pattern and stoichiometric ratio. The nickel derivative of meso-substituted tetraphenyl

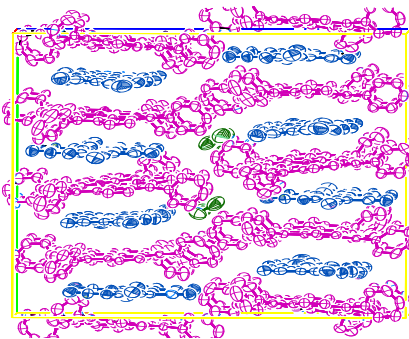


Figure 2. $[H_2(tpp)][F_4TCNQ](CH_2Cl_2)$

porphyrin, $[\text{Ni}(\text{tpp})]_2[\text{F}_4\text{TCNQ}](\text{CHCl}_3)$ presented in (Figure 4), produced similar crystal dimensions with its corresponding unmetallated compound.

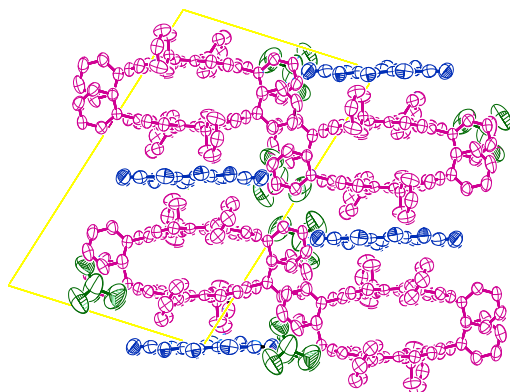


Figure 3. $[\text{H}_2(\text{tpp})]_2[\text{F}_4\text{TCNQ}](\text{CHCl}_3)$

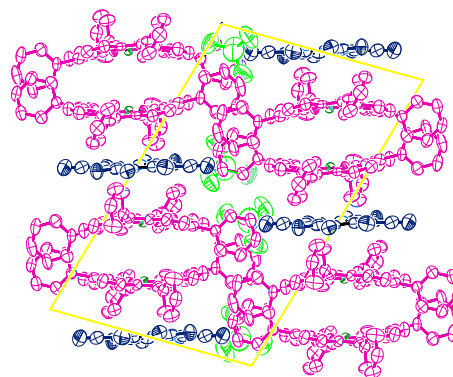


Figure 4. $[\text{Ni}(\text{tpp})]_2[\text{F}_4\text{TCNQ}](\text{CHCl}_3)$

Charge transfer characteristics of the complexes were investigated through comparison of the bond lengths and distinct vibrational modes of the acceptor molecules in each complex with those of known ionic and neutral states of the acceptor. The results show that there exist small degrees of charge transfer in the complexes. This was further confirmed by the charge transfer energy of the complexes determined from diffuse reflectance spectra. Also, consulting the ionicity diagram (Figure 5) formulated by Torrance³, the CT complexes prepared can be classified as neutral compounds. Although the combination of donors and acceptors was attempted for a rather wide range of ΔE (difference between the oxidation potential of the donor and reduction potential of the acceptor), the CT complexes obtained were only restricted in a narrow ΔE range. Attempts to expand the ΔE range are now under way, and the details of the results will be presented.

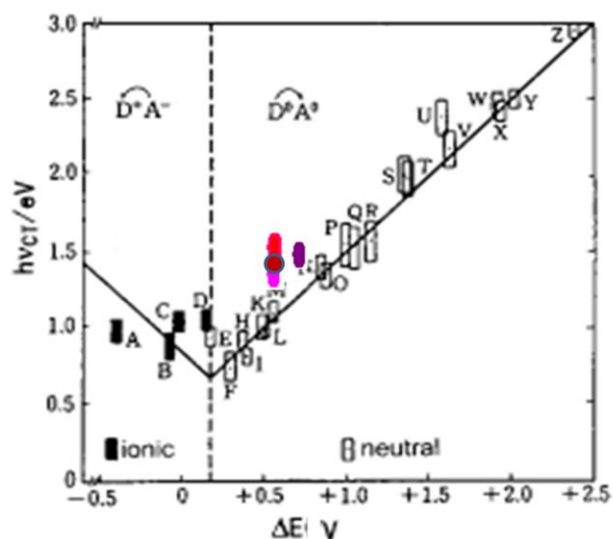


Figure 5. Ionicity Diagram³ for CT Complexes

- $[\text{H}_2(\text{tmp})][\text{TCNQ}]$
- $[\text{H}_2(\text{tpp})]_2[\text{F}_4\text{TCNQ}](\text{CHCl}_3)$
- $[\text{H}_2(\text{tpp})][\text{F}_4\text{TCNQ}]\text{CH}_2\text{Cl}_2$
- $[\text{Ni}(\text{tpp})]_2[\text{F}_4\text{TCNQ}](\text{CHCl}_3)$

¹Ulman A, et al., *J. Heterocyclic Chem.*, 19, 409-413, (1982) ; McGhee E, et al. *Inorg. Chem.* 30, 803-808, (1991); Johnstone R.A.W., et al., *Heterocycles*, 43, 7, 1423-1437, (1996)

²Pace L, et al., *Inor. Chem.* 21, 1, 199-207, (1982)

³Torrance JB, et al., *Phys. Rev. Lett.* 46, 253, (1981)