Vertically Linked Ruthenium(II) Porphyrin Oligomers

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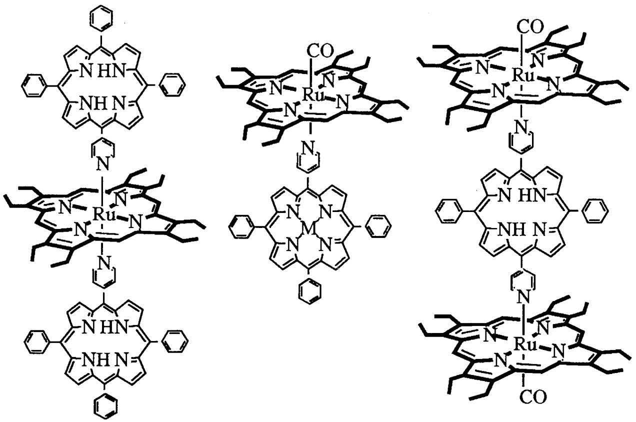
A novel porphyrin trimer linked vertically, Ru(OEP)(H_2PyP$_3$P)$_2$ **1**, was synthesized and characterized.The trimer showed intriguing MLCT bands. The preparation of a series of three porphyrin oligomers, Ru(OEP)(CO)(H_2PyP$_3$P) **2**, Ru(OEP)(CO)(ZnPyP$_3$P) **3**, and [Ru(OEP)(CO)]$_2$(trans-H_2Py$_2$P$_2$P) **4** were also reported.

Polymacrocyclic porphyrins recently developed by Sanders and coworkers aiming at synthetic enzymes presented precious data for host guest chemistry and possible mechanisms of stereoselective catalytic reactions.[1-3] Further, there are many versatile studies of porphyrin oligomers such as spacer- or directly-linked porphyrin oligomers,[4-7] entwined porphyrin conjugates,[8] and facial porphyrins.[9] Especially, the studies of interaction between metal centers and between porphyrins in these oligomers have played much important key roles for understanding many biological processes as well as photochemical, electrochemical, magnetic, and catalytic natures, and solar energy conversion mechanisms. Those oligomers were essentially built up by linking porphyrins in the lateral direction of porphyrin planes, which caused much effect on the electronic interaction between porphyrin units. On the other hand, there have been no systematic study on the porphyrin oligomers linked perpendicularly and virtually nothing is known on the interaction between porphyrins of such systems. There are only a few reports on such oligomers so far to our knowledge, i.e., [ZnPyP$_3$P]$_n$ oligomers equilibrated in solutions,[10,11] and a ternary ruthenium complex which was used to prove the coordination of trans-H_2Py$_2$P$_2$P in the cavity of polymacrocyclic zinc porphyrins.[2,3]

We report here the synthesis and characterization of a novel porphyrin trimer, Ru(OEP)(H_2PyP$_3$P)$_2$ **1**, in addition to the preparation of a series of three porphyrin oligomers, Ru(OEP)(CO)(H_2PyP$_3$P) **2**, Ru(OEP)(CO)(ZnPyP$_3$P) **3**, and [Ru(OEP)(CO)]$_2$(trans-H_2Py$_2$P$_2$P) **4**.[12] The porphyrin ligands with pyridyl groups in these oligomers are coordinated to the metal centers of parent ruthenium(II) porphyrins perpendicularly as shown in Figure 1. All these oligomers except **1** contain CO ligands at the trans positions to coordinating pyridyl porphyrins. Only the ternary porphyrin **1** showed an intriguing electronic interaction, i.e., metal to ligand charge transfer (MLCT) bands.

Ruthenium(II) porphyrin oligomers of **1** ~ **4** were synthesized by treating Ru(OEP)(CO)(MeOH) with corresponding porphyrin ligands, H_2PyP$_3$P, ZnPyP$_3$P, or trans-H_2Py$_2$P$_2$P as shown in Scheme 1. Treating **2** with zinc acetate also gave **3**. The elemental analyses and all spectral data of FAB-MS, IR, ^{1}H NMR, and UV-vis supported the formation of the oligomers.



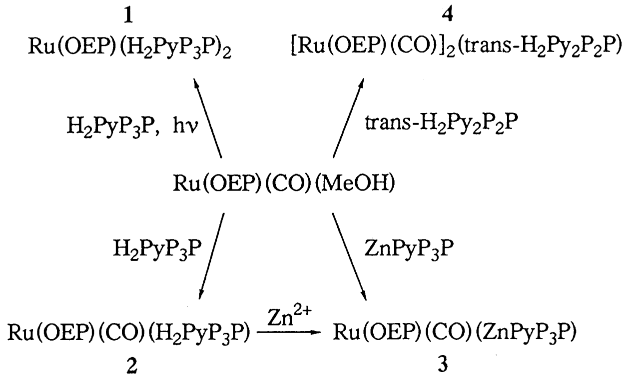
1

M : 2H$^+$ **2**
Zn^{2+} **3**

4

Figure 1. Idealized drawing of the oligomers.

Scheme 1.



FAB-MS measurements gave parent signals of **1**, **2**, and **3** at 1865, 1277, and 1340 (m/z$^+$) respectively. For **4**, the signal observed at 1939 (m/z$^+$) was too small to support the formation of [Ru(OEP)(CO)]$_2$(H_2Py$_2$P$_2$P) (m.w. = 1940). However, the signals appeared at 1279 and 1250 (m/z$^+$) due to the respective fragments of [Ru(OEP)(CO)](H_2Py$_2$P$_2$P) and [Ru(OEP)](H_2Py$_2$P$_2$P) supported the formation of [Ru(OEP)(CO)]$_2$(trans-H_2Py$_2$P$_2$P). The presence or absence of CO ligands and inner NH for corresponding oligomers was confirmed by IR measurements.

Sharpness of the ^{1}H NMR signals of the sample solutions suggested the diamagnetism of **1** ~ **4** as expected for Ru(II) porphyrins. The chemical shifts for 2,6- and 3,5-protons of the pyridyl groups of the porphyrin ligands of H_2PyP$_3$P and trans-H_2Py$_2$P$_2$P were taken as diagnosis of the coordination of pyridyl groups at the axial position of ruthenium porphyrin. The 2,6- and 3,5-protons were observed at significantly higher fields around 1~2 and 5 ppm, respectively, compared to the corresponding chemical shifts of those of free H_2PyP$_3$P or trans-H_2Py$_2$P$_2$P porphyrins which appeared around 9 and 8 ppm, respectively. Similar remarkable upfield chemical shifts have been reported for the protons of pyridyl groups in the ruthenium ternary complex **3** analogue,[3] in aggregated ZnPyP$_3$P,[10] and in

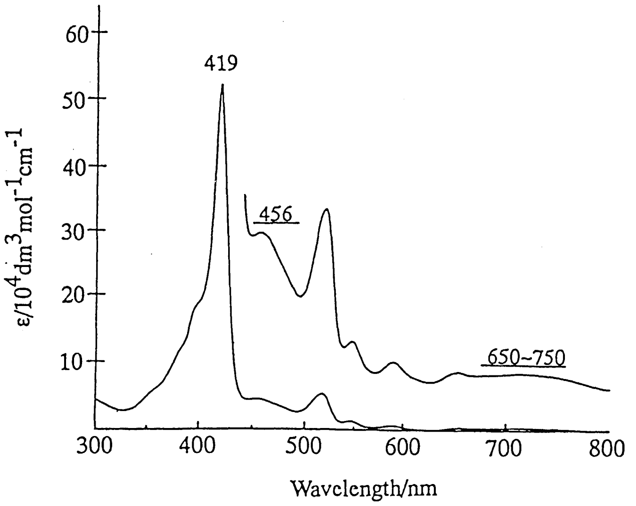


Figure 2. UV-vis spectrum of **1** in toluene at room temperature.

Zn(TPP)py.[13] The results clearly indicated that H_2PyP_3P and trans-$H_2Py_2P_2P$ are coordinated to the central ruthenium metal of Ru^{II}(OEP)CO or Ru^{II}(OEP) cores through the pyridyl groups. An inner proton (NH) signals of **1**, **2**, and **4** were observed around -3 ppm. Integral intensities of these signals confirmed that **1**~ **4** consisted of corresponding porphyrin units.

The UV-vis spectra of **2**~ **4** having CO ligands are essentially composed of those of free H_2PyP_3P porphyrins and core ruthenium OEP porphyrins. However, as Figure 2 shows, **1** exhibits two new extra bands at 456 and 650-750 nm, besides the bands originated from Ru(OEP) and H_2PyP_3P. These extra bands which were similarly observed for Ru(OEP)(py)$_2$[14] decreased in intensity by the oxidation of the ruthenium ion to form $[Ru^{III}(OEP)(H_2PyP_3P)_2]^+$ using $(NH_4)_2Ce(NO_3)_6$. The bands also shifted to longer wavelength in more polar solvents. Thus the bands should be assigned to MLCT from ruthenium to horizontal porphyrin rings or to vertical ligand porphyrin rings. The charge transfer may indicate possible intramolecular electron transfer, as observed for spacer-bridged ruthenium complexes.[5,15]

This work provides a systematic route for constructing perpendicularly linked porphyrin oligomers and polymers. A full investigation for potential functions of these new oligomers especially for photochemical and electrochemical natures, and further structural analyses are currently in progress.

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11 Abbreviations : PyP_3P = 5-pyridyl-10,15,20-triphenylporphyrinato dianion, OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion, TPP = 5,10,15,20-tetraphenylporphyrinato dianion, H_2PyP_3P = 5-pyridyl-10,15,20-triphenylporphyrin, trans-$H_2Py_2P_2P$ = 5,15- dipyridyl-10,20-diphenylporphyrin
12 Elemental analyses of these oligomers were satisfactory.
1: The oligomer was prepared by the reaction of Ru(OEP)(CO)(MeOH) with H_2PyP_3P in toluene under argon atmosphere followed by photoirradiation with pyrex-filtered visible light using a mercury lamp (yield: 40%). UV-vis/nm (ε/10^4 dm^3 mol^{-1} cm^{-1}) (in $C_6H_5CH_3$) 399 (sh), 419 (53.9), 456 (5.40), 516 (6.38), 546, 588, 652; IR/cm^{-1} (KBr mull) νNH 3316; ^{1}H NMR/ppm vs TMS (270 MHz, C_6D_6) 10.06 (meso, s), 4.09 (-CH_2-, q, J=7.56 Hz), 2.08 (-CH_3, t, J=7.56 Hz), 8.79, 8.77, 8.25, 6.93 (pyrrole β, d, J=5.13 Hz), -2.89 (inner NH, s), 8.01, 7.91 (phenyl *o*-, d, J=8.10 Hz), ~7.54 (phenyl *m,p*-, m), 5.31 (py 3,5-, d, J=6.75 Hz), 2.82 (py 2,6-, d, J=6.75 Hz)
2: The toluene solution containing Ru(OEP)(CO)(MeOH) and H_2PyP_3P was refluxed for 30 min under argon atmosphere, and evaporated to dryness. The product was purified using a silica gel column and recrystallized from toluene-haxane (yield; 67.5%). UV-vis/nm (ε/10^4 dm^3 mol^{-1} cm^{-1}) (in CH_2Cl_2) 395 (30.4), 418 (40.1), 514 (3.16), 550 (2.98), 590 (0.543), 646 (0.397); IR/cm^{-1} (KBr mull) νCO 1945, νNH 3320; ^{1}H NMR/ppm vs TMS (270 MHz, CD_2Cl_2) 10.01 (meso, s), 4.08 (-CH_2-, q, J=7.43 Hz), 1.96 (-CH_3, t, J=7.43 Hz), 8.69, 8.65, 8.36, 7.16 (pyrrole β, d, J=5.13 Hz), -3.41 (inner NH, s), 8.04, 7.95 (phenyl *o*-, dd, J=7.56, 1.35 Hz), 7.68 (phenyl *m,p*-, m), 5.77 (py 3,5-, dd, J=5.40, 1.35 Hz), 1.23 (py 2,6-, d, J=5.40 Hz)
3: The oligomer was synthesized by a method similar to **2** using Zn(PyP_3P) in place of H_2PyP_3P (yield: 88.3%). UV-vis/nm (ε/10^4 dm^3 mol^{-1} cm^{-1}) (in CH_2Cl_2) 395 (28.2), 419 (51.3), 516 (1.52), 548 (4.22), 586 (0.440); The IR and ^{1}H NMR spectra confirmed the formation of **3**.
4: The oligomer was prepared similarly to **2** using trans-$H_2Py_2P_2P$ (yield: 45%). UV-vis/nm (ε/10^4 dm^3 mol^{-1} cm $^{-1}$) (in CH_2Cl_2) 395 (51.3), 421 (38.7), 515 (4.69), 550 (6.30), 591 (0.525), 648 (0.366); The IR and ^{1}H NMR spectra are also consistent with the structure.
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