Synthesis of Fullerene-Porphyrin Complex

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C_{60}-porphyrin complex (**1**) has been synthesized for the first time. In this complex, two functional molecules are linked by a direct metal-C_{60} bond. Characterization of **1** is performed with a ^{1}H and ^{13}C NMR and an electrospray ionization mass-spectroscopy (ESI-MS). The UV/Vis spectrum of **1** in benzene showed the strong absorption positioned at 280 and 326 nm assigned to the electronic transitions in C_{60} moiety, which were red-shifted by 3 nm and blue-shifted by 7 nm with respect to those of pristine C_{60}, respectively. A new absorption band at λ_{max}=780 nm appeared in a longer-wavelength region. This band was assigned to metal-to-ligand charge transfer (MLCT) transition from ruthenium to fullerene.

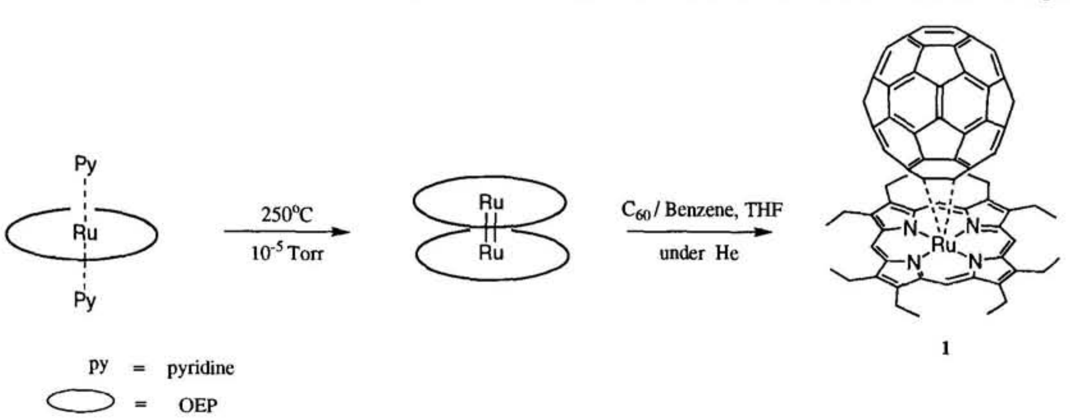
Buckminsterfullerene, C_{60}, has a symmetrically peculiar and shapely structure, entirely made of carbons almost with the sp^2-hybridized state. The conjugated π-electron system widely-spread over the spherical surface of C_{60} possesses the distinctive electronic configuration[1,2] due to the unique symmetry. A number of C_{60} derivatives have been synthesized toward application of the distinctive π-electron system.[3] Among them, C_{60} has often been connected with other functional moieties.[4-7] However, the π-conjugation is not delocalized over the whole complex in most of those complexes. That is, the orbital interaction between the moieties would be weak and all the interactions would depend mainly on the distance. In order to delocalize the π-conjugation over the whole complex, the π-systems of the other functional moieties need to be near to the π-system of C_{60} not in perpendicular but in parallel manner.

Meanwhile, it is known that C_{60} plays the role of a π-ligand η^2-coordinated to the transition metals[8-13] and that Ru-porphyrin forms a complex in which a ethylene is η^2-coordinated to the Ru metal.[14-16] In this article, we would like to report a novel type of C_{60} complex (**1**), in which a C_{60} is linked directly with ruthenium octaethyl-porphyrin (Ru(OEP)) through a coordination.

Bis((octaethylporphyrinato)ruthenium(II))($(Ru(OEP))_2$) was synthesized[17,18] following the method similar to that reported by Collman et al.[14-16] A 10 mL of benzene/THF (100/1 v/v) solution of C_{60} (1.10×10^{-2} mmol) was added to solid $(Ru(OEP))_2$ (5.25×10^{-3} mmol) under He (Scheme 1). The color of the solution immediately changed from purple to dark brown. After 30 min, the solvent was removed by evaporation and the brown precipitates were obtained. This product was hardly soluble in common organic solvents and very air-sensitive. The product was immediately examined without further purification. The structure **1** in which a C_{60} is η^2-coordinated to the Ru metal of Ru-porphyrin was expected, which was confirmed as in what follows.

The ^{1}H-NMR spectrum (*o*-dichlorobenzene-d_4) of **1** showed two broad and two singlet signals of δ = 1.29, 4.12 ppm (TMS std.) and δ = 8.38, 8.46 ppm, respectively. The signals in the region δ = 1.29, 4.12 ppm were assigned to hydrogen atoms in the ethyl groups of OEP. The signals in the region δ = 8.38, 8.46 ppm were assigned to hydrogen atoms at the *meso* sites of OEP. No signals assignable to hydrogen atoms of THF moiety were detected in our observation although there was possibility that a THF is also coordinated to the Ru metal.[14]

The ^{13}C-NMR spectrum (*o*-dichlorobenzene-d_4) of **1** showed a broad signal in the region δ = 143.7-141.0 ppm arising from C_{60}.[13] There was no peak derived from the pristine C_{60}. The peaks of δ = 140.1 and 138.4 ppm should occur from C_α and C_β, respectively, of OEP. The peaks observed at δ = 96.7 ppm were assigned to the OEP *meso* carbon atoms and the peaks at δ = 31.9, 22.7 ppm to the OEP ethyl carbon atoms. An additional signal appeared at δ = 66.8 ppm. It could be considered that this signal is due to the residual solvent, because THF was used as the solvent in the synthesis of this complex, and because the ^{13}C-NMR spectrum (*o*-dichlorobenzene-d_4) of the pristine THF showed two signals (δ = 67.5, 25.6 ppm). Although we also synthesized $Ru(OEP)(THF)_2$[14-16] and measured ^{13}C-NMR spectrum (*o*-dichlorobenzene-d_4) in order to clarify the assignment of that signal, a signal near δ = 66.8 ppm was not detected at all. Therefore, it was probable that the signal at 66.8 ppm could be assigned to the sp^3 carbon atoms of C_{60} moiety.[19] In order to confirm the above assignment, ^{1}H-^{13}C correlation NMR spectrum (*o*-dichlorobenzene-d_4) of **1** by HMQC[20] was also measured. It was shown that the ^{13}C signal at δ = 66.8



Scheme 1.

ppm had no correlation with any ^1H signals. Therefore, the additional signal was assigned to the sp^3 carbon atoms in C_{60} moiety.[19]

Furthermore, we tried to identify **1** by several kinds of mass spectroscopies. Fast atom bombardment (FAB) mass-spectra (MS) using *m*-nitrobenzylalchol (NBA) as a matrix did not show any C_{60} moiety signal but a strong peak for Ru(OEP) (m/z = 634 (M^+)). In this case, the dark brown solution of **1** was added to the matrix immediately resulting in color change into green. Atmospheric pressure chemical ionization (APCI) -MS in positive- and negative-ion modes also showed no molecular ion peak of **1**. Moreover, we measured on an electrospray ionization (ESI) mass-spectral technique in positive- and negative-ion modes. A weak peak assignable to **1** (m/z 1426.9 ($(M+THF)^+$)) was observed in positive mode, while the spectrum in negative-ion mode showed no molecular ion peak of **1**. No peaks assignable to other conceivable complexes such as (RuOEP : C60) = (2 : 1) and (1 : 2) ones were detected.

The UV/Vis absorption spectra of benzene solution of the compound **1** and C_{60} at room-temperature are shown in Figure 1. The absorption spectrum of the pristine C_{60} consists of four major strong absorption bands in the range 200 – 400 nm and a weak one in the region 400-630 nm assigned to the forbidden electronic transition.[21,22] The spectrum of **1** contained two strong absorption bands positioned at 281 and 326 nm. The former band was blue-shifted by 7 nm and the latter red-shifted by 3 nm with respect to those of the pristine C_{60} and these two bands became broader. The strong absorption bands positioned at 407 nm was derived from Ru(OEP). The spectrum of **1** also contains the absorption bands positioned at 520, 545 nm, which would be derived from the Q band of Ru(OEP). Moreover, a new absorption band at λ_{max}=780 nm appeared in a long-wavelength region. No absorption bands were observed above 700 nm in the absorption spectrum of the pristine C_{60}. Moreover, that absorption band did not seem to belong to Ru(OEP) moiety, since such band were not observed for carbonyl (methanol) (octaethylporphyrinato) ruthenium(II) and bis (pyridine) (octaethylporphyrinato) ruthenium(II). We assigned that absorption band to a metal-to-ligand charge transfer (MLCT) transition as well as that of the C_{60}-platinum complex.[23] This absorption band shifted to 803 nm with the use of toluene as solvent (see also Figure 1).

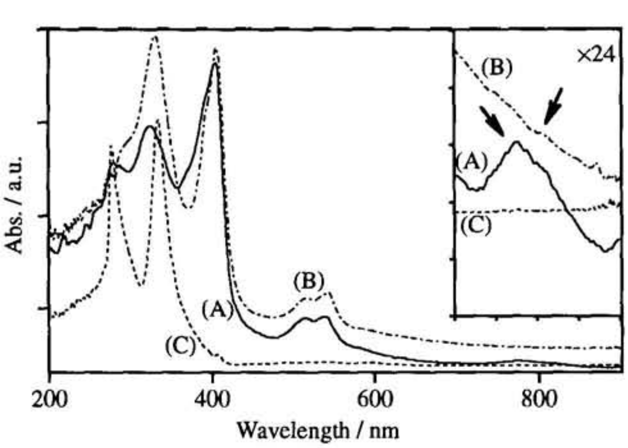


Figure 1. UV/Vis spectra of (A) **1** in benzene (solid line), (B) **1** in toluene (dash-dotted line), and (C) C_{60} in benzene (broken line). The arrows in the inset show the CT-band spectra.

Incidentally, the two shifted absorption bands mentioned above immediately turned into those of pristine C_{60} upon exposure to air. This signifies that **1** was decomposed into C_{60} and porphyrin. Further investigations are now in progress.

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References and Notes

1 R. C. Haddon, L. E. Brus, and K. Raghavachari, *Chem. Phys. Lett.*, **125**, 459 (1986).
2 J. Cioslowski, "Electronic Structure Calculations on Fullerenes and Their Derivatives," Oxford University Press, New York (1995).
3 A. Hirsch, *Synthesis*, **1995**, 895.
4 H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *J. Am. Chem. Soc.*, **118**, 11771 (1996).
5 H. Imahori and Y. Sakata, *Adv. Mater.*, **9**, 537 (1997).
6 N. Martín, I. Pérez, L. Sánchez, and C. Seoane, *J. Org. Chem.*, **62**, 5690 (1997).
7 D. Gust, T. A. Moore, and A. L. Moore, *Res. Chem. Intermed.*, **23**, 621 (1997).
8 P. J. Fagan, J. C. Calabrese, and B. Malone, *Science*, **252**, 1160 (1991).
9 A. L. Balch, J. W. Lee, B. C. Noll, and M. M. Olmstead, *J. Am. Chem. Soc.*, **114**, 10984 (1992).
10 I. J. Mavunkal, Y. Chi, S. - M. Peng, and G. - H. Lee, *Organometallics*, **14**, 4454 (1995).
11 H. - F. Hsu and J. R. Shapley, *J. Am. Chem. Soc.*, **118**, 9192 (1996).
12 K. Tang, S. Zheng, X. Jin, H. Zeng, Z. Gu, X. Zhou, and Y. Tang, *J. Chem. Soc., Dalton Trans.*, **1997**, 3585.
13 A. N. Chernega, M. L. H. Green, J. Haggitt, and A. H. H. Stephens, *J. Chem. Soc., Dalton Trans.*, **1998**, 755.
14 J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, and L. J. Wright, *J. Am. Chem. Soc.*, **107**, 4570 (1985).
15 J. P. Collman, P. J. Brothers, L. McElwee-White, and E. Rose, *J. Am. Chem. Soc.*, **107**, 6110 (1985).
16 J. P. Collman, C. E. Barnes, P. N. Swepston, and J. A. Ibers, *J. Am. Chem. Soc.*, **106**, 3500 (1984).
17 In the synthesis, carbonyl (methanol) (octaethylporphyrinato) ruthenium(II) was obtained in yield of 40.5%, and bis (pyridine) (octaethylporphyrinato) ruthenium(II) in yield of 80.7 %.
18 Octaethylporphyrin, (H_2(OEP)), was purchased from Tokyo Chemical Industry. Ruthenium trichloride was purchased from Wako Pure Chemicals. C_{60} was purchased from Bucky USA. All the solvents were distilled and degassed by freeze-pump-thaw method under He before the measurements. *o*-Dichlorobenzene-d_4 for the NMR measurements were degassed and stored in the presence of Na metal. Other reagents were of the best commercial grade and used without further purification.
19 M. Rasinkangas, T. T. Pakkanen, and T. A. Pakkanen, *J. Organometallic Chem.*, **476**, C6 (1994).
20 A. Bax, R. H. Griffey, and B. L. Hawkins, *J. Magn. Reson.*, **55**, 301 (1983).
21 S. Larsson, A. Volosov, and A. Rosén, *Chem. Phys. Lett*, **137**, 501 (1987).
22 S. Kazaoui, R. Ross, and N. Minami, *Solid State. Commun.*, **90**, 623 (1994).
23 H. Kunkely and A. Vogler, *Inorg. Chim. Acta*, **250**, 375 (1996).
24 ^1H and ^{13}C NMR spectra were obtained on either a JEOL EX-400MHz or a Bruker AVANCE DRX-500MHz NMRs. FAB-MS measurements were carried out with a JEOL JMS-700. ESI- and APCI-MS measurements were carried out with a Finnigan Mat TSQ-7000. UV/Vis absorption spectra were recorded on either Shimadzu UV-2200 or MPS-2000 spectrophotometers. All the spectra for **1** and Ru(OEP)$(THF)_2$ were measured under inert atmosphere.