Synthesis of Closely Spaced Porphyrin-Fullerene

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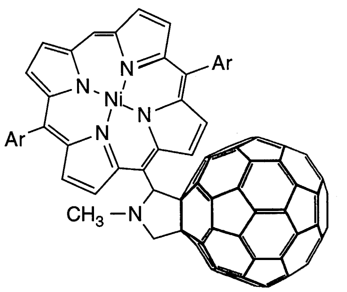
(Received November 20, 1995)

A porphyrin-linked fullerene where a C_{60} moiety is covalently linked to the meso position of 5,15-diarylporphyrin with a pyrolidine spacer was prepared. ^{1}H NMR, electronic absorption, and electrochemical studies show that there is a considerable interaction between the two chromophores.

Since the development of the gram-scale isolation of fullerenes,[1] very rich chemistry of fullerenes[2,3] has been established in a very short period. Owing to an electron-accepting ability C_{60} forms charge-transfer (CT) complexes with superconducting[4] or ferromagnetic properties.[5] However, electronic interaction of C_{60} with other π-systems is not well understood. Porphyrins constitute large π-systems and have been widely employed as both an electron acceptor and an electron donor. Therefore, a pair of C_{60} and porphyrin is a good combination for the better understanding of the electronic interaction. The intriguing issue of the interaction can be solved experimentally by placing the porphyrin moiety in the vicinity of C_{60}. Since this cannot be achieved intermolecularly,[6] it is necessary to make a linkage between C_{60} and porphyrin chromophores with small number of covalent bonds. Although there are a few reports about porphyrin-linked C_{60} with different linkage,[7-9] interaction between the two chromophores remains unclear. Now we report the synthesis of porphyrin-linked fullerene **1** where the C_{60} moiety is covalently linked to the meso position of 5,15-diarylporphyrin with only two intervening bonds.



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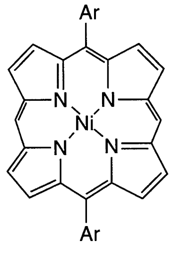

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Ar = 3,5-$(t\text{-Bu})_2C_6H_3$

Porphyrin-linked fullerene **1** was obtained by the 1,3-dipolar cycloaddition of azomethine ylide to C_{60}.[10] Thus, a mixture of N-methylglycine (50 molar equivalent), 10,20-bis(3,5-di-*t*-butylphenyl)-5-formylporphyrinatonickel(II)[11] (1 molar equivalent) and C_{60} (2 molar equivalent) was heated in toluene under reflux in the presence of molecular sieve 3A for 3 days. Purification of the reaction mixture by flash column chromatography with benzene afforded porphyrin-linked fullerene **1** quantitatively based on the starting porphyrin. On the other hand, no reaction took place for 5-formyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) under the same conditions described above, presumably due to the steric hindrance.

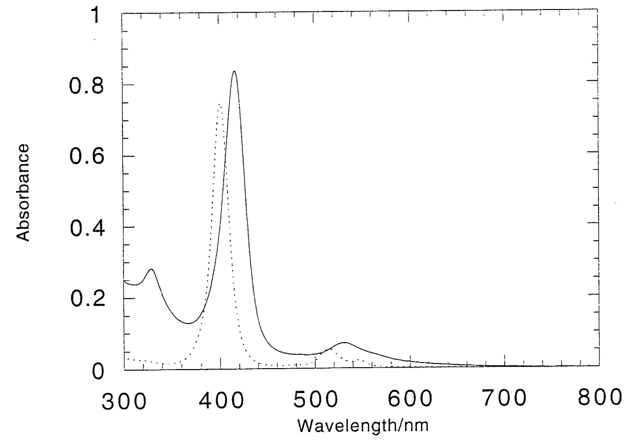

Figure 1. Electronic absorption spectra of **1** (——; 4.0 x 10^{-6} mol dm^{-3}) and **2** (····; 4.0 x 10^{-6} mol dm^{-3}) in tetrahydrofuran.

Structure of **1** was confirmed by spectroscopic analysis including ^{1}H-, ^{13}C-, 2D-COSY NMR, and FAB mass spectra.[12] The ^{1}H NMR spectrum of **1** show that all eight β protons are magnetically unequivalent and two of them are shifted to downfield. One of the signals at 9.86 ppm displays relevant NOE only with the singlet at 7.36 ppm and no coupling with the signals at 11.40 ppm. Thus, the doublets at 9.86 and 11.40 ppm can be assigned to the β protons vicinal to the meso carbon connected to the pyrolidine ring. The corresponding protons of **2** show a signal at 9.19 ppm. The large downfield shifts (0.67 and 2.21 ppm) for the two of eight β-protons in **1** is due to the deshielding effect that is originating from the C_{60} π-electrons.[13] The methyne proton of the pyrolidine ring in **1** is also downfield-shifted by about 2 ppm with respect to those of the usual pyrolidine ring, owing to the ring current effect of the porphyrin. These results clearly indicate that the C_{60} moiety in **1** is in close proximity to the porphyrin ring. In the electronic absorption spectrum of **1** in THF the bands due to the C_{60} moiety could not be well observed in the region of 400-800 nm because of the low intensity. However, the Soret band as well as Q-band of the porphyrin chromophore are shifted to longer wavelengths by 16-17 nm relative to those of **2** and the Q-band appears as a single band with a shoulder, indicating that there is a significant interaction between the two chromophores (Figure 1).[7-9,14] However, no appreciable CT bands were observed, despite the close disposition of the two chromophores. Redox potentials of **1** and **2** were measured by cyclic voltammetry (CV) and differential potential voltammetry (DPV) in dichloromethane (Figure 2). While the first oxidation (+0.98 V vs. Ag/AgCl) and the sixth reduction potential of **1** (-1.66 V) are irreversible, five successive reversible reductions were observed at -0.53, -0.64, -0.94, -1.04, -1.41 V. These are not simply explained by the sum of **2** (-1.34, +1.03 V vs. Ag/AgCl) and the 6,6-closed C_{60} derivative

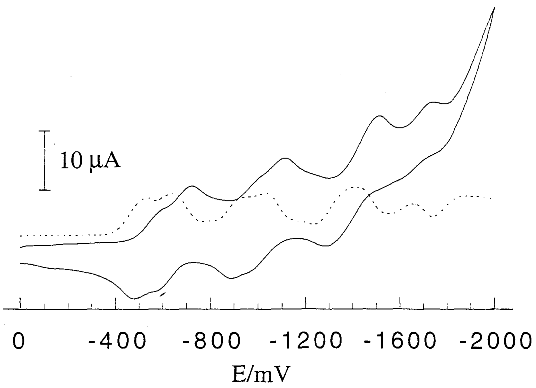

Figure 2. Cyclic voltammograms (——) and differential pulse voltammograms (····) of **1** (0.001 mol dm^{-3}) in 0.1 mol dm^{-3} tetrabutylammonium perchlorate in dichloromethane. Ag/AgCl was the reference electrode; the ferrocene/ferricinium couple was used as external redox standard. Sweep rate, 100 mV s^{-1} (CV) and 20 mV s^{-1} (DPV); pulse amplitude, 50 mV; pulse width, 50 ms; and pulse period, 200 ms.

(-1.58, -1.04, -0.59 V vs. Ag/AgCl)[7] and will be the subject of further investigations. However, through-space or through-bond orbital interactions between the chromophores may cause the change in **1**.[15]

The possibility that the observed large change in absorption spectra and redox potentials originates from the deformation of the porphyrin ring may be eliminated by the fact that chemical shifts of most protons of the porphyrin ring in **1** are almost the same as those in **2** and therefore, the porphyrin ring in **1** seems to be planar. The fairly large interaction observed in **1** comes from direct or indirect overlap between p-orbitals of C_{60} and porphyrin parts. For such overlap the high electron density in HOMO level of porphyrin ring may play an important role.

This work was supported by the Grant-in Aids (No. 07213220 and 07454166 to Y. S.) from the Ministry of Education, Science, Sports and Culture, Japan. H. I. thanks Kansai Research Foundation for Technology Promotion and Foundation Advanced Technology Institute for financial support.

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9 During the course of this research, a similar porphyrin-linked C_{60} compound has been reported. As C_{60} is linked via the β position instead of the meso position of the porphyrin ring, the interaction between the two chromophores is weaker than the present compound **1**. T. Drovetskaya, C. A. Reed, and P. Boyd, *Tetrahedron Lett.*, **36**, 7971 (1995).

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11 C.-H. Lee and J. S. Lindsey, *Tetrahedron*, **50**, 11427 (1994); A. W. Johnson and D. Oldfield, *J. Chem. Soc. (C)*, **1966**, 794. Syntheses of **1** and **2** will be reported elsewhere in detail.

12 It is reported that 1,3-dipolar cycloaddition of azomethine ylide to C_{60} gives the 6,6-closed structure.[10] Because of poor solubility and intensive broadening of the spectrum, all the signals in ^{13}C-NMR spectrum of **1** could not be assigned. **1**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.56 (s, 36H), 3.01 (s, 3H), 4.68 (d, 1H, J=10 Hz), 5.39 (d, 1H, J=10 Hz), 7.36 (s, 1H), 7.73 (t, 2H, J=2 Hz), 7.86 (d, 4H, J=2 Hz), 8.83 (d, 1H, J=5 Hz), 8.85 (d, 1H, J=5 Hz), 8.86 (d, 1H, J=5 Hz), 8.91 (d, 1H, J=5 Hz), 9.05 (d, 1H, J=5 Hz), 9.06 (d, 1H, J=5 Hz), 9.70 (s, 1H), 9.86 (d, 1H, J=5 Hz), 11.40 (d, 1H, J=5 Hz). MS (FAB) 1519 (M+H$^+$). UV-vis (THF) λmax 329, 417, 531, 564 (sh) nm; **2**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.52 (s, 36H), 7.78 (t, 2H, J=2 Hz), 7.94 (d, 4H, J=2 Hz), 9.00 (d, 4H, J=5 Hz), 9.19 (d, 4H, J=5 Hz), 9.94 (s, 2H). MS (FAB) 743 (M+H$^+$). UV-vis (THF) λmax 401, 515, 547 nm.

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14 The band at around 330 nm in **1** is due to the C_{60} moiety in **1**.[10] Having different substitution pattern at the meso position, **2** is not well suited as a reference for **1**. However, no suitable compound has not been reported so far.

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