Synthesis and Photophysical Property of Porphyrin-Linked Fullerene

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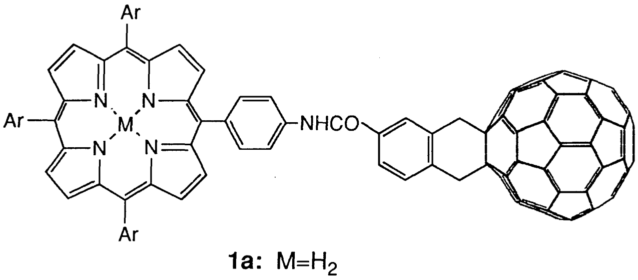
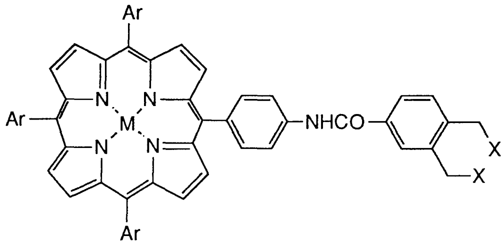
Porphyrin-linked fullerenes were prepared by the Diels-Alder reaction of bisbromomethylbenzene derivative to C_{60}. The absorption spectra and electrochemical measurements indicate that there is little interaction between the porphyrin and the C_{60} moieties. Intramolecular electron transfer from the excited singlet state of zincporphyrin to C_{60} was observed by picosecond transient absorption measurements.

Since the first report on mass production of C_{60} by Krätschmer et al.,[1] the chemistry and derivatization of fullerenes[2] have been extensively studied for the understanding of their unique physical and chemical properties. Among various characteristics of C_{60} the facile electron-accepting ability is one of the most remarkable point. Considering that C_{60} has the first reduction potential similar to that of benzoquinone[3] which is a most frequently employed electron acceptor in photosynthetic models, C_{60} is expected to be an electron acceptor in artificial photosynthetic models.[4] Compared with benzoquinone, C_{60} has the following characteristics. (1) Both neutral (C_{60}) and anionic (C_{60}^{-},C_{60}^{2-},C_{60}^{3-}) species are stable.[3,5] (2) Absorption band of C_{60}^{-} at around 1000 nm[5] may enable the accurate analysis of electron transfer (ET) dynamics. (3) The diameter of C_{60} (7.0 Å) is comparable to that of pheophytin, which is the first electron acceptor in biological systems.[4] (4) The lowest singlet excited state of C_{60} locates below that of porphyrin.[6] Although there are a number of reports on the participation of C_{60} in intermolecular ET processes,[6] there exist only a quite limited number of donor-linked C_{60}[7,8] and no example of C_{60}-linkage to porphyrin,[9] which is the most important chromophore both in natural photosynthetic systems and in artificial models. Here we report on our first synthesis and photophysical property of porphyrin-linked fullerenes **1a**,**b**. In the molecular design of **1** we introduced *tert*-butyl groups into *meso*-phenyl rings of porphyrin to increase solubility in usual organic solvents, since C_{60} and porphyrin are notorious for low solubility in these solvents.

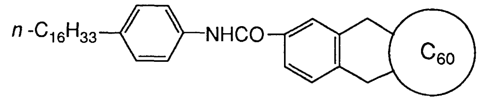
Dibromide **2** was obtained by the coupling reaction of the corresponding aminoporphyrin with 3,4-bis(bromomethyl)-benzoic acid in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine and N-methylmorpholine in THF in 24% yield. The Diels-Alder reaction of **2** and C_{60} using potassium iodide and 18-crown-6 in toluene gave **1a** in 50 % yield.[10] Reference compounds **3a** and **4** were obtained by the coupling reaction of the aminoporphyrin and 3,4-dimethylbenzoic acid and by the Diels-Alder reaction of the corresponding 1,2-bis(bromomethyl)-benzene derivative and C_{60}, respectively. Zinc complexes **1b** and **3b** were prepared by treatment of **1a** and **3a** with zinc acetate in $CHCl_3$. As expected, **1a**,**b** are easily soluble in a variety of solvents, such as benzene, chloroform, and THF. Various spectral data (^{1}H-, ^{13}C-, 2D-COSY NMR, IR, and FAB and TOF mass spectra) supported the expected strucure for **1a**,**b**.[11] In ^{1}H NMR spectra the signals of the methylene protons of the cyclohexene ring appeared as singlet, indicating that the rate of the ring inversion in the cyclohexene ring is faster than the NMR time scale at room temperature. It has already been established on the basis of chemical shifts, X-ray analysis, and MO calculations that the Diels-Alder cycloaddition of *ortho*-quinodimethane with C_{60} occurs at the 6,6-ring junction of the C_{60} framework with closed transannular bond.[12,13] In ^{13}C NMR spectra of **1**, there exist signals (**1a**: 63.79 ppm; **1b**: 63.87 ppm), which are quite close to the reported value (66-69 ppm) for the quaternary carbon at the 6,6-ring junction of the Diels-Alder adduct. This fact clearly shows that **1** has also the 6,6-closed structure. Redox potentials of **1** (**1a**: -1.24, -1.01, -0.64, +0.97 V ; **1b**: -1.40, -1.01, -0.65, +0.77 V vs. Ag/AgCl) in CH_2Cl_2 using 0.1 M Bu_4NClO_4 as a supporting electrolyte are roughly explained by the sum of **3** (**3a**: -1.19, +0.94 V ; **3b**: -1.37, +0.74 V vs. Ag/AgCl) and **4** (-1.04, -0.59 V vs. Ag/AgCl). However, C_{60} part of **1** is much perturbed and the reduction potentials are shifted to more negative direction by ca. 0.1 V compared with C_{60} (-0.90, -0.49 V vs. Ag/AgCl).[14] Absorption spectra of **1** in THF are nearly identical to that of **3** except weak absorption bands at around 300-400 and 700 nm assigned to C_{60} chromophore.[12] No additional bands



1a: M=H_2
1b: M=Zn
Ar=3,5-(t-Bu)$_2C_6H_3$



2: X=Br, M=H_2
3a: X=H, M=H_2
3b: X=H, M=Zn



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due to charge transfer or perturbation of the porphyrin chromophore were observed, indicating that there is no appreciable interaction in the ground state between the porphyrin and C_{60} moieties. Fluorescence spectra of **1** are quenched as compared with those of **3** (0.13 for **1a** and 0.03 for **1b** in THF), showing the rapid quenching of the excited singlet state of the porphyrin moiety by C_{60}.

Intramolecular ET from the excited singlet state of zincporphyrin moiety to the C_{60} moiety was observed for **1b** by picosecond transient absorption measurements in THF.[15] Immediately after excitation of **1b** with 590-nm picosecond pulse, the bleaching of the ground-state porphyrin absorption of the Q-band at 560 nm and an intense absorption with a maximum at near 470 nm assigned to $S_n \leftarrow S_1$ band of the porphyrin were mainly observed. Along with the rapid decay of the 470-nm band, new broad bands with maxima at 660 nm and 920 nm appeared. Although both absorption of C_{60}^{-} [5,6] and $S_n \leftarrow S_1$ of C_{60}[6] appear around 900-1000 nm, concomitant rise (60 ps) and decay (500 ps) of 660-nm and 920-nm bands clearly show that 660-nm band is ascribed to the zinc porphyrin cation $P(Zn)^+$ and 920-nm band is to C_{60}^{-}. In accordance with this interpretation, 470-nm band has biphasic decay with 60 ps and 500 ps, which are corresponding to the decay of $^1P(Zn)$ and that of $P(Zn)^+$, respectively. The present results show that C_{60} is a promising candidate as a building block in artificial photosynthesis. The detailed dynamical behavior, in particular, the orientation and solvent dependence of these molecules will be reported elsewhere.

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9 Porphyrin-linked fullerene, which has different linkage compared with ours, has been prepared at the same time. P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, and D. Gust, *Photochem. Photobiol.*, in press.

10 Synthesis of **1-4** will be reported elsewhere in detail.

11 **1a**: ^{1}H NMR (270 Mz, $CDCl_3$) δ −2.89 (br s, 2H), 1.55 (s, 18H), 1.56 (s, 36H), 3.83 (br s, 4H), 7.77 (t, J=1.9 Hz, 2H), 7.78 (d, J=7.3Hz, 1H), 7.80 (t, J=1.9 Hz, 1H), 7.98 (d, J=1.9 Hz, 4H), 8.03 (d, J=8.3 Hz, 2H), 8.04 (d, J=1.9 Hz, 2H), 8.23 (d, J=8.3 Hz, 2H), 8.34 (s, 1H), 8.45 (d, J=7.3 Hz, 1H), 8.79 (d, J=4.8 Hz, 2H), 8.83 (d, J=4.8 Hz, 2H), 8.86 (s, 4H), 9.03 (br s, 1H). MS (FAB) 1818 ((M+1)$^+$). **1b**: ^{1}H NMR (270 Mz, $CDCl_3$) δ 1.45 (s, 36H), 1.53 (s, 18H), 5.12 (br s, 4H), 7.69 (d, J=7.3Hz, 1H), 7.72 (t, J=1.9 Hz, 2H), 7.75 (t, J=1.9 Hz, 1H), 7.80 (d, J=8.3 Hz, 2H), 7.83 (d, J=1.9 Hz, 4H), 7.92 (d, J=1.9 Hz, 2H), 8.25 (d, J=8.3 Hz, 2H), 8.33 (s, 1H), 8.44 (d, J=7.3 Hz, 1H), 8.76 (d, J=4.8 Hz, 2H), 8.81 (d, J=4.8 Hz, 2H), 8.90 (s, 4H), 9.26 (br s, 1H). MS (FAB) 1880 (M$^+$).

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