

Synthesis and Photophysical Behavior of Porphyrins with Two C₆₀ Units

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Two C₆₀ units were covalently linked to 5,10- (*cis*-) or 5,15- (*trans*-) positions at a *meso*-tetraphenylporphyrin via pyridine spacers. ¹H NMR, UV-visible absorption, and fluorescence spectroscopy showed that there is a considerable interaction among the chromophores in *cis*-isomers due to the close proximity of the two C₆₀ moieties.

Fullerene chemistry has been developed rapidly because of the potential application in material science.¹ Fullerenes have been shown to be a good electron acceptor as well as a sensitizer in photochemical and photophysical processes.² We have reported the acceleration effect of C₆₀ in photoinduced charge separation and the deceleration effect in charge recombination due to the small reorganization energy of C₆₀.³ Thus, fullerenes seem to be promising building blocks in artificial photosynthesis. Although there are a number of reports about donor-linked C₆₀ compounds,⁴⁻⁶ no report concerning poly-C₆₀-linked donor has appeared so far. Here we report the synthesis and physical properties of porphyrin-(C₆₀)₂ **1** and **2**.

Compounds **1** and **2** were obtained by 1,3-dipolar cycloaddition from the corresponding formyl porphyrins,⁷ *N*-methylglycine, and C₆₀ in toluene.⁸ Similarly, **3** was also prepared as a reference compound. The purification of **1-3** was carried out by preparative thin layer chromatography, and their structures were confirmed by ¹H NMR and MALDI-TOF-MS.⁹ Mono-C₆₀ derivative **3** showed the parent peak (*M*+*H*⁺=1726), while only the fragment peaks due to the elimination of the C₆₀ moieties and the C₆₀ itself were detected for bis-C₆₀ derivatives **1** and **2**.

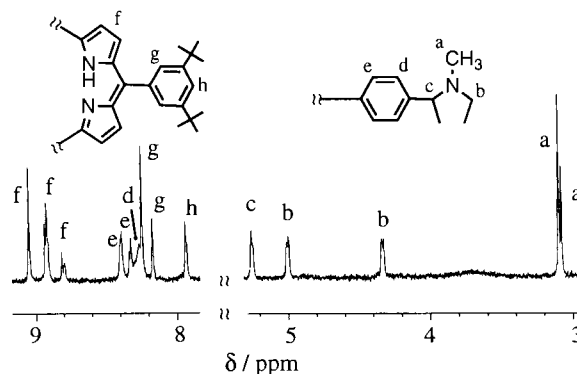
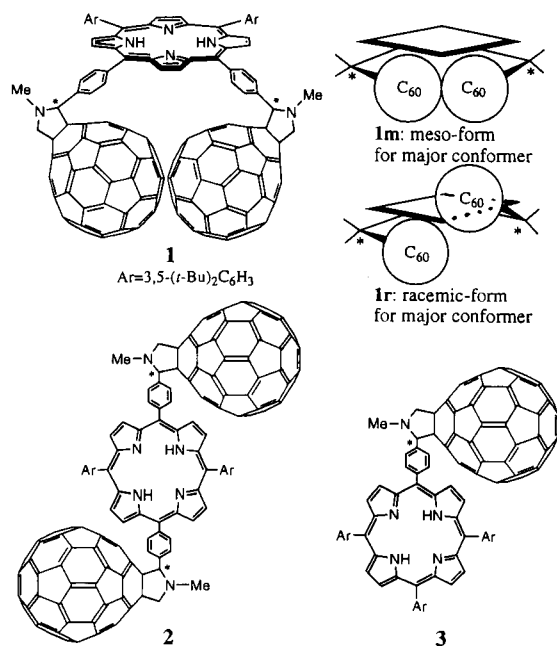


Figure 1. 600 MHz ¹H NMR of **1r** (110 °C) in *o*-dichlorobenzene-*d*₄.

The thin layer chromatograms of *cis*-**1** displayed four bands (CS₂:CHCl₃=9:1) in spite of two possible configurational isomers. The isolated products from the first (highest) and the second bands were determined to be *meso* (**1m**) and *racemic* (**1r**) isomers, respectively, by HPLC experiments using a chiral column (Regis Whelk-01 SS). Interestingly, the isolated *meso* and *racemic* isomers in solution at room temperature became equilibrated mixtures with the products being appeared to the third and the fourth (lowest) bands, respectively. These findings should be explainable only by rotational isomerism caused by π - π attractive interactions¹⁰ between the two C₆₀ skeletons. The ¹H NMR spectrum of an equilibrated mixture of **1r** at 110 °C (Figure 1) demonstrated that the couples of signals due to the protons a, e, f, and g appeared in a ratio of 3:1. The major component (fourth band) can be assigned, on the basis of the downfield shifts by the anisotropic effects of the C₆₀, to a conformer where the two C₆₀ units are in the close proximity; the minor one to an isomer where the C₆₀ moieties are apart. Preliminary molecular mechanics calculation for **1** using CAChe shows that the two C₆₀ moieties are in van der Waals contact in the most stable conformation.¹⁰ Quite similar phenomena were observed with **1m**. In *trans*-isomer **2**, no rotational isomerism could be detected and the structures corresponding to the upper and the lower bands on a TLC plate were assigned to *racemic* (**2r**) and *meso* (**2m**) isomers, respectively, by similar methods described above.

In the electronic absorption spectra of **1-3** in CS₂ the Soret bands as well as the Q bands are similar in the peak positions, while relative intensities of the Q bands in **1** are quite different from those in **2** and **3**, indicating that there is a significant interaction in the ground state among the chromophores in **1**. Fluorescence spectra of **1-3** were measured in CS₂ excited at the Soret band under the same concentration. Fluorescence spectrum of **3** is strongly quenched compared with that of tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (relative intensity=0.02), showing the rapid quenching of the excited singlet state of the porphyrin by the C₆₀. Fluorescence intensities of **1r**, **1m**, **2r**, and **2m** are

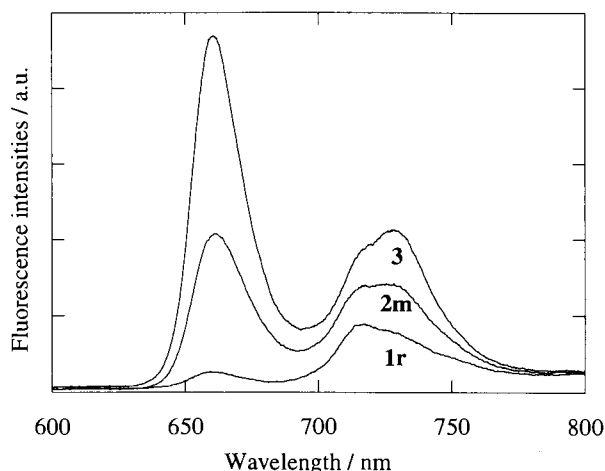


Figure 2. Fluorescence spectra of **1r**, **2m**, and **3** excited at 420 nm in CS₂.

much lower than that of **3**. Typical examples are shown in Figure 2. It should be noted here that fluorescence spectra of **1** are different in the shape and the peak positions compared with those of **2** and **3**, suggesting the substantial interaction among the chromophores in the excited state of **1**. Improvement of the solubilities in these compounds will make it easier to analyze the photodynamics including electron transfer processes as well as the physical properties. We are working on this line.

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- 1r** (major): ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.53 (s, 2H), 1.54 (s, 36H), 3.10 (s, 6H), 4.31 (d, 2H, J=7.9 Hz), 4.99 (d, 2H, J=7.9 Hz), 5.24 (s, 2H), 7.94 (br.m, 2H), 8.24 (s, 4H), 8.26 (br.m, 4H), 8.40 (d, 4H, J=7.0 Hz), 8.82 (br.m, 2H), 8.92 (br.m, 4H), 9.04 (br.m, 2H). **1r** (minor): ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.53 (s, 2H), 1.54 (s, 36H), 3.08 (s, 6H), 4.31 (d, 2H, J=7.9 Hz), 4.99 (d, 2H, J=7.9 Hz), 5.23 (s, 2H), 7.94 (s, 2H), 8.17 (s, 4H), 8.26 (br.m, 4H), 8.32 (d, 4H, J=7.0 Hz), 8.82 (br.m, 2H), 8.92 (br.m, 4H), 9.04 (br.m, 2H). MALDI-TOF-MS 950 (M+H⁺-(C₆₀)₂), 720 (C₆₀). **1m** (major): ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.53 (s, 2H), 1.54 (s, 36H), 3.10 (s, 6H), 4.34 (d, 2H, J=9.1 Hz), 5.00 (d, 2H, J=9.1 Hz), 5.27 (s, 2H), 7.93 (s, 2H), 8.17 (s, 4H), 8.33 (br.d, 4H), 8.40 (br.d, 4H), 8.82 (br.m, 2H), 8.92 (br.m, 4H), 9.04 (br.m, 2H). **1m** (minor): ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.54 (s, 2H), 1.54 (s, 36H), 3.08 (s, 6H), 4.34 (d, 2H, J=9.1 Hz), 5.00 (d, 2H, J=9.1 Hz), 5.27 (s, 2H), 7.93 (s, 2H), 8.17 (s, 4H), 8.33 (br.d, 4H), 8.40 (br.d, 4H), 8.82 (br.m, 2H), 8.94 (br.m, 4H), 9.06 (br.m, 2H). MALDI-TOF-MS 950 (M+H⁺-(C₆₀)₂), 720 (C₆₀). **2r**: ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.52 (s, 2H), 1.51 (s, 36H), 3.10 (s, 6H), 4.33 (d, 2H, J=8.1 Hz), 4.99 (d, 2H, J=8.1 Hz), 5.26 (s, 2H), 7.91 (s, 2H), 8.17 (s, 4H), 8.27 (d, 4H, J=8.4 Hz), 8.34 (d, 4H, J=8.4 Hz), 8.81 (br.d, 4H), 8.95 (d, 4H, J=4.8 Hz). MALDI-TOF-MS 950 (M+H⁺-(C₆₀)₂), 720 (C₆₀). **2m**: ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.52 (s, 2H), 1.51 (s, 36H), 3.10 (s, 6H), 4.33 (d, 2H, J=8.4 Hz), 4.99 (d, 2H, J=8.4 Hz), 5.25 (s, 2H), 7.92 (s, 2H), 8.17 (s, 4H), 8.28 (br.d, 4H), 8.34 (d, 4H, J=7.7 Hz), 8.81 (br.d, 4H), 8.95 (d, 4H, J=4.8 Hz). MALDI-TOF-MS 950 (M+H⁺-(C₆₀)₂), 720 (C₆₀). **3**: ¹H-NMR (600 MHz, *o*-dichlorobenzene-*d*₄, 90°C) δ -2.42 (s, 2H), 1.51 (s, 54H), 3.10 (s, 3H), 4.32 (d, 1H, J=8.5 Hz), 4.99 (d, 1H, J=8.5 Hz), 5.25 (s, 1H), 7.93 (s, 3H), 8.18 (s, 6H), 8.27 (d, 2H, J=7.6 Hz), 8.35 (d, 2H, J=7.6 Hz), 8.82 (d, 2H, J=4.8 Hz), 8.92 (s, 4H), 8.96 (d, 2H, J=4.8 Hz). MALDI-TOF-MS 1726 (M+H⁺), 1006 (M+H⁺-C₆₀). It was difficult to assign the β protons on the porphyrin and the meta protons on the meso-phenyl rings in **1** because of broadening and overlapping of the signals.
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