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A Convenient Synthesis of Polyyne-bridged Porphyrin Dimers

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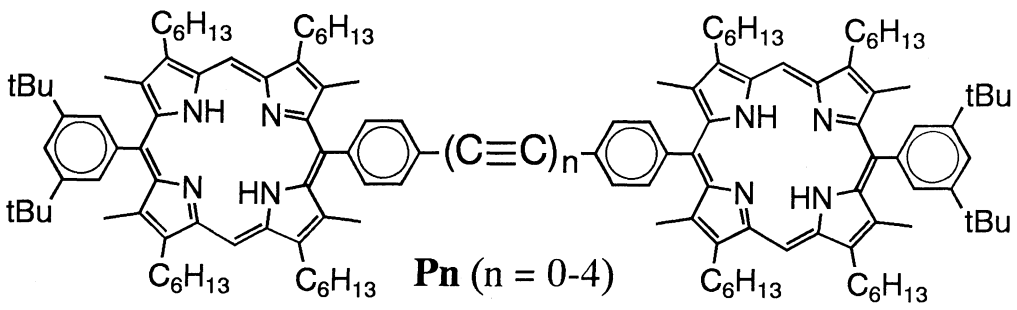
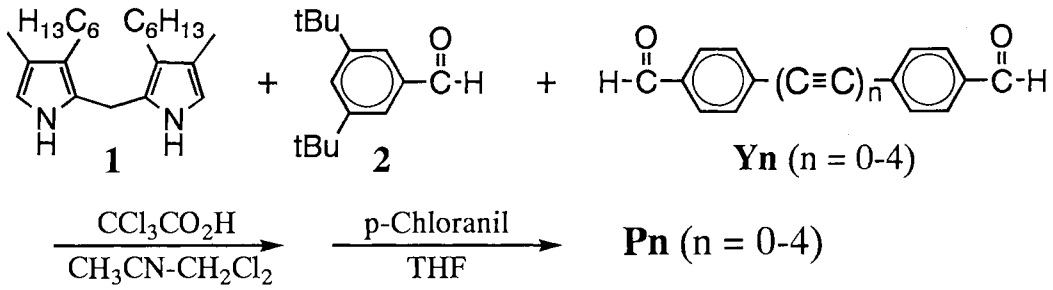
A convenient synthetic procedure of a series of polyyne-bridged porphyrin dimers from diphenylpolyyne dialdehydes is reported. Trichloroacetic acid catalyzed double condensation of diphenylpolyyne dialdehydes with bis(3-hexyl-4-methyl-2-pyrrolyl)-methane and 3,5-di-*tert*-butylbenzaldehyde in acetonitrile-dichloromethane followed by p-chloranil oxidation gave a set of diporphyrin model compounds (**Pn**, n=0-4) bridged by conjugated triple bonds.

Electron transfer is an essentially important process and plays a crucial role in a variety of chemical and biological processes. In order to understand the fundamental mechanism of photoinduced electron-transfer reactions, a lot of conformationally restricted model compounds have been synthesized.[1] Many investigations have been focused on the issue of distance and energy-gap dependence of electron transfer rate with donor-acceptor models bridged by saturated hydrocarbons[2-4] or aromatic rings.[5,6] Recently, porphyrin model compounds bridged by highly polarizable, linear, π-conjugated spacers have been investigated intensively.[7] However, systematic studies on donor-acceptor models bridged by these spacers with variable length are



relatively limited because of synthetic difficulties. Such spacers may participate in enhancing electron exchange interactions of donor and acceptor,[8] thus increasing the electron-transfer rate. The distance-dependence of electron-transfer rate through these π-conjugated spacers is therefore expected to be much weaker.[9] This sort of phenomena has attracted considerable interest in relation to its application to molecular wires.[10] It will be important to investigate the nature of linear π-conjugated systems that affect electron transfer rate.

We have synthesized a series of polyyne-bridged diporphyrins to investigate the medium effect of such conjugated spacer.[11] In these models the center-to-center distances are strictly defined by the number of the intervening triple bonds. But the synthetic yields were rather low, precluding further characterization of their metal substituted derivatives. In recent years, however, synthetic methods of multiple porphyrin cyclization have been advanced and convenient one-pot procedure of double porphyrin cyclization has been developed in our laboratory.[12] In this paper, a successful extension of this procedure to the synthesis of a series of polyyne-bridged porphyrin dimers from diphenylpolyyne dialdehydes is reported.



Synthetic procedure is as follows: Dialdehyde (**Yn**, 0.1 mmol),[13] dipyrromethane (**1**, 1.0 mmol), and 3,5-di-*tert*-butylbenzaldehyde (**2**, 0.8 mmol) were dissolved in a mixture of CH_3CN (5.5 ml) and CH_2Cl_2 (2.5 ml). When the solubility of dialdehyde is not enough, the content of CH_2Cl_2 could be increased up to that of CH_3CN. Trichloroacetic acid (0.3 mmol) dissolved in CH_3CN (2 ml) was added to this solution and the mixture was stirred for 1 day under N_2 in the dark at room temperature. Then, p-chloranil (1.6 mmol) dissolved in THF (20 ml) was added and the resulting solution was stirred for further 1 day. After evaporation of the solvent, the residue was dissolved in a small amount of $CHCl_3$ and passed through a short activated alumina column (Wako, 200 mesh). The product was purified by column chromatography on silica gel (Merck, Kieselgel 7736, eluent as CH_2Cl_2-hexane). Recrystallization from $CHCl_3$-CH_3OH gave polyyne-bridged porphyrin dimer (**Pn**) as violet crystals. Synthetic yields were 24% (**P0**), 26% (**P1**), 28% (**P2**), 30% (**P3**), and 46% (**P4**) based on the amount of **Yn** used.

It is worthwhile to note that this synthetic method does not affect acid-labile polyyne-functionality. The

diporphyrin products give satisfactory spectral data[14] consistent with the assigned structures, and exhibit the absorption and fluorescence spectra those are quite similar to those reported for the related compounds.[11] In addition, these products are found to be stable enough in the metalation of Zn(II) or Fe(III) ions, thereby allowing an access to these hybrid metal complexes. Characterization of optical properties of these compounds and metal-substituted derivatives for donor-acceptor model compounds are now undergoing.

This synthetic procedure will be applicable to an efficient one-pot synthesis of porphyrin dimers bridged with various kinds of conjugated molecular systems.

References

1) M. R. Wasielewski, *Chem. Rev.*, **92**, 435 (1992) and references therein.

2) G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, and J. R. Miller, *J. Phys. Chem.*, **90**, 3673 (1986); G. L. Closs, P. Piotrowiak, J. M. MacInnis, and G. R. Fleming, *J. Am. Chem. Soc.*, **110**, 2652 (1988); G. L. Closs, M. D. Johnson, J. R. Miller, and P. Piotrowiak, *ibid.*, **111**, 3751 (1989).

3) B. A. Leland, A. D. Joran, P. M. Felker, J. J. Hopfield, A. H. Zewail, and P. B. Dervan, *J. Phys. Chem.*, **89**, 5571 (1985).

4) H. Oevering, J. W. Verhoeven, M. N. Paddon-Row, and J. M. Warman, *Tetrahedron*, **45**, 4751 (1989).

5) D. Heiler, G. McLendon, and P. Rogalskyj, *J. Am. Chem. Soc.*, **109**, 604 (1987); A. Helms, D. Heiler, and G. McLendon, *ibid.*, **113**, 4325 (1991).

6) H.Heitele and M. E. Michel-Beyerle, *J. Am. Chem. Soc.*, **107**,8286 (1985); H. Heitele, M. E. Michel-Beyerle, and P. Finckh, *Chem. Phys. Lett.*, **134**, 273 (1987).

7) D. P. Arnold and G. A. Heath, *J. Am. Chem. Soc.*, **115**, 12197 (1993); V. S.-Y. Lin, S. G. DiMagno, and M. J. Therien, *Science*, **264**, 1105 (1994); H. Imahori, Y. Tanaka, T. Okada, and Y. Sakata, *Chem. Lett.*, **1993**, 1215.

8) S. Larsson, *J. Chem. Soc., Faraday Trans. 2*, **79**, 1375 (1983).

9) M. R. Wasielewski, D. G. Johnson, W. A. Svec, K. M. Kersey, D. E. Cragg, and D. W. Minsek, "Photochemical Energy Conversion," ed by J. R. Norris and D. Meisel, Elsevier, New York (1989), p. 135.

10) T. S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.-M. Lehn, and J. Malthete, *Proc. Natl. Acad. Sci. U.S.A.*, **83**, 5355 (1986).

11) K. Maruyama and S. Kawabata, *Bull. Chem. Soc. Jpn.*, **63**, 170 (1990).

12) A. Osuka, B. Liu, and K. Maruyama, *Chem. Lett.*, **1993**, 949; A. Osuka, N. Tanabe, R. Zhang, and K. Maruyama, *ibid.*, **1993**, 1505; A. Osuka, B. Liu, and K. Maruyama, *J. Org. Chem.*, **58**, 3582 (1993).

13) K. Maruyama and S. Kawabata, *Bull. Chem. Soc. Jpn.*, **62**, 3498 (1989).

14) **P0** : MS 1933 ($[M+1]^+$)[15]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (4H, s, meso), 8.35 (4H, d, J = 8.0 Hz, Ar), 8.32 (4H, d, J = 8.0 Hz, Ar), 7.95 (4H, d, J = 2.0 Hz, Ar), 7.82 (2H, t, J = 2.0 Hz, Ar), 4.02-4.10 (16H, m, hex-1), 2.75 (12H, s, Me), 2.49 (12H, s, Me), 2.20-2.29 (16H, m, hex-2), 1.74-1.82 (16H, m, hex-3), 1.53 (36H, s, t-Bu), 1.47-1.55 (16H, m, hex-4), 1.35-1.46 (16H, m, hex-5), 0.93 (12H, t, J = 7.3 Hz, hex-6), 0.92 (12H, t, J = 7.3 Hz, hex-6), -2.32 (4H, br, NH); UV {λ_{max} in CH_2Cl_2 (relative intensity, %)} 412 (100), 505 (8.4), 538 (1.8), 575 (2.8), 629 nm (0.4); Fluorescence {λ_{max} in CH_2Cl_2 (relative intensity)} 630 (1.0), 698 nm (1.8).

P1 : MS 1957 ($[M+1]^+$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (4H, s, meso), 8.20 (4H, d, J = 7.8 Hz, Ar), 8.11 (4H, d, J = 7.8 Hz, Ar), 7.93 (4H, d, J = 1.5 Hz, Ar), 7.82 (2H, t, J = 1.5 Hz, Ar), 3.98-4.08 (16H, m, hex-1), 2.64 (12H, s, Me), 2.48 (12H, s, Me), 2.17-2.27 (16H, m, hex-2), 1.74-1.82 (16H, m, hex-3), 1.52 (36H, s, t-Bu), 1.46-1.58 (16H, m, hex-4), 1.33-1.43 (16H, m, hex-5), 0.93 (12H, t, J = 7.3 Hz, hex-6), 0.92 (12H, t, J = 7.3 Hz, hex-6), -2.36 (4H, br, NH); UV {λ_{max} in CH_2Cl_2 (relative intensity, %)} 413 (100), 507 (8.4), 538 (2.0), 575 (2.8), 629 nm (0.6); Fluorescence {λ_{max} in CH_2Cl_2 (relative intensity)} 629 (1.0), 697 nm (1.6).

P2 : MS 1981 ($[M+1]^+$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (4H, s, meso), 8.15 (4H, d, J = 7.8 Hz, Ar), 8.02 (4H, d, J = 7.8 Hz, Ar), 7.93 (4H, d, J = 1.6 Hz, Ar), 7.81 (2H, t, J = 1.6 Hz, Ar), 3.98-4.04 (16H, m, hex-1), 2.58 (12H, s, Me), 2.47 (12H, s, Me), 2.17-2.25 (16H, m, hex-2), 1.72-1.79 (16H, m, hex-3), 1.51 (36H, s, t-Bu), 1.45-1.53 (16H, m, hex-4), 1.33-1.43 (16H, m, hex-5), 0.92 (12H, t, J = 7.1 Hz, hex-6), 0.91 (12H, t, J = 7.2 Hz, hex-6), -2.39 (4H, br, NH); UV {λ_{max} in CH_2Cl_2 (relative intensity, %)} 413 (100), 507 (8.4), 538 (2.0), 575 (3.0), 629 nm (0.6); Fluorescence {λ_{max} in CH_2Cl_2 (relative intensity)} 630 (1.0), 697 nm (1.5).

P3 : MS 2005 ($[M+1]^+$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (4H, s, meso), 8.10 (4H, d, J = 8.0 Hz, Ar), 7.97 (4H, d, J = 8.0 Hz, Ar), 7.93 (4H, d, J = 1.8 Hz, Ar), 7.81 (2H, t, J = 1.8 Hz, Ar), 3.96-4.02 (16H, m, hex-1), 2.52 (12H, s, Me), 2.47 (12H, s, Me), 2.16-2.24 (16H, m, hex-2), 1.71-1.78 (16H, m, hex-3), 1.51 (36H, s, t-Bu), 1.45-1.52 (16H, m, hex-4), 1.34-1.40 (16H, m, hex-5), 0.92 (12H, t, J = 7.3 Hz, hex-6), 0.91 (12H, t, J = 7.3 Hz, hex-6), -2.39 (4H, br, NH); UV {λ_{max} in CH_2Cl_2 (relative intensity, %)} 414 (100), 506 (8.8), 539 (2.0), 575 (3.0), 630 nm (0.6); Fluorescence {λ_{max} in CH_2Cl_2 (relative intensity)} 629 (1.0), 695 nm (1.6).

P4 : MS 2029 ($[M+1]^+$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (4H, s, meso), 8.11 (4H, d, J = 7.8 Hz, Ar), 7.96 (4H, d, J = 7.8 Hz, Ar), 7.92 (4H, d, J = 1.5 Hz, Ar), 7.81 (2H, t, J = 1.5 Hz, Ar), 3.95-4.03 (16H, m, hex-1), 2.51 (12H, s, Me), 2.46 (12H, s, Me), 2.05-2.25 (16H, m, hex-2), 1.70-1.78 (16H, m, hex-3), 1.51 (36H, s, t-Bu), 1.43-1.53 (16H, m, hex-4), 1.35-1.42 (16H, m, hex-5), 0.91 (24H, t, J = 7.3 Hz, hex-6), -2.39 (2H, br, NH), -2.42 (2H, br, NH); UV {λ_{max} in CH_2Cl_2 (relative intensity, %)} 414 (100), 507 (9.0), 540 (2.4), 575 (3.6), 630 nm (0.6); Fluorescence {λ_{max} in CH_2Cl_2 (relative intensity)} 630 (1.0), 697 nm (1.5).

15) The mass spectra were measured by a JEOL HX-110 spectrometer; the positive-FAB ionization method, accelerating voltage 10 kV, 3-nitrobenzylalcohol-$CHCl_3$ matrix.

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