A Cyclic Dimer of Metalloporphyrin Forms a Highly Stable Inclusion Complex with C_{60}

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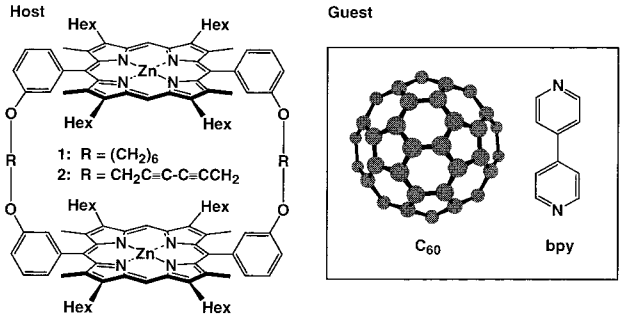
Host molecules for inclusion of fullerenes are of great importance because of their application to extraction and chemical modification of fullerenes.[1] In particular, inclusion via π-electronic donor−acceptor interactions is highly interesting in view of possible supramolecular modulation of electronic properties of fullerenes. Herein we report that a face-to-face cyclic dimer of zinc porphyrin (**1**) forms a highly stable 1:1 inclusion complex with C_{60} via donor−acceptor interactions.



Zinc porphyrin cyclic dimer **1** was synthesized by hydrogenation of **2** having rigid diacetylenic spacers (Scheme 1). A benzene solution of **1** upon mixing with C_{60} showed a marked color change from bright reddish purple to dark red. In the electronic absorption spectrum of a mixture of **1** and C_{60}, the Soret absorption band of **1** was observed to shift bathochromically from 410.5 to 417.5 nm, suggesting an electronic interaction of **1** with C_{60} (Figure 1).[2] Interestingly, when an equimolar mixture of **1** and C_{60} was subjected to TLC on alumina with benzene as eluent, only a single spot was observed at $R_f = 0.13$ without any other spots at 0.72 and 0.85 due to **1** and C_{60}, respectively. On the other hand, when either **1** or C_{60} was present in excess with respect to the counterpart, the TLC trace showed an additional spot due to free **1** or C_{60}. These observations indicate that **1** and C_{60} form a highly stable complex. Accordingly, the complex between **1** and C_{60} could be easily isolated by column chromatography on alumina.

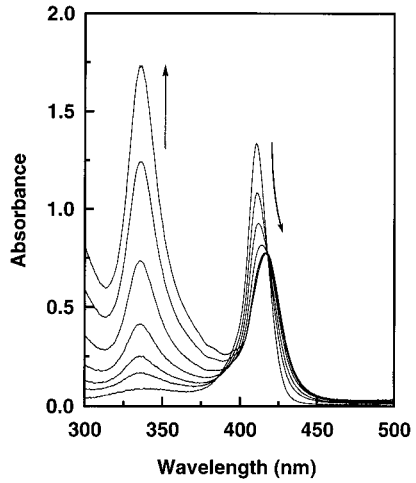


Figure 1. Spectroscopic titration of receptor **1** with C_{60} in benzene at 25 °C: $[\mathbf{1}] = 1.96 \times 10^{-6}$ M; $[C_{60}]/[\mathbf{1}] = 0$, 0.74, 1.48, 2.96, 5.91, 10.35, 14.77.

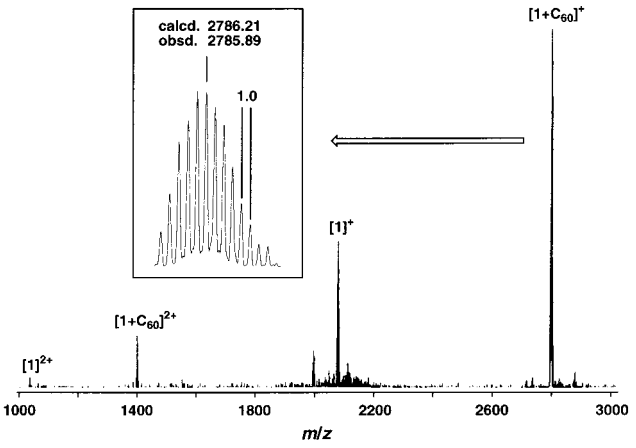


Figure 2. ESI-MS spectrum of a THF solution of a mixture of **1** and C_{60}.[3]

When benzene solutions of **1** and C_{60} (1.9×10^{-6} M) were mixed at varying volume ratios (Job's plots) at 25 °C, the change in absorbance at 410.5 nm displayed a maximum at a mole ratio **1**:C_{60} of unity. Furthermore, electrospray ionization mass spectrometry (ESI-MS) of a THF solution of a mixture of **1** and C_{60} clearly showed two sets of isotopic distributions centered at *m*/*z* 2785.89 and 1393.12 (Figure 2),[3] which correspond to the mono and dication, respectively, of a 1:1 complex between **1** and C_{60}. To determine the binding constant of the complexation of **1** with C_{60}, we titrated a benzene solution of **1** with C_{60} at 25 °C, where the absorption spectral change showed a clear isosbestic point at 418.0 nm (Figure 1). From the change in absorbance at 410.5

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[||] Responsible for ESI-MS.

(1) Selected examples of C_{60} receptors: (a) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström. *J. Chem. Soc., Chem. Commun.* **1992**, 604. (b) Diederich, F.; Effing, J.; Jonas, U.; Jullien, L.; Plesnivy, T.; Ringsdorf, H.; Thilgen, C.; Weinstein, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1599. (c) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229. (d) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699. (e) Yoshida, Z.; Takekuma, H.; Takekuma, S.; Matsubara, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1597. (f) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 997.

(2) Several covalently linked porphyrin/C_{60} systems have been reported to show similar red shifts in the Soret absorption bands. For selected examples, (a) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771. (b) Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100*, 15926. (c) Baran, P. S.; Monaco, R. R.; Khan, A. U.; Schuster, D. I.; Wilson, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 8363. (d) Bourgeois, J.-P.; Diederich, F.; Echegoyen, L.; Nierengarten, J.-F. *Helv. Chim. Acta* **1998**, *81*, 1835. (e) Dietel, E.; Hirsch, A.; Eichhorn, E.; Rieker, A.; Hackbarth, S.; Röder, B. *Chem. Commun.* **1998**, 1981. (f) Cheng, P.; Wilson, S. R.; Schuster, D. I. *Chem. Commun.* **1999**, 89.

(3) C_{60} was added to a THF solution of **1** (2.2×10^{-4} M), and the mixture was sonicated for 20 min and subjected to ESI-MS (JEOL Type JMS-700T) with a four-sector (BEBE) tandem mass spectrometer. Conditions: needle volt, 2.0 kV; current, 300−700 nA; acceleration volt, 5.0 kV; resolution, 5000; chamber temperature, 150 °C; flow rate, 10 μL min^{-1}.

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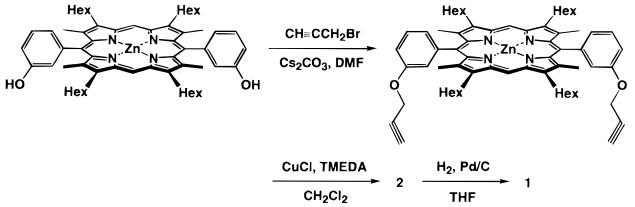
Scheme 1



nm, the binding constant of the 1:1 complexation was evaluated to be 6.7×10^5 M^{-1}.[4] To the best of our knowledge, this is the highest binding constant reported to date for host−guest interactions with C_{60} in organic solvents.[1f] In sharp contrast, cyclic dimer **2**, having rigid diacetylenic spacers between the two zinc porphyrin units, showed no spectral change at the visible region upon mixing with C_{60} under similar conditions.

Host molecule **1** in solution exists as a mixture of conformational isomers due to its flexible spacers:[5] ^{1}H NMR spectrum of **1** in C_6D_6 at 25 °C showed two sets of three singlet signals at δ 10.60−9.57 and 3.07−2.67 ppm due to meso and β-methyl resonances, respectively. ^{1}H NMR saturation transfer profile[6] of **1** indicated that such conformational isomers are transformed with one another at a rate slower than the NMR time scale. On the other hand, when an equimolar amount of 4,4′-bipyridine (bpy)[7] with respect to **1** was added to the solution, the ^{1}H NMR spectrum became much simplified to show single meso (δ 10.53) and β-methyl (δ 3.06) signals together with two upfield-shifted doublet signals due to bpy (δ 8.79, 7.05 → 3.42, 2.09). Thus, bpy was incorporated between the two zinc porphyrin units in an induced-fit fashion.[8] A similar NMR spectral change was observed upon addition of C_{60} to a C_6D_6 solution of **1**, where the meso and β-methyl resonances showed singlet signals at δ 10.32 and 2.87 ppm, respectively. These results indicate the formation of an inclusion complex between **1** and C_{60} (Figure 3). When the inclusion complex was mixed with an equimolar amount of bpy,[7] C_{60} was released quantitatively from the cavity, to form a complex of **1** coordinated with bpy.

^{13}C NMR spectrum of the inclusion complex of **1** and C_{60} in C_6D_6 at 30 °C showed a single signal due to the included C_{60} at δ 140.10 ppm, which is upfield-shifted from that of free C_{60} (δ 143.21). Such an upfield shift is considered to reflect the shielding effect and/or the electronic effect of the zinc porphyrin π-cloud. Cyclic voltammetry of an equimolar mixture of **1** and C_{60} in CH_2Cl_2 showed that the first reduction of C_{60} occurs at −1.11 V vs Fc/Fc^+.[9] Comparison of the observed redox potential with that of free C_{60} ($E_{1/2} = -1.05$ V) indicates that C_{60} becomes less subject to reduction upon complexation with **1**. Therefore, it is likely that a π-electronic interaction is operative between **1** and C_{60} in the inclusion complex.[10]

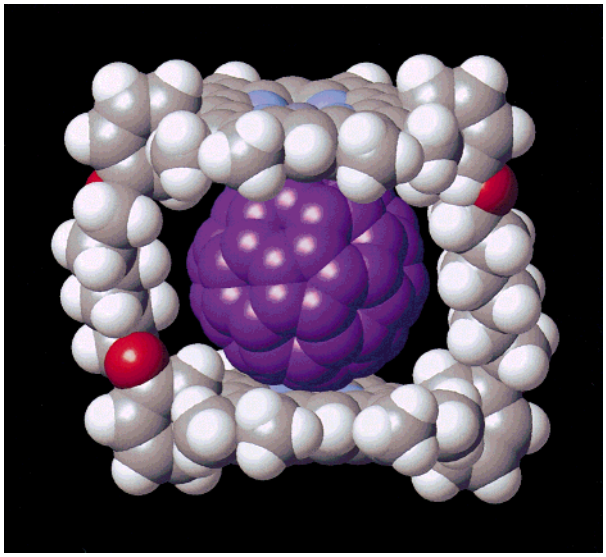


Figure 3. A computer-generated molecular model of the inclusion complex between **1** and C_{60}, optimized with a CAChe molecular mechanics calculation. For ease of calculation, the peripheral hexyl groups of **1** were replaced by methyl groups.

In conclusion, we have developed a novel macrocyclic receptor for the inclusion of C_{60} via π-electronic donor−acceptor interactions, where the very high binding constant (6.7×10^5 M^{-1}) enables chromatographic separation of C_{60}. The change in redox potentials of the included C_{60} also suggests a potential utility of the *supramolecular approach* for the modulation of the electronic properties of fullerenes.

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Supporting Information Available: Details for synthesis and characterization of **1** and **2**, together with ^{1}H NMR spectral profiles of **1**, an equimolar mixture of **1** and 4,4′-bipyridine (bpy), and that of **1** and C_{60} in C_6D_6 at 25 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Spectral change was analyzed by a nonlinear curve fitting method ($R^2 = 0.999417$).

(5) For ^{1}H NMR spectra, see Supporting Information. Presence of conformational isomers in analogous dimeric porphyrin systems has been reported in Golubchikov, O. A.; Mamardashvili, N. Zh.; Semeikin, A. S. *Zh. Org. Khim.* **1993**, *29*, 2445.

(6) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University: Oxford, U.K., 1987.

(7) The binding constant of bpy in benzene at 25 °C was 3.2×10^8 M^{-1}, as determined spectroscopically.

(8) Bampos, N.; Marvaud, V.; Sanders, J. K. M. *Chem. Eur. J.* **1998**, *4*, 335.

(9) Cyclic voltammograms of C_{60} in the absence and presence of **1** were recorded in CH_2Cl_2 (10^{-4} M) on a BAS Type CV−27 voltammetry controller with Bu_4NPF_6 (0.1 M) at Pt using a Ag wire pseudo reference electrode and recalculated against internal Fc/Fc^+.

(10) A comparable cathodic shift of the reduction potential has been reported in ref 2d.