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Synthesis of a C_3 Symmetric Host Molecule for C_{60} Bearing a Bicyclic Triarylphosphate Framework

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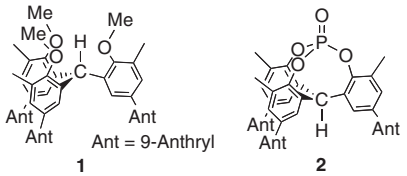
A fluorescent host molecule bearing a bicyclic triarylphosphate framework was synthesized. Its inclusion behavior to C_{60} was revealed by fluorescent titration. Cocrystallization of the host and C_{60} resulted in the formation of an inclusion complex in the crystalline state.

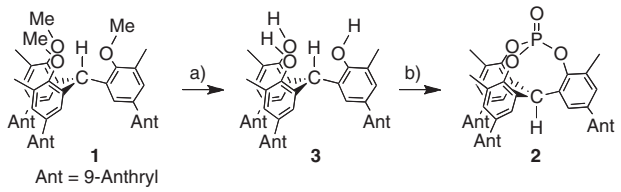
Inclusion behavior of calix[*n*]arenes to fullerenes was first reported by Atwood et al. and Shinkai et al., independently in 1994.[1,2] Since these findings, various calix[*n*]arene-based host molecules have been designed.[3] These host molecules interact with fullerenes by utilizing concave/convex complementality principle. Recently, some other bowl-shaped host molecules for C_{60} have been reported, for example, "fly trap" corranulene,[4] double corranulene containing molecular tweezers,[5] and extended tribenzotriquinacenes.[6] We have recently reported the triarylmethane-based host molecule **1**.[7] In host **1**, three anthryl groups construct the cavity, and **1** can work as a fluorescent host molecule. Because host **1** has a flexible framework, however, the shape and size of the cavity could not be fixed suitable for inclusion of a C_{60} molecule. Cocrystallization of **1** with C_{60} revealed that interaction between **1** and C_{60} occurred by side-on mode. To improve the inclusion ability of host **1**, the flexibility of the host molecule should be restricted. Thus, a novel host molecule **2**, in which three methoxy groups are replaced by a phosphoryl group, was designed (Scheme 1). Here we report the synthesis of the novel host molecule **2** based on a bicyclic triarylphosphate framework and the investigation of inclusion ability to C_{60}.

The host molecule **2** was prepared from the previously reported trianthryltriarylmethane **1** according to Scheme 2.[12] Three methoxy groups of **1** were demethylated by BBr_3 giving triarylmethane **3** (92%). The reaction of **3** with phosphoryl chloride in the presence of triethylamine afforded the host molecule **2** in 53% yield. The ^{1}H and ^{13}C NMR spectra of **2** in solution indicated the C_3 symmetric structure. UV–vis spectra of **2** showed its absorption maxima at 388 nm. The absorption maximum of **2** is not much different from those of host **1** ($\lambda_{max} = 385$ nm) and 9-anisylanthracene ($\lambda_{max} = 384$ nm), indicating that the electronic communication between anthracene moieties in **2** does not exist at the ground state.

Single crystals of **2** were obtained by the slow evaporation of a saturated CH_2Cl_2/CH_3CN solution and the molecular



Scheme 1. Triarylmethane host **1** and bicyclic phosphate host **2**.



Scheme 2. Synthesis of bicyclic host **2**. (a) BBr_3, CH_2Cl_2 (92%); (b) NEt_3, then Cl_3PO, toluene (53%).

Figure 1. ORTEP drawing of host **2** (50% probability). Solvent molecules and H atoms except for the methine hydrogen are omitted for the clarity.

structure was determined by X-ray crystallographic analysis (Figure 1).[8,9] A solvent molecule was contained in the unit cell. Although the solvent molecules could not be determined due to the severe disorder, the molecular structure of **2** was determined. Three anthryl groups constructed the shallow cavity, and its depth was estimated to be 4.0 Å. The distances between the centroids of the anthracenes are 10.4, 10.3, and 9.6 Å, respectively (avg. 10.1 Å). The size of the cavity is suitable for the inclusion of C_{60} fullerene.

Since the cavity of **2** was constructed from the fluorescent anthracene moiety, its inclusion behavior to C_{60} was investigated by fluorescent titration. Fluorescent quenching of aromatic compounds upon complexation with fullerene can be a useful tool for the detection of interaction due to high sensitivity of fluorescent spectra. Indeed, several studies of estimation of interaction between fullerene and organic hosts using fluorescent quenching have been reported.[10] In these reports, the Stern–Volmer plot[11] was used for analysis of the interaction. If the fluorescent quenching occurs by static quenching, the Stern–Volmer constant is nearly equal to the association constant, and can be used as an index for the complexation ability of organic hosts.

The titration was carried out by addition of various concentration solutions of C_{60} to a constant concentration solution of host molecule **2**. Fluorescent intensity was diminished by increasing the concentration of C_{60}. The change of fluorescent spectra is shown in Figure 2a. Stern–Volmer plots were prepared for these spectral changes according to eq 1 and the results are shown in Figure 2b. The Stern–Volmer plot showed the linearity in the region of the molar ratio of C_{60}

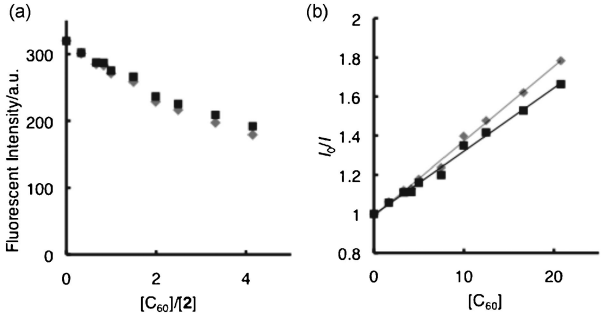


Figure 2. (a) Change of the fluorescent intensity of **2** upon addition of C_{60} ($[\mathbf{2}] = 5.01 \times 10^{-6}\,M^{-1}$; diamond, $\lambda_F = 402\,nm$; square, $\lambda_F = 422\,nm$). (b) Stern–Volmer plot for the fluorescent spectral change (diamond, $\lambda_F = 402\,nm$; square, $\lambda_F = 422\,nm$).

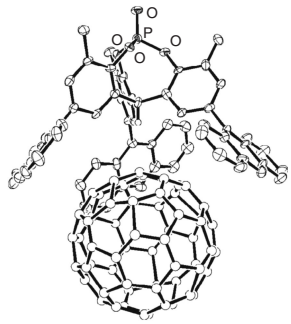


Figure 3. Crystal structure of the cocrystallite of **2** and C_{60} (50% probability for **2**; sphere diagram for C_{60}). Solvent molecules and H atoms except for the methine hydrogen are omitted for clarity.

against **2** as 0–6 equiv. The linearity of the Stern–Volmer plot means the formation of 1:1 complex between **2** and C_{60}. The Stern–Volmer constant was estimated to be $(3.5 \pm 0.2) \times 10^4$ M^{-1}. It is almost the same or smaller than those of fluorescent macrocyclic hosts (10^4–$10^5\,M^{-1}$).[10]

$$I_0/I = 1 + K_{SV}[Q] \quad (1)$$

I: fluorescent intensity of host

K_{SV}: Stern–Volmer constant

[Q]: concentration of quencher (guest)

Cocrystallization of the host molecule **2** and C_{60} was carried out by the slow evaporation of toluene/CH_3CN solution of the 1:1 mixture of **2** and C_{60}. Dark brown single crystals suitable for X-ray crystallographic analysis were obtained. The molecular structure is shown in Figure 3.[8,9] C_{60} was highly disordered and it could not be completely modeled, but C_{60} was found to be included in the inside of the cavity. This result makes a sharp contrast to the side-on interaction between the flexible triarylmethane host **1** with C_{60}.[7] The solid-state structure of **2** in the presence of C_{60} was not much different from that in the absence of C_{60}, while they were quite different for **1**. Such differences indicated that **2** is preorganized for inclusion of C_{60}. However, its Stern–Volmer constant $[(3.5 \pm 0.2) \times 10^4\,M^{-1}]$ is smaller than that of **1** $[(4.6 \pm 0.2) \times 10^4\,M^{-1}]$. The molecular structure of **1** is adjusted to the suitable structure for interaction with C_{60}. It can be therefore concluded that **1** is an induced-fit host and the interaction of **1** with C_{60} is controlled by enthalpy.

In summary, the bicyclic triarylphosphate C_3 symmetric host **2** was prepared and inclusion behavior toward C_{60} was investigated and compared with more flexible triarylmethane host **1**, indicating that **2** worked as a preorganized host for inclusion of C_{60}.

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References and Notes

1 J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229.
2 T. Suzuki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1994**, 699.
3 a) A. Ikeda, Y. Suzuki, M. Yoshimura, S. Shinkai, *Tetrahedron* **1998**, *54*, 2497. b) M. Makha, M. J. Hardie, C. L. Raston, *Chem. Commun.* **2002**, 1446. c) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 259. d) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem., Int. Ed.* **1998**, *37*, 997. e) J. L. Atwood, L. J. Barbour, C. L. Raston, I. B. N. Sudria, *Angew. Chem., Int. Ed.* **1998**, *37*, 981. f) J. L. Atwood, L. J. Barbour, M. W. Heaven, C. L. Raston, *Angew. Chem., Int. Ed.* **2003**, *42*, 3254.
4 a) P. E. Georghiou, A. H. Tran, S. Mizyed, M. Bancu, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 6158. b) S. Mizyed, P. E. Georghiou, M. Bancu, B. Cuadra, A. K. Rai, P. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **2001**, *123*, 12770.
5 A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842.
6 P. E. Georghiou, L. N. Dawe, H.-A. Tran, J. Strübe, B. Neumann, H.-G. Stammler, D. Kuck, *J. Org. Chem.* **2008**, *73*, 9040.
7 J. Kobayashi, Y. Domoto, T. Kawashima, *Chem. Commun.* **2009**, 6186.
8 Crystal data for **2** (CCDC-754769): monoclinic, $P2_1/n$, $a = 13.141(2)$, $b = 28.937(6)$, $c = 14.463(3)$ Å, $\beta = 98.628(3)°$, $V = 5737.4(18)$ Å^3, $Z = 4$, $R1 = 0.1276$ ($I > 2\sigma(I)$), w$R2 = 0.3939$ (all data). Crystal data for **2**·C_{60} (CCDC-754770): monoclinic, $P2_1/n$, $a = 13.324(6)$, $b = 45.654(18)$, $c = 13.833(6)$ Å, $\beta = 105.894(3)°$, $V = 8093(6)$ Å^3, $Z = 4$, $R1 = 0.1414$ ($I > 2\sigma(I)$), w$R2 = 0.4306$ (all data).
9 G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Determination*, University of Göttingen, Germany, **1997**.
10 a) L. H. Tong, J.-L. Wietor, W. Clegg, P. R. Raithby, S. I. Pascu, J. K. M. Sanders, *Chem.—Eur. J.* **2008**, *14*, 3035. b) K. A. Nielsen, G. H. Sarova, L. Martín-Gomis, F. Fernández-Lázaro, P. C. Stein, L. Sanguinet, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos, J. O. Jeppesen, *J. Am. Chem. Soc.* **2008**, *130*, 460. c) K. A. Nielsen, W.-S. Cho, G. H. Sarova, B. M. Petersen, A. D. Bond, J. Becher, F. Jensen, D. M. Guldi, J. L. Sessler, J. O. Jeppesen, *Angew. Chem., Int. Ed.* **2006**, *45*, 6848. d) Z.-Q. Wu, X.-B. Shao, C. Li, J.-L. Hou, K. Wang, X.-K. Jiang, Z.-T. Li, *J. Am. Chem. Soc.* **2005**, *127*, 17460. e) T. Haino, H. Araki, Y. Fujiwara, Y. Tanimoto, Y. Fukazawa, *Chem. Commun.* **2002**, 2148. f) D. I. Schuster, J. Rosenthal, S. MacMahon, P. D. Jarowski, C. A. Alabi, D. M. Guldi, *Chem. Commun.* **2002**, 2538. g) M.-X. Wang, X.-H. Zhang, Q.-Y. Zheng, *Angew. Chem., Int. Ed.* **2004**, *43*, 838. h) H.-Y. Gong, X.-H. Zhang, D.-X. Wang, H.-W. Ma, Q.-Y. Zheng, M.-X. Wang, *Chem.—Eur. J.* **2006**, *12*, 9262. i) T. Kawase, K. Tanaka, N. Fujiwara, H. R. Darabi, M. Oda, *Angew. Chem., Int. Ed.* **2003**, *42*, 1624. j) T. Kawase, K. Tanaka, Y. Seirai, N. Shiono, M. Oda, *Angew. Chem., Int. Ed.* **2003**, *42*, 5597.
11 B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2001**.
12 Supporting Information is available electronically on the CSJ-Journal Web Site, http://www.csj.jp/journals/chem-lett/index.html.

