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A Dendritic Porphyrin Receptor for C_{60} Which Features a Profound Positive Allosteric Effect

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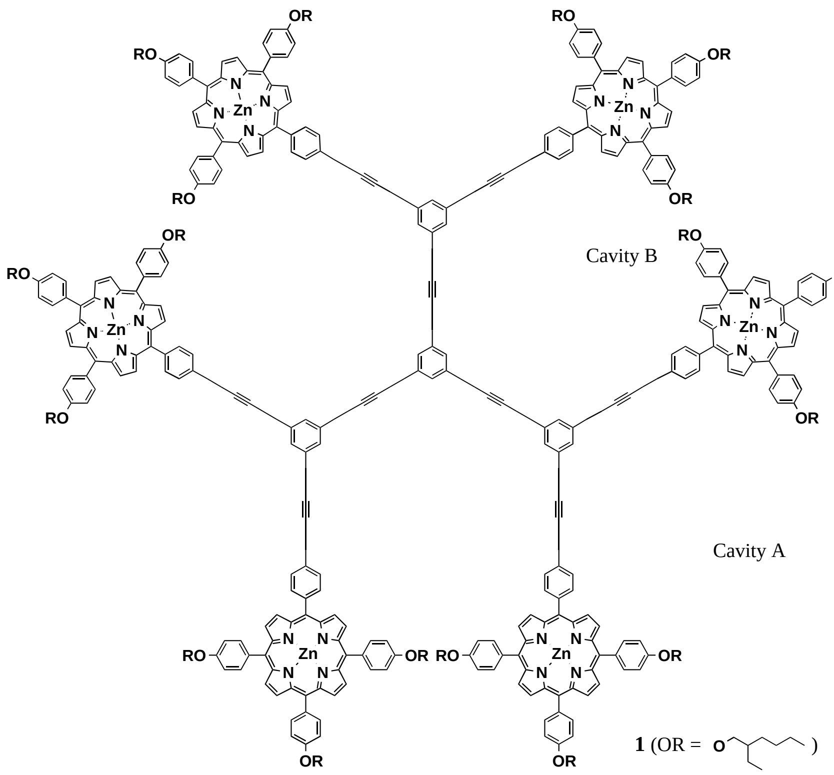
The developmental investigation of the novel application of dendrimers and dendritic compounds has been of recent concern.[1] Dendrimers, as host molecules have attracted a great deal of attention because of their unique topology, well-defined structures, and unusual guest-binding behaviors compared to general polymers.[2] As [60]fullerene (C_{60}) exhibits outstanding new chemical and physical properties, the molecular design of C_{60} receptors is a growing research area.[3] For the crystal state, several articles have shown that porphyrin derivatives cocrystallize with C_{60} because of an attractive force between C_{60} and a porphyrin-ring center.[4] In organic solvents, Aida and co-workers[5] and Reed and co-workers[6] have shown that the porphyrin dimers have exceptionally high affinity for C_{60}. Herein, we describe a rigid star-shaped D_3-symmetric receptor **1**[7] bearing six porphyrin moieties linked with one another through phenylacetylene units. The dendritic receptor **1** has three rotational axes which affect the spatial arrangement of porphyrins (Figure 1), and the shape of the three clefts, each of which consists of two porphyrin planes. We have already demonstrated that the subunits for guest binding, which are rationally arranged around a rotational axis such as metal ion,[8] C–C bond,[9] or butadiynylene,[10] work cooperatively to bind guest molecules in a nonlinear fashion (positive homotropic allosterism). In addition, we have found that this effect is useful to bind guest molecules which are difficult to bind with a linear, 1:1 guest-binding fashion. As shown in Figure 1, when two porphyrins sandwich one C_{60} molecule, the complexation site successively suppresses the rotational freedom of the remaining porphyrin "tweezers". This "domino" effect is expected to be effective for the binding of three equivalents of C_{60} in an allosteric manner to attain high C_{60} affinity.



The formation of the **1**-C_{60} complex in toluene was indicated by a change in the UV/Vis absorption spectra induced by successive addition of C_{60} to **1** (Figure 2). The λ_{max} of the Soret band (428 nm) slightly shifts to longer wavelength (429 nm) with a tight isosbestic point (435 nm in Soret band region). The spectral characteristics are coincident with those of recent findings for a few porphyrin–C_{60} complexation systems.[5, 6]

To estimate the stoichiometry between **1** and C_{60}, ^{1}H NMR spectra for [**1**]:[C_{60}] = 1:0–1:5 at 25 °C were measured in [D_8]toluene ([**1**] = 0.50 mM). The resonance signals of the *meso*-aryl protons and β-pyrrole protons shifted upfield on C_{60} addition (see Supporting Information). As shown in Figure 3, a plot of $\Delta\delta$ versus [C_{60}]/[**1**] has a clear inflection point at [C_{60}]/[**1**] = 3.0. This value supports the view that the complex is

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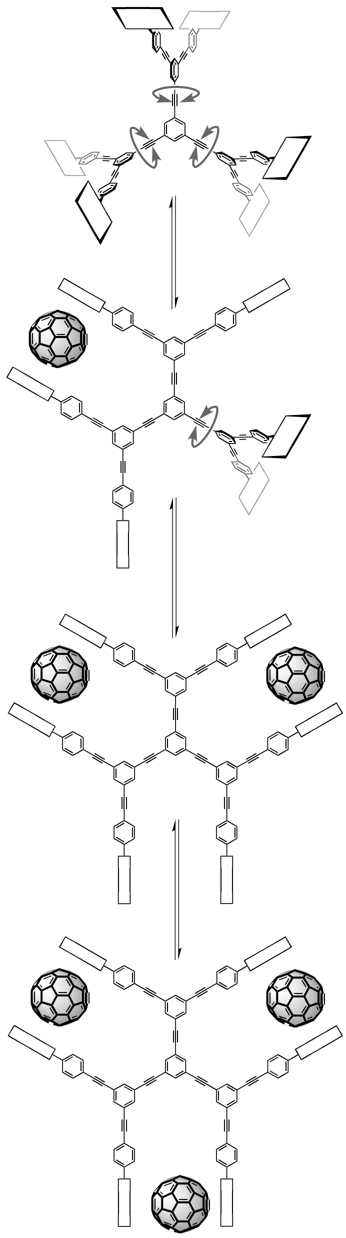


Figure 1. Rotational axes of **1**.

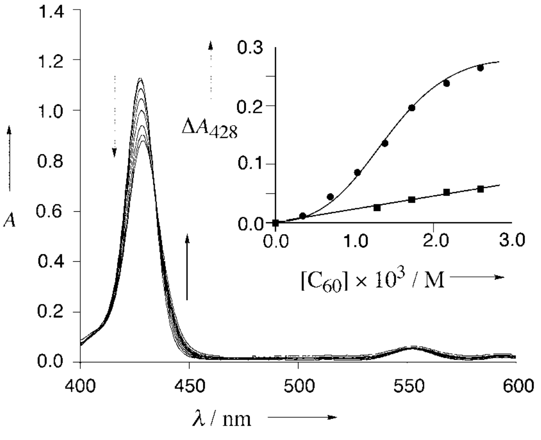


Figure 2. Absorption spectral change of **1** (5.3×10^{-6} M) in toluene at 25 °C: $[C_{60}] = 0-2.6\times10^{-3}$ M, 1 mm cell. Inset: plot of ΔA_{428} (●: **1**, ■: **2**) versus $[C_{60}]$. To normalize the porphyrin concentration, we set [**2**] to 3 × [**1**].

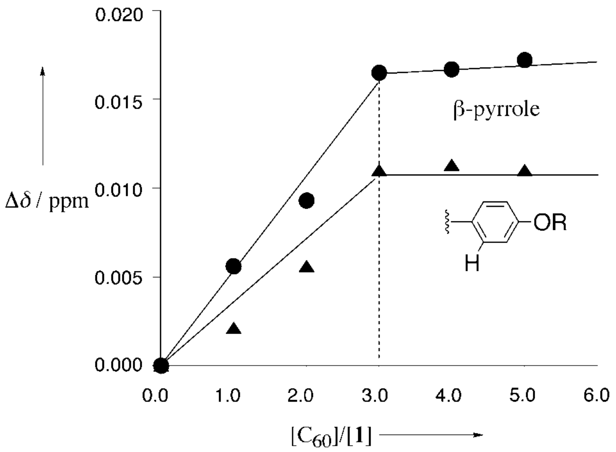
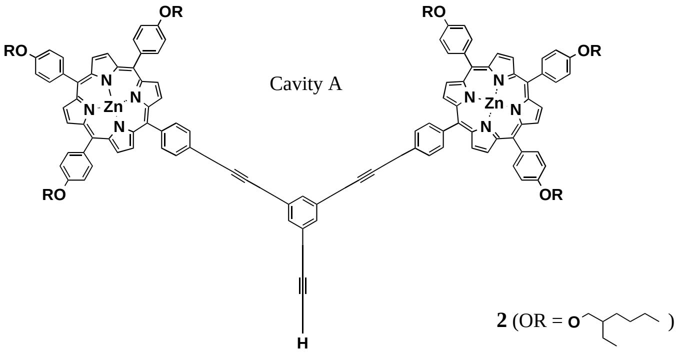


Figure 3. Plots of chemical-shift change versus $[C_{60}]$/[**1**] where [**1**] was kept constant (0.5 mM): 400 MHz, $[D_8]$toluene, 25 °C.

formed with a 1:3 **1**:C_{60} stoichiometry. These trends in the C_{60}-induced chemical-shift changes in the ^{1}H NMR spectra are consistent with those of recent reports on porphyrin–C_{60} complexation systems.[5, 6]

Very interestingly, a plot of the absorbance change at 428 nm (ΔA_{428}) versus $[C_{60}]$ featured a sigmoidal curve, which indicates that the binding of C_{60} to **1** occurs according to a well-defined cooperative phenomenon (inset of Figure 2).[8a,b] This guest-binding profile was analyzed with the Hill equation: $\log(y/(1-y)) = n\log[\text{guest}] + \log K$, where K and n are the association constant and Hill coefficient, respectively, and $y = K/([\text{guest}]^{-n} + K)$.[11] From the slope and the intercept of the linear plot, we obtained $K = 1.4\times10^{8}\,(\mathrm{M}^{-3})$ for 1:3 **1**-C_{60} complex (correlation coefficient 0.995) and $n = 2.8$. The binding of the first C_{60} suppresses the rotation of two complexing porphyrin rings and consequently suppresses the rotation of two other neighboring porphyrin rings in same axes. The binding of the second C_{60} suppresses the rotation of residual two free porphyrin rings (Figure 1). Therefore, as the number of the bound guests increases, the loss of Gibbs free energy decreases. In fact, the results obtained by the analysis based on the Hill equation show that the K value is sufficiently large and the Hill coefficient is close to 3.0, which allows a highly cooperative binding of three C_{60} guests.

Compound **1** has two different kinds of porphyrin tweezers: one composed of two porphyrins in the same branch (cavity A in compound **1**) and the other composed of two porphyrins in the two adjacent branches (cavity B in compound **1**). To evaluate which cavity is acting as a real binding site in solution, we measured the UV/Vis absorption spectroscopy of model compound **2** bearing only cavity A. We confirmed that addition of C_{60} scarcely induces a spectral change in model compound **2**. From a plot of ΔA_{428} versus $[C_{60}]$, we estimated the K value to be lower than $10\,\mathrm{M}^{-1}$. This result is consistent with examination of the computational models, which show that cavity A (distance between parallel-oriented porphyrins, 2.29 nm) is too large to sandwich C_{60}. Furthermore, if C_{60} were bound to cavity A, compound **1** should not exhibit the allosteric effect because the three phenylacethylene axes can rotate quite independently. On the other hand, the distance between parallel-oriented porphyrins in cavity B is



2 (OR = O)

estimated to be 1.18 nm, which is comparable with the size of C_{60} (diameter, 1.00 nm).[12] One can thus consider that cavity B is acting as a real binding site.

In conclusion, the present study demonstrated that the dendritic receptor **1** binds three C_{60} guests in the positive allosteric manner with high Hill coefficient of 2.8. With the aid of this effect, the K value is considerably enhanced. In addition, the findings have important implications because molecular recognition can be coupled with the control of various chemical and physical functions inherent to the porphyrin–fullerene interaction, such as solubilization of C_{60} in polar solvents, photochemical electron or energy transfer as a photosynthetic model, electrochemical redox reactions, etc.

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Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxide Ligand

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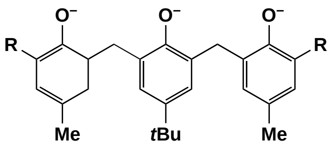
The efficient activation of dinitrogen under mild conditions is a challenging topic in chemistry because of its important applications. Although dinitrogen complexes of almost transition metals have been prepared,[1] there are few examples of well-characterized transition-metal compounds which are capable of cleaving the N≡N bond.[2] As part of studies aimed at developing new ancillary ligands to support reactive metal centers, we have found it attractive to employ linked aryloxide ligands ($R\text{-}L^{3-}$; R = *t*Bu, Me; Scheme 1),[3, 4, 5] to determine complex geometry and to limit ligand mobility. Furthermore, their steric size can be easily regulated by substituents at *ortho* positions of the outer aryloxides. We chose to investigate the chemistry of niobium complexes with the $R\text{-}L^{3-}$ ligands in dinitrogen activation. Herein we describe the reductive N≡N-bond cleavage by the combination of $LiBHEt_3$ and a niobium complex supported by a tridentate aryloxide ligand.



Scheme 1. Ligands, $R\text{-}L^{3-}$ (R = *t*Bu, Me).

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