Thermodynamic Insight into the Origin of a Calix[n]arene-[60]fullerene Interaction and its Application to a Porphyrin-[60]fullerene Energy Transfer System

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Abstract. The calixarene-fullerene interaction, which causes only a slight change in the absorption spectra, has been substantiated by calorimetric measurements: the ΔH° values are comparable with those obtained from the association constants estimated by a spectroscopic method. Furthermore, we determined the association constant between homooxacalix[3]arene and [60]fullerene derivatives with a porphyrin moiety by fluorescence spectra.

Key words: calixarene, [60]fullerene, porphyrin, inclusion complex, calorimetry, fluorescence spectra.

1. Introduction

Recently, it was shown that certain calix[*n*]arenes and their analogues can interact with [60]fullerene even in solution [1–9]. However, this proposal has so far been derived only on the basis of a change in the absorption spectra at around 430 nm or the chemical shift in NMR spectroscopy [1b, 4c]. In order to obtain direct evidence for the formation of the calix[*n*]arene-[60]fullerene complexes in solution, various mass spectrophotometric methods (SIMS, ESIMS, MALDI-TOF, ESI-TOF, etc.) were applied but failed. Is there any other complementary experimental method by which one can firmly evidence the complex formation? A similar controversial process once appeared in the history of calixarene chemistry: i.e., it was not clear for a long period whether certain small molecules (such as chloroform, toluene, acetone, etc.), which were known by X-ray crystallographic studies to be included in the cavity of calix[*n*]arenes in the solid state [10, 11], are also included in the cavity in solution. This problem was clearly solved by a calorimetric method, which

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unambiguously showed the inclusion of these molecules [12]. In this paper, we address the first calorimetric data for inclusion of [60]fullerene and [70]fullerene in homooxacalix[3]arene (**1**) and compare the $\Delta H°$ values with those obtained from the conventional spectroscopic method. In addition, we refer to a possible application of the calix[n]arene-[60]fullerene interaction to the control of energy transfer in a porphyrin-[60]fullerene conjugate (**2**). In this study, compound **3** was used as a reference for **2**.

2. Experimental

2.1. MATERIALS

Compounds **2** and **3** were synthesized according to the method similar to Ref. 13 and identified by IR and ^{1}H NMR spectral evidence and elemental analyses.

Compound **2**: mp >340°C (decomp.); m/z (FAB$^+$) 1666 (M + H$^+$); δ_H (600 MHz; CDCl$_3$; TMS; 25 °C) −2.44 (2H, s, NH), 1.15 (3H, t, CH$_2$CH_3), 2.43 and 2.48 (6H and 3H, s each, ArCH$_3$), 3.43–3.49, 3.58–3.60, 4.33–4.35, and 4.44–4.46 (6H, 2H, 2H and 2H, respectively, m each, CH$_2$O), 4.22 (2H, q, CH_2CH$_3$), 7.31, 7.38, 8.10, 8.17, 8.33, and 8.66 (4H, 2H, 4H, 2H, 2H and 2H, respectively, d each, ArH) and 8.75, 8.90, 8.92, and 8.95 (2H each, d each, pyrrole) (Found: C, 79.38; H, 3.23; N, 3.16. C$_{119}$H$_{52}$N$_4$O$_8$· 1.3CHCl$_3$ requires C, 79.35; H, 2.95; N, 3.07%).

Compound **3**: m.p. >340 °C (decomp.); δ_H (250 MHz; CDCl$_3$; TMS; 25 °C) −2.78 (2H, s, NH), 1.24 (3H, t, CH$_2$CH_3), 2.70 (9H, s, ArCH$_3$), 3.42 (2H, s, CH$_2$C=O), 3.76–3.80, 3.92–4.02, 4.32–4.36 and 4.67–4.71 (6H, 2H, 2H and 2H, respectively, m each, CH$_2$O), 4.17 (2H, q, CH_2CH$_3$), 7.55, 8.09, 8.30 and 8.45 (6H, 6H, 2H and 2H, respectively, d each, ArH) and 8.76–8.89 (8H, m, pyrrole) (Found: C, 75.20; H, 5.85; N, 5.72. C$_{59}$H$_{54}$N$_4$O$_8$ requires C, 74.82; H, 5.74; N, 5.91%).

2.2. CALORIMETRIC MEASUREMENTS

The enthalpy values ($\Delta H_c°$: subscript 'c' denotes the data determined by calorimetry) for inclusion of [60]fullerene and [70]fullerene by **1** were measured at 25 °C by an isothermal titration microcalorimeter (TAM2277; Thermometric AB, Sweden) controlled by Digitam 3.0 Software. To the solution of [60]fullerene or [70]fullerene in toluene (2.0 cm^3, [[60]fullerene] or [[70]fullerene] = 1.00 × 10^{-3} mol dm^{-3}) was injected into a toluene solution (5.0 × 10^{-6} dm^3) of **1** (2.00 × 10^{-4} mol dm^{-3}) at ten-minute intervals by using a computer-controlled syringe pump (612 Lund Pump 2) from a gastight syringe (Hamilton 1725LT) through a stainless steel cannula. The solution was stirred by a turbine at a constant speed of 80 rpm. The heat flow was detected by highly sensitive thermopiles surrounded by a heat sink stabilized at the desired temperature. The data are the average values of three repeated runs.
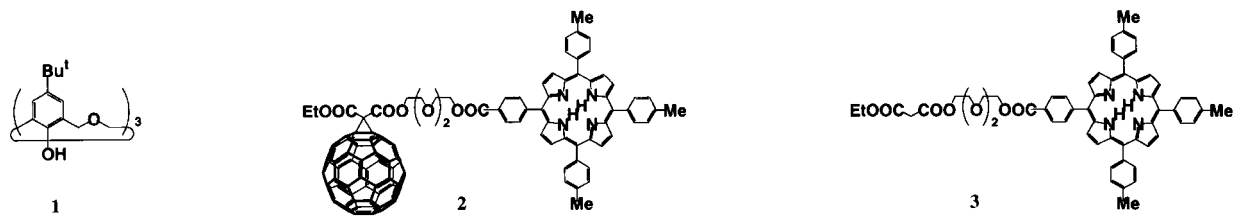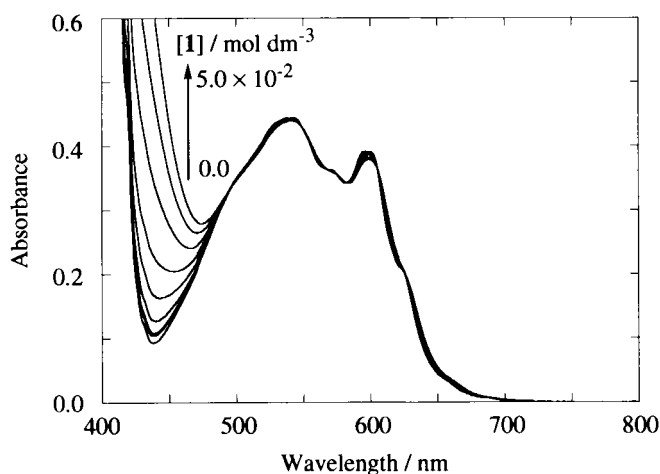
Compounds **1**–**3**.

Figure 1. Absorption spectral change in the **1**–[60]fullerene system: 30 °C, [**1**] = 0–5.00 × 10^{-2} mol dm^{-3}, [[60]fullerene] = 5.00 × 10^{-4} mol dm^{-3}, toluene.

2.3. ABSORPTION AND FLUORESCENCE SPECTROSCOPIC MEASUREMENTS

The ΔH_a° and ΔS_a° (subscript 'a' denotes the data determined by absorption spectroscopy) values for inclusion of [60]fullerene and [70]fullerene by **1** were measured by the association constants (K_{ass}) at five different temperatures (15, 20, 30, 40 and 50 °C) [14]. The K_{ass} values were estimated at each temperature using the absorbance increase at 425 nm for the **1**–[60]fullerene system and that at 470 nm for the **1**–[70]fullerene system. The values summarized in Table I are the average of three repeated experiments. The details of the measurement conditions are described in the caption to Figure 1.

The methods employed in the estimation of association constants (K_{ass}) between **1** and **2** (or **3**) were based on observing changes in absorption and fluorescence intensities of solutions where the relative concentration of **1** was increased with respect to **2** (or **3**). All association constants were determined in toluene at 25 °C. The $A–A_o$ or I/I_o–[**1**] plots were analyzed using a nonlinear least-square curve fitting.

2.4. MISCELLANEOUS

^{1}H NMR, UV-Vis and fluorescence spectra were recorded with a Bruker DRX 600 spectrometer, a Shimadzu UV-2500PC spectrometer and a Shimadzu F-4500 spectrometer, respectively.

Table I. Thermodynamic parameters obtained from the absorption spectral changes

Parameter	**1**–[60]Fullerene	**1**–[70]Fullerene
K_{ass} (dm^3 mol^{-1} at 30 °C)	34.0 ± 1.5	34.4 ± 1.1
ΔG_a° (kJ mol^{-1} at 30 °C)	-8.9 ± 0.5	-8.9 ± 0.5
ΔH_a° (kJ mol^{-1})	-11.9 ± 0.5	-12.5 ± 0.5
ΔS_a° (J mol^{-1} K^{-1})	-10.0 ± 2.0	-11.9 ± 3.0

[a][**1**] = 0–50.0 × 10^{-3} mol dm^{-3}, [[60]fullerene] = 5.00 × 10^{-4} mol dm^{-3}, [[70]fullerene] = 5.00 × 10^{-5} mol dm^{-3}, toluene.

3. Results and Discussion

3.1. CALORIMETRIC MEASUREMENTS

We obtained $\Delta H_c^\circ = -10.8 \pm 0.3$ kJ mol^{-1} for the **1**–[60]fullerene system and $\Delta H_c^\circ = -9.1 \pm 0.2$ kJ mol^{-1} for the **1**–[70]fullerene system. These calorimetric data clearly support the view that as predicted on the basis of the spectroscopic experiments [1–9], both [60]fullerene and [70]fullerene are included in the cavity of **1**.

3.2. DETERMINATION OF THE THERMODYNAMIC PARAMETERS

In order to compare these calorimetric data with the ΔH_a° and ΔS_a° (subscript 'a' denotes the data determined by absorption spectroscopy) values obtained from the absorption spectral change, we estimated the association constants (K_{ass}) at the five different temperatures (15, 20, 30, 40 and 50 °C) [14]. The typical spectral change in the **1**–[60]fullerene system is shown in Figure 1. The results are summarized in Table I.

One can discuss several important features of the calixarene-fullerene interaction on the basis of the examination of Table I. Firstly, the absorption spectral ΔH_a° values are nearly comparable with the calorimetric ΔH_c° values. This supports the view that the spectral method has a justifiable basis for the determination of the K_{ass} values although the spectral change is very small. Secondly, the ΔS_a° term features small negative values. When the $T\Delta S_a^\circ$ values are compared with the ΔH_a° values at 300 K, the entropy term corresponds to only one-fourth of the enthalpy term. This means that fullerene inclusion does not accompany a large entropy loss, but is predominantly governed by the enthalpy term. Thirdly, we surmised that there was a difference in the rotational freedom between [60]fullerene and [70]fullerene: [60]fullerene with ultimate symmetry scarcely loses its rotational freedom in the homooxacalix[3]arene cavity whereas the rotation of [70]fullerene with lower symmetry is partially restricted when it is included in the homooxacalix[3]arene cavity [12, 13]. This difference should be reflected by the entropy term, so that the answer for this hypothetical rationale should be obtained by determination of ΔH_a° and
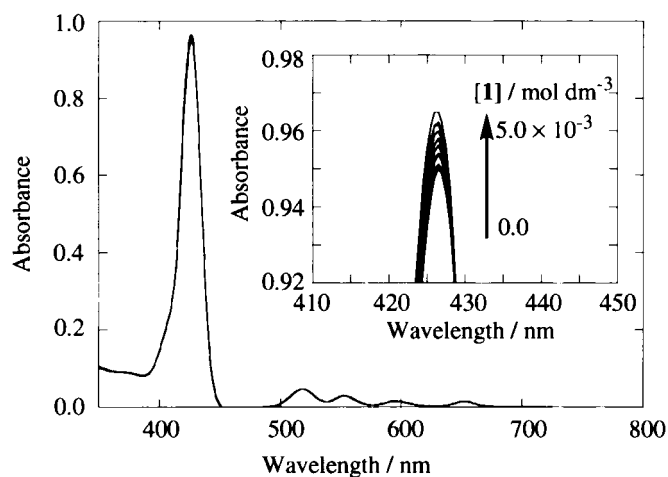
Figure 2. Absorption spectral changes in the **1–2** system: 25 °C, **[1]** = 0–5.00 × 10^{-3} mol dm^{-3}, **[2]** = 5.0 × 10^{-5} mol dm^{-3} toluene. Cell length; 1 mm.
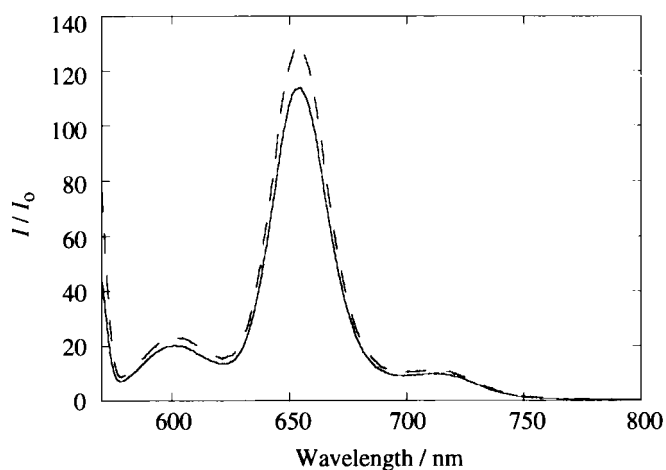

Figure 3. Fluorescence spectra of **2** (5.0 × 10^{-5} mol dm^{-3}), in the absence of **1** (–) and presence of **1** (– – –) (5.00 × 10^{-3} mol dm^{-3}): 25 °C, toluene, excitation 550 nm.

ΔS_s° for the complexation process. The ΔS_a° for the **1**–[70]fullerene system is more negative than that for the **1**–[60]fullerene system. Although this trend is compatible with the above hypothesis, the difference seems to be too small to justify it. This means that **1** is flexible enough to fit to [60]fullerene and [70]fullerene.

3.3. DETERMINATION OF THE K_{ass} VALUES BY THE FLUORESCENCE INTENSITY

We applied the **1**–[60]fullerene interaction to the control of a porphyrin-[60]fullerene energy transfer system, expecting that this interaction should suppress the energy transfer efficiency [15]. The Soret band for **2** is weaker than that for **3** and the absorption maximum shifts to longer wavelength by 5 nm. This implies that the porphyrin-[60]fullerene interaction already exists in the ground state. As shown in Figure 3, the fluorescence intensity for **2** is markedly reduced by intramolecular quenching of the porphyrin excited state by the intramolecular [60]fullerene moiety. Addition of **1** to this system increased both the absorbance and the fluorescence intensity (Figures 2 and 3): from a plot of A_{427} in **2** vs. [**1**] in the absorption spectral change the K_{ass} for the association between **1** and the [60]fullerene moiety in **2** was estimated to be 1.0 (± 0.3) $\times$ 10^3 dm^3 mol^{-1}. Likewise, the fluorescence maximum of the porphyrin moiety (655 nm) increased to $I/I_o = 1.12$ in the presence of **1** (5.0×10^{-3} mol dm^{-3}). We believe that the intramolecular fluorescence quenching is partially released by the **1**–[60]fullerene interaction.

4. Conclusion

The present study has shown clear evidence for the calixarene-fullerene interaction on the basis of the calorimetric method. This has justified the absorption spectroscopic method used so far as an analytical method for the calixarene-fullerene interaction [16]. The conclusion is important for the design of functionalized calixarene-fullerene conjugate systems and the expeditious detection of the interactive processes.

Acknowledgement

References

1. (a) A. Ikeda, M. Yoshimura, and S. Shinkai: *Tetrahedron Lett.* **38**, 2107 (1997); (b) A. Ikeda, M. Yoshimura, H. Udzu, C. Fukuhara, and S. Shinkai: *J. Am. Chem. Soc.* **121**, 4296 (1999); (c) For the X-ray structure of a [60]fullerene-homooxacalix[3]arene complex, see K. Tsubaki, K. Tanaka, T. Kinoshita, and K. Fuji: *J. Chem. Soc., Chem. Commun.* 895 (1998).
2. A. Ikeda, Y. Suzuki, M. Yoshimura, and S. Shinkai: *Tetrahedron* **54**, 2497 (1998) and references cited therein.
3. (a) K. Araki, K. Akao, A. Ikeda, T. Suzuki, and S. Shinkai: *Tetrahedron Lett.* **37**, 73 (1996); (b) S. Shinkai and A. Ikeda: *Gazz. Chim. Ital.* **127**, 657 (1997).
4. (a) T. Haino, M. Yanase, and Y. Fukazawa: *Angew. Chem. Int. Ed. Engl.* **36**, 259 (1997); (b) T. Haino, M. Yanase, and Y. Fukazawa: *Tetrahedron Lett.* **38**, 3739 (1997); (c) M. Yanase, T. Haino, and Y. Fukazawa: *Tetrahedron Lett.* **40**, 2781 (1999).

5. J. L. Atwood, L. J. Barbour, C. L. Raston, and I. B. N. Sudria: *Angew. Chem. Int. Ed. Engl.* **37**, 981 (1998).

6. J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston, and R. S. Burkhalter: *J. Chem. Soc., Chem. Commun.* 1449 (1996).

7. N. S. Isaacs, P. J. Nichols, C. L. Raston, C. A. Sandova, and D. J. Young: *J. Chem. Soc., Chem. Commun.* 1839 (1997).

8. T. Haino, M. Yanase, and Y. Fukazawa: *Angew. Chem. Int. Ed. Engl.* **37**, 997 (1998).

9. J. S. Wang and C. D. Gutsche: *J. Am. Chem. Soc.* **120**, 12226 (1998).

10. (a) R. Ungaro, A. Pochini, G. D. Andreetti, and P. Domiano: *J. Chem. Soc., Perkin Trans. 2* 197 (1985); (b) R. Ungaro, A. Pochini, G. D. Andreetti, and V. Sangermano: *J. Chem. Soc., Perkin Trans. 2* 1979 (1984). (c) G. D. Andreetti, R. Ungaro, and A. Pochini, *J. Chem. Soc., Chem. Commun.* 1005 (1979).

11. G. D. Andreetti and F. Ugozzoli: In J. Vicens and V. Böhmer (eds.), *Calixarenes*, Kluwer, Dordrecht (1991), pp. 87–123. See also the references cited therein.

12. A. F. D. de Namor, M. T. G. Pardo, L. Munoz, D. A. P. Tanaka, F. J. S. Velarde, and M. C. Cabaleiro, *J. Chem. Soc., Chem. Commun.* 855 (1992).

13. (a) P. S. Baran, R. R. Monaco, A. U. Khan, D. I. Schuster, and S. R. Wilson: *J. Am. Chem. Soc.* **119**, 8386 (1997); (b) E. Dietel, A. Hirsch, J. Zhou, and A. Rieker: *J. Chem. Soc., Perkin Trans. 2* 1357 (1998).

14. We previously estimated these values in the narrow temperature range (15–30 °C), which might result in erroneous values: Ref. 3b.

15. For recent publications on porphyrin-fullerene interactions, see (a) H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *J. Am. Chem. Soc.* **118**, 11771 (1996); (b) H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, and Y. Sakata *Chem. Lett.* 265 (1995); (c) H. Imahori and Y. Sakata: *Chem. Lett.* 199 (1996); (d) D. Carbonera, M. Di Valentin, C. Corvaja, G. Agostini, G. Giacometti, P. A. Liddel, D. Kucianskas, A. L. Moore, T. A. Moore, and D. Gust, *J. Am. Chem. Soc.* **120**, 4398 (1998).

16. Recently we found that an electrochemical method is also applicable for this purpose: M. Kawaguchi, A. Ikeda, S. Shinkai, and I. Neda: *J. Incl. Phenom.* **37**, 253 (2000).