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Molecular Design of Calixarene-based Host Molecules for Inclusion of C_{60} in Solution

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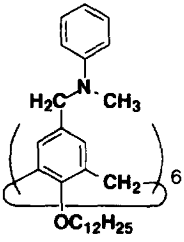
Abstract: Calix[6]arenes bearing *N,N*-dialkylaniline units or *m*-phenylenediamine units were synthesized to capture C_{60} in organic solution: the association constants ($7.9\text{-}1.1 \times 10^2$ dm^3mol^{-1}) were the largest values obtained so far, indicating that calix[6]arene acts as an excellent platform to facilitate the cooperative action of the donor groups.

In 1994, we[1] and Atwood *et al.*[2] discovered that *p-tert*-butylcalix[8]arene selectively includes C_{60} in carbon soot and forms the precipitate with 1:1 stoichiometry. This is a very novel and very useful purification method to obtain C_{60} in the large quantity and with the high purity. However, when this complex was solubilized in solution (*e.g.*, by heating or using good solvents), it dissociated to each component, and any spectroscopic indication for the complex formation could not be found.[3] This means that this complex can stably exist only in the solid state. So far, inclusion complexes of C_{60} are obtained only in an aqueous system with cyclodextrins and water-soluble calixarenes.[4] However, C_{60} is soluble (although sparingly) in certain organic solvents: therefore, it seems more practical and favorable for C_{60} to be treated in organic solvents, for example, for further derivatization and functionalization.

The purpose of the present study is to find out such host molecules that can form inclusion complexes in organic solvents. The survey of the past references taught us that the charge-transfer interaction with *N,N*-dialkylaniline derivatives is the sole non-covalent interaction useful to capture C_{60} in organic solvents.[5] Here, we decided to introduce *N,N*-dialkylaniline units or *m*-phenylenediamine units into calix[n]arenes. When they are introduced into the upper rim in calix[6]arene, the size of the extended cavities becomes comparable with that of calix[8]arene. Furthermore, the treatment of calix[6]arene is much easier than that of calix[8]arene. Taking these advantages into consideration, we designed and synthesized **1** and **2**. We have found that these calix[6]arene-based host molecules can bind C_{60} with appreciably-large association constants in organic solvents.

Compound **1** was synthesized from calix[6]arene-37,38,39,40,41,42-hexol according to Scheme 1. The *n*-dodecyl group was chosen to enhance the solubility in organic solvents. Compound **2** was synthesized according to Scheme 2, referring to the synthetic methods used for the preparation of 'stapled' calix[n]arenes.[6] The products were identified by IR and ^{1}H NMR spectroscopic analyses and elemental analyses. Compounds **3** and **4** were used as reference compounds for **1** and **2**, respectively.



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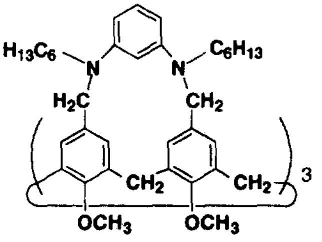

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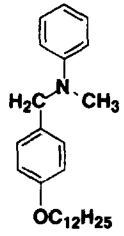

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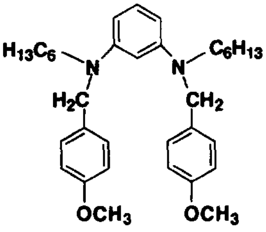

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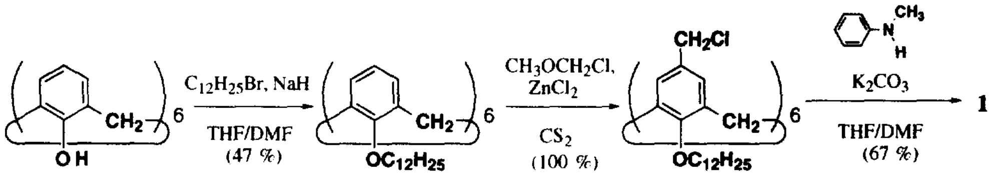
Scheme 1



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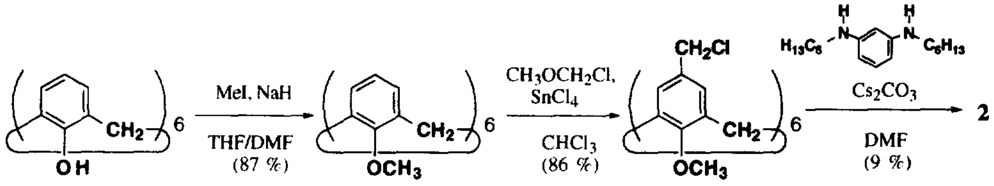
Scheme 2



7 8

The absorption spectra for a C_{60} + **1** system in toluene are shown in Fig. 1. With increasing **1** concentration the absorption band at 539 nm (which is an absorption maximum of C_{60} but where **1** does not absorb) increased. A plot of [**1**] *vs.* A_{539} (corrected for the absorbance of C_{60}) could be analyzed by the Benesi-Hildebrand equation for a 1:1 complex[7, 8] and the association constant (K) was estimated to be 7.9 dm^3 mol^{-1} ($r = 0.999$). A C_{60} + **3** system ($[C_{60}] = 0.50$ mmol dm^{-3} constant ; [**3**] = 0.24 - 0.70 mol dm^{-3}) also resulted in a similar spectral change and the K was estimated to be 0.20 dm^3 mol^{-1} ($r = 0.998$). This value was comparable with those determined for *N,N*-dialkylanilines.[5] We also tested 37,38,39,40,41,42-hexadodecyloxycalix[6]arene **5** but the perceptible spectral change was not observed for 500 - 700 nm region even in the presence of excess **5**. The results indicate that the increased absorbance in Fig. 1 is attributed to the charge-transfer interaction between C_{60} and dialkylaniline units in **1** and integration of donor groups is effective to enhance the association constant.

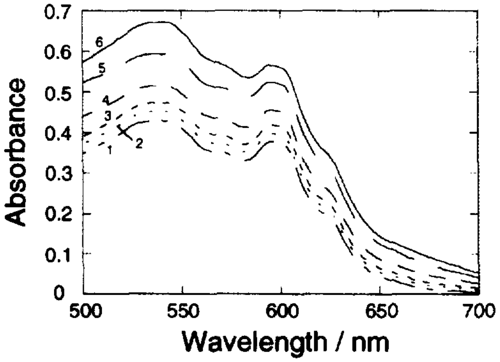


Fig. 1. Absorption spectra of C_{60} (5.0×10^{-4} mol dm^{-3}) in the presence of **1** in toluene at 25 °C: 10^3 mol^{-1} $dm^3 \times$ [**1**] = (1) 0, (2) 3.8, (3) 7.6, (4) 15.2, (5) 30.4, (6) 103.

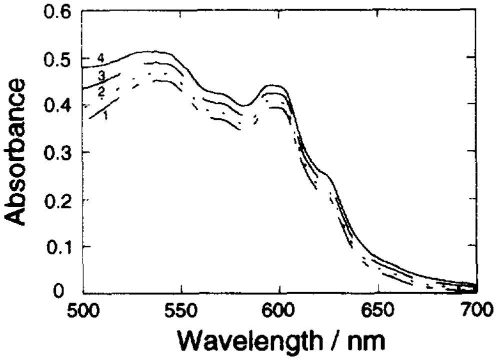


Fig. 2. Absorption spectra of C_{60} (5.0×10^{-4} mol dm^{-3}) in the presence of **2** in toluene at 25 °C: 10^3 mol^{-1} $dm^3 \times$ [**2**] = (1) 0, (2) 2.0, (3) 6.0, (4) 10.

To exploit a host molecule with the greater binding ability we synthesized **2**, the *m*-phenylenediamine units which should act as better donors than the *N*,*N*-dialkylaniline units in **1**. The spectral change observed for a C_{60} + **2** system is shown in Fig. 2: the broad absorbance increase was observed at 500 - 700 nm. By the analysis of a plot of [**2**] vs. A_{600} (corrected for the absorbance of C_{60}) by the Benesi-Hildebrand equation[7, 8] we obtained K = 1.1×10^2 dm^3 mol^{-1} (r = 0.999).[9] The similar treatment of **4** ([C_{60}] = 0.50 mmol dm^{-3} constant ; [**4**] = 0.010 - 0.040 mol dm^{-3}) gave K = 0.43 dm^3 mol^{-1} (r = 0.997). Comparison of the data for **1** ~ **4** establishes that reference compound **4** has the K greater only by 2-fold than **3** whereas host compound **2** has the K greater by 14-fold than **1**. To the best of our knowledge, the $K = 1.1 \times 10^2$ dm^3 mol^{-1} obtained in this study is the largest association constant achieved so far in organic solvents.[5] The large K enhancement of **2** relative to **1** is accounted for by (i) the stronger donation ability of the m-phenylenediamine unit relative to the N,N-dialkylaniline unit and (ii) the higher preorganization by stapling two calix[6]arene phenyl units. The proposed structure including the cooperative action of donor groups is shown in Fig. 3.

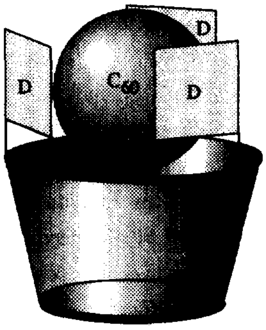


Fig. 3. Proposed structure including the cooperative action of donor groups

In conclusion, the present study successfully demonstrates that the inclusion complexes of C_{60} in solution can be stably formed with host molecules in which donor groups such as *N*,*N*-dialkylaniline or *m*-phenylenediamine are preorganized on an appropriate platform. Undoubtedly, calix[6]arene is one of the best platforms for this purpose.

REFERENCES AND NOTES

1. Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.*, **1994**, 699-702.
2. Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature*, **1994**, 368, 229-231.
3. Suzuki, T.; Shinkai, S.; unpublished results: also see Suzuki, T.; Nakashima, K.; Shinkai, S. *Tetrahedron Lett.*, **1995**, 36, 249-252.
4. Anderson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.*, **1992**, 604-606; Yoshida, Z.; Takekuma, H.; Matsubara, Y. *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 1597-1599; R. M. Williams and J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, **1992**, 111, 531-532.
5. Sun, Y.-P.; Bunker, C. E.; Ma, B. *J. Am. Chem. Soc.*, **1994**, 116, 9692 and references cited therein.
6. Ikeda, A.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 2671-2673. Compound **1:** ^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$, 408 K), δ 0.80 (t, J = 6.9 Hz, $\mathit{CH_3}CH_2$, 18H), 0.86-1.92 [overlapped, $CH_3\mathit{(CH_2)_{10}}$, 120H], 2.30-2.95 (bs, NCH_3, 18H), 2.97-4.62 (overlapped, OCH_2, NCH_2, $ArCH_2Ar$, 36H), 5.95-6.93 (overlapped, ArH, 30H), 6.97-7.10 (m, ArH, 12H). Compound **2:** ^{1}H NMR (400 MHz, $C_6D_5CD_3$, 303 K), δ 0.90 (t, J = 7.0 Hz, $\mathit{CH_3}CH_2$, 18H), 1.26-1.32 [overlapped, $CH_3\mathit{(CH_2)_3}$, 36H], 1.58 (m, $NCH_2\mathit{CH_2}$, 12H), 2.98 (t, J = 7.0 Hz, $N\mathit{CH_2}CH_2$, 12H), 3.11 (s, CH_3O, 18H), 3.74 (s, $ArCH_2Ar$, 6H), 3.98 (s, $ArCH_2Ar$, 6H), 4.36 (s, $ArCH_2N$, 12H), 6.30 (s, ArH, 3H), 6.58 (d, J = 8.2 Hz, ArH, 6H), 6.78 (s, ArH, 6H), 6.88 (s, ArH, 6H), 7.15 (t, J = 7.9 Hz, ArH, 3H).
7. Benesi, H.; Hildebrand, J. H. *J. Am. Chem. Soc.*, **1949**, 71, 2703; Since **1** and **2** exist in great excess over C_{60}, one can regard that only the 1:1 complex formation is monitored by the spectroscopic change.
8. We tried to estimate the stoichiometry by making a Job plot from ^{1}H NMR and absorption spectral changes but failed. The difficulty is related to the small K and the weak CT band. At [**2**] $\approx$ [C_{60}] $\approx$ 10^{-3} mol dm^{-3} region the interaction is still too weak to obtain reliable results. We measured the ^{1}H NMR (400 MHz) spectra of a 1:1 mixture of C_{60} and **2** (3.0 mol dm^{-3} each) in toluene-d_8 at -85 - 30 °C. However, we could not detect the significant shift (the largest up-field shift was 0.0046 ppm for the calix[6]arene ArH protons).
9. The K value was scarcely affected by the wavelength used (>550 nm).

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