

Synthesis and Spectroscopic Properties of C₆₀ Functionalized Calix[8]arene (Calixfullerene)

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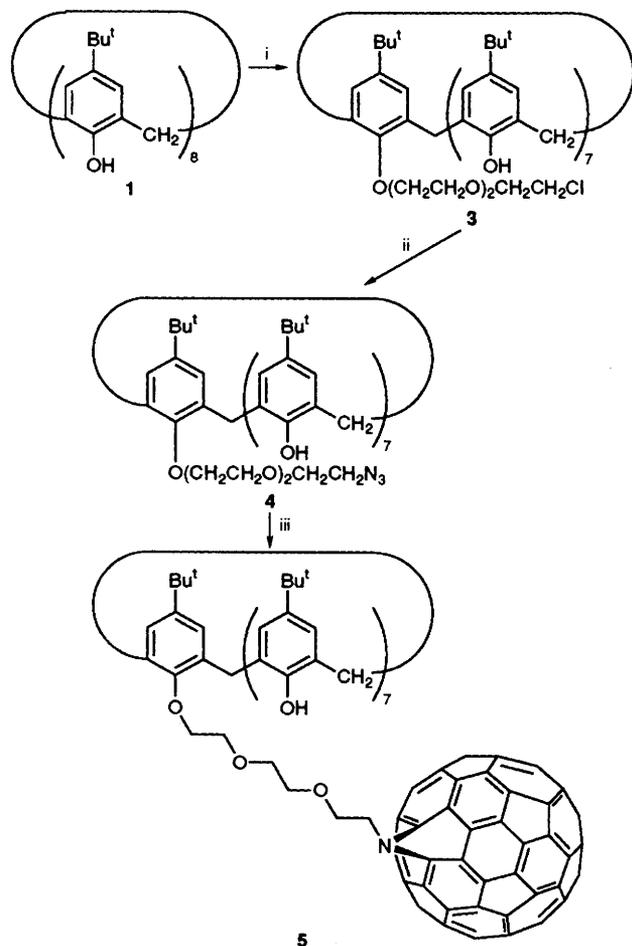
C₆₀ functionalized calix[8]arene connected by a polyether chain has been prepared and its spectroscopic properties have been examined.

In host-guest chemistry, preparations of C₆₀¹⁻³ functionalized crown ethers have been reported,³ but few reports on the inclusion of C₆₀ in cyclodextrins⁴ and calixarenes⁵ have been made. Recently, Atwood's group⁶ and our group⁷ found that from toluene solution, C₆₀ and calix[8]arene form a green-yellow precipitate, assigned as a 1:1 complex. However, the structure of the complex is still unknown since the precipitate decomposes when it redissolves at high temperature. These facts prompted us to synthesize the C₆₀ functionalized calix[8]arene **5** which can form an intramolecular inclusion complex of C₆₀ in the calix[8]arene cavity.

Treatment of calix[8]arene **1** with Cl(CH₂CH₂O)₃Ts **2**⁸ in the presence of 4 equiv. of NaH in THF under reflux afforded mono-substituted calix[8]arene **3** in 38% yield (70% based on consumed **1**). This is the first example of introducing an alkyl group into one of the eight hydroxy groups in calix[8]arene and may be synthetically useful.^{9,10} Without purification of the azide **4**, which was obtained by treatment of **3** with NaN₃ in Me₂SO, a mixture of **4** and 2 equiv. of C₆₀ was refluxed for 24 h¹¹ in chlorobenzene to afford calixfullerene **5** in 19% yield

from **3** (60% based on consumed C₆₀). The purification of **5** was carried out by column chromatography (silica gel, eluent: CH₂Cl₂-hexane (2:1) (Scheme 1).[†]

Calixfullerene **5** is a pale-green solid which decomposes at 330 °C and is soluble in most organic solvents. Fig. 1 shows the ¹H NMR spectrum of **5** in CDCl₃ at 25 °C (300 MHz). Four singlets (δ 9.0–9.5) (intensity 2:2:1:2) can be assigned to the seven phenolic hydroxy groups of the calix[8]arene moiety. The ¹³C NMR spectrum of **5** in CDCl₃ at 25 °C (75 MHz) shows 58 peaks (δ 125–150), which are assignable to aromatic carbons. From the symmetry of **5**, one can assign 26 peaks to the calix[8]arene carbons (four different carbons in a C₆₀-carrying phenyl unit and a distal phenyl unit and six different carbons in residual four phenyl units). Therefore, the remaining 32 peaks are assignable to the C₆₀ carbons. Recently, Hawker's group reported the ¹³C NMR spectrum of functionalized C₆₀ **6**, which is useful as a reference compound for **5**, which showed 32 peaks in the aromatic region: they concluded that the structure of **6** is an azaannulene structure with 6,5



Scheme 1 Reagents and conditions: i, NaH (4 equiv.), Cl(CH₂CH₂O)₃Ts **2**, THF, reflux, 14 h; ii, NaN₃, Me₂SO, 70 °C, 12 h; iii, C₆₀, PhCl, reflux

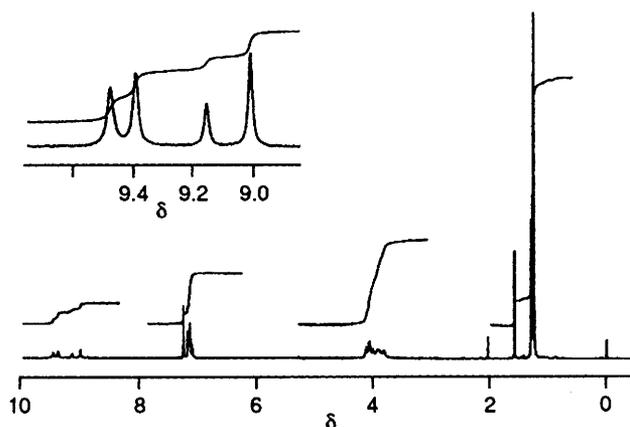


Fig. 1 ¹H NMR spectrum of **5** in CDCl₃ (25 °C, 300 MHz)

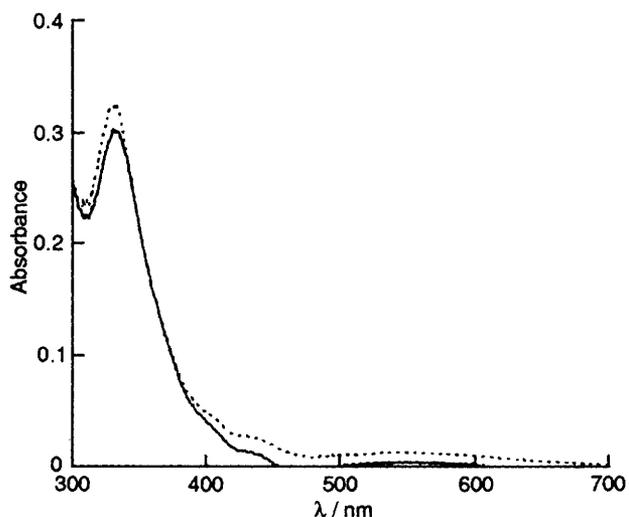


Fig. 2 UV-VIS spectra of **5** (solid line) and a mixture of **3** and **6** (dotted line) in CH₂Cl₂ at 25 °C (1.0 × 10⁻⁵ mol dm⁻³)

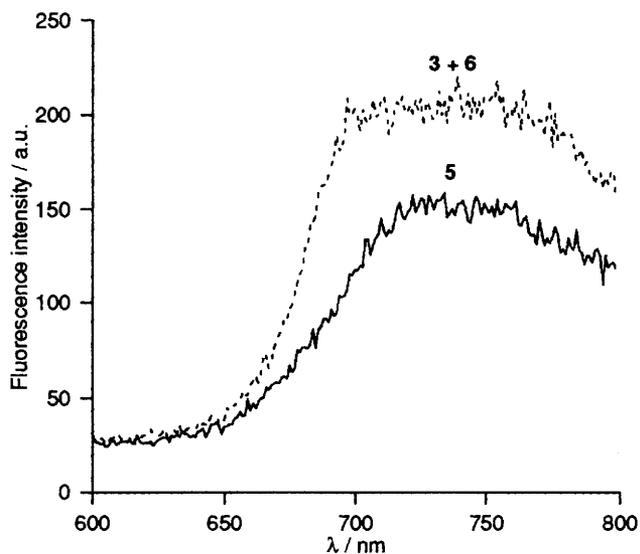
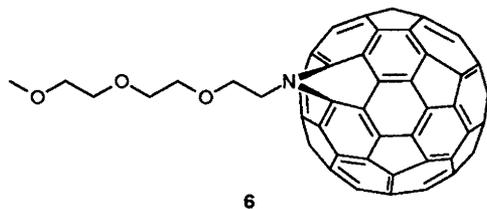


Fig. 3 Fluorescence spectra of **5** (solid line) and a mixture of **3** and **6** (dotted line) in CH_2Cl_2 at 25°C ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$, excitation: 349 nm). At 349 nm two samples have the same extinction coefficient.



junction.¹² Because of the good agreement of the number and the chemical shifts of C_{60} carbon peaks, the structure of this calixfullerene **5** can also be determined as the azaannulene structure with 6,5 junction as shown in Scheme 1. The mass spectrum of **5** shows a $(M + 1)$ ion peak ($m/z = 2146$), strong C_{60}^+ and (calix[8]arene + 1)⁺ peaks ($m/z = 720$ and 1426, respectively). Elemental analysis proved satisfactory.

Fig. 2 shows the UV-VIS spectra of **5** and a mixture of mono-substituted C_{60} **6** and mono-substituted calix[8]arene **3** as the reference in dichloromethane (25°C , $1.0 \times 10^{-5} \text{ mol dm}^{-3}$). For **5**, the extinction coefficient at λ_{max} 330 nm is decreased and the absorption at 500–600 nm is weakened, suggesting the isolation of C_{60} by intramolecularly linked calix[8]arene.^{6,7} The fluorescence spectra¹³ of **5** and a mixture of **6** and **3** in dichloromethane show very different spectra ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$, excitation: 349 nm) (Fig. 3). The decrease in the fluorescence intensity caused by connecting calix[8]arene with C_{60} would arise from intramolecular interaction of calix[8]arene and C_{60} . The shape of the spectrum is also different from that of the reference **6**, supporting certain interactions between C_{60} and calix[8]arene.

Studies on details of self-complexation and X-ray crystallographic analysis of **5** are now being carried out and will be published in the near future.‡

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Footnotes

† Spectroscopic data for **5**: 330°C (decomp.); $^1\text{H NMR}$ (CDCl_3) δ 1.24 (18H, s), 1.25 (18H, s), 1.27 (18H, s), 1.27 (9H, s), 1.27 (9H, s), 3.82–4.16 (28H, m), 7.10–7.18 (16H, m), 9.01 (2H, s), 9.16 (1H, s), 9.40 (2H, s), 9.48 (2H, s); $^{13}\text{C NMR}$ (CDCl_3) δ 21.06, 30.50, 31.42, 31.51, 31.54, 31.56, 32.43, 32.55, 32.88, 33.96, 34.00, 34.03, 34.29, 51.72, 60.39, 70.42, 70.54, 71.10, 71.21, 74.82, 125.27, 125.55, 125.75, 125.70, 125.82, 125.86, 125.92, 126.00, 126.62, 126.68, 126.89, 127.36, 127.60, 127.69, 127.88, 128.03, 128.09, 133.42, 133.58, 135.70, 136.06, 136.87, 137.22, 137.56, 137.88, 138.24, 138.96, 140.52, 140.58, 141.31, 142.45, 142.51, 142.64, 142.66, 142.94, 143.02, 143.13, 143.22, 143.40, 143.49, 143.67, 143.84, 143.92, 143.99, 144.17, 144.26, 144.31, 144.56, 144.65, 144.89, 146.47, 146.61, 146.96, 147.26, 147.66, 147.89, 148.36, 150.35; IR (KBr) ν/cm^{-1} 2959, 1483, 1361, 1203, 1118, 874, 527; MS (SIMS⁺) (rel. int.) 2145 (3.9), 1426 (10.4), 720 (100%).

‡ After submission of this paper, we found that the dynamic $^1\text{H NMR}$ spectra (between 313 K and 193 K) of **5** in $(\text{CD}_3)_2\text{CO}-\text{CDCl}_3$ (5 : 1) support the presence of two species. There is an exchange between these two species as determined by NOESY and ROESY spectra. Moreover, only one species is observed in the dynamic $^1\text{H NMR}$ spectra of **3** in $(\text{CD}_3)_2\text{CO}-\text{CDCl}_3$ (5 : 1). Therefore, the two species found in the dynamic $^1\text{H NMR}$ spectra of **5** are assignable to a self-inclusion compound and a non-self-inclusion compound. The details of the dynamic $^1\text{H NMR}$ spectra of **5** will be published in the near future.

References

- For example: R. M. Baum, *Chem. Eng. News*, 1993, **71**(38), 31.
- For example: F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157; R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; A. Hirsch, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1138; T. Suzuki, *Kagaku Kogyo*, 1994, **47**, 654 and references cited therein.
- F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf and C. Thilgen, *Helv. Chim. Acta*, 1993, **76**, 2445; S. R. Wilson and Y. Wu, *J. Chem. Soc., Chem. Commun.*, 1993, 784; S. R. Wilson and Q. Lu, *Tetrahedron Lett.*, 1993, **34**, 8043; S. R. Wilson, N. Kaprinidis, Y. Wu and D. I. Schuster, *J. Am. Chem. Soc.*, 1993, **115**, 8495; S. R. Wilson and Y. Wu, *J. Am. Chem. Soc.*, 1993, **115**, 10334; S. N. Davey, D. A. Leigh, A. E. Moody, L. W. Tetler and F. A. Wabe, *J. Chem. Soc., Chem. Commun.*, 1994, 397; A. Gügel, A. Kraus, J. Spickermann, P. Belik and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 559.
- T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. Wennerstöm, *J. Chem. Soc., Chem. Commun.*, 1992, 604; D. M. Guldi, H. Hungerbühler, E. Janata and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, 1993, 84; D. Zhang, J. Chen, Y. Yang, R. Cai, X. Shen and S. Wu, *J. Incl. Phen.*, 1993, **16**, 245; P. Boulas, W. Kutner, M. T. Jones and K. M. Kadish, *J. Phys. Chem.*, 1994, **98**, 1282.
- R. M. Williams and J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, 1992, **111**, 531.
- J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229.
- T. Suzuki, K. Nakashima and S. Shinkai, *Chem. Lett.*, 1994, 699.
- J. F. W. Keana, Y. Wu and G. Wu, *J. Org. Chem.*, 1987, **52**, 2571.
- Monoarylation of calix[8]arene, see: R. Muthukrishnan and C. D. Gutsche, *J. Org. Chem.*, 1979, **44**, 3962.
- Polyalkylation of calix[8]arene, see: P. Neri, E. Battoccolo, F. Cunsolo, C. Geraci and M. Piattelli, *J. Org. Chem.*, 1994, **59**, 3880.
- Similar conditions, see: M. Prato, C. Li and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 1148; C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1994, 925.
- C. J. Hawker, P. M. Saville and J. W. White, *J. Org. Chem.*, 1994, **59**, 3503.
- Fluorescence of C_{60} see: J. Catalán and J. Elguero, *J. Am. Chem. Soc.*, 1993, **115**, 9249.