Preferential separation of fullerene[84] from fullerene mixtures by encapsulation†‡

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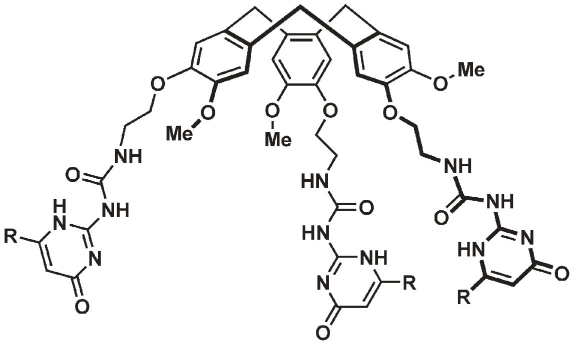
The encapsulation of fullerenes with a cyclotriveratrylene derivative, capable to self assemble into a dimer by means of three strong 4-ureidopyrimidinone quadruple hydrogen bonds is described. The system shows preference for C_{84}, allowing its easy enrichment directly from fullerene mixtures.

Since their discovery,[1,2] the isolation of high order fullerenes ($>C_{70}$) is a challenging topic due to their low abundance, poor solubility and difficult separation. To date, the most reliable method to purify higher fullerenes is by multiple runs of cyclic HPLC, which makes these elusive materials very expensive.[3] Alternative methods, based on supramolecular interactions, have been recently described. For example, a new double calix[5]arene container successfully extracts higher fullerenes, especially C_{94} and C_{96}, from fullerene mixtures.[4] Raising the temperature above 100 °C promotes a conformational *syn–anti* isomerization with release of the captured fullerene. In another approach, macrocyclic dimers of zinc porphyrins were employed to extract fullerenes $\geqslant C_{76}$ directly from mixtures, allowing the enrichment of rare fullerenes C_{102}–C_{110} after several extractions.[5] Despite these elegant designs, chromatography is still required at some step of the process.

Among fullerenes, C_{84} is the third most abundant member of the family, after C_{60} and C_{70}.[1,6] A total of 24 isomers of C_{84} are predicted by calculations obeying the isolated pentagon rule (IPR).[7] The ^{13}C NMR spectra of C_{84} of samples obtained by the standard graphite arc method, is consistent with a 2 : 1 thermodynamic mixture of the isoenergetic D_2 and D_{2d} symmetry isomers. Due to the limited accessibility of pure C_{84} its chemistry has been poorly developed, mainly aimed at separating the different isomers or testing the reactivity.[8] With regard to potential applications, a C_{84}-based field effect transistor was developed by Shibata *et al.*[9] and pioneering work has been done in the field of nonlinear optics and superconductivity.[10] Hummelen and co-workers[11] have developed organic transistors based on methanofullerene [6,6]-phenyl-C_{84}-butyric acid methyl ester ([84]PCBM), the higher analogue of [60]PCBM and [70]PCBM derivatives with reported good electron-transporting properties. [84]PCBM-based transistors, unlike its lower analogues, are stable to air and light, and are capable of functioning even after exposure to ambient air for long-standing periods of time. In this context, an easy, inexpensive and expeditious access to C_{84} would be highly desirable.



1 R=$C_{11}H_{23}$

Fig. 1 Structure of compound **1**.

We previously reported that cyclotriveratrylene (CTV)-based receptor **1** (Fig. 1) bearing three 4-ureidopyrimidinone (UPy) moieties dimerizes *via* three robust four-fold hydrogen bonding arrays into a supramolecular self-assembled capsule ($\mathbf{1}_2$) able to selectively encapsulate C_{70} over C_{60}. This nanocapsule was subsequently applied to the isolation of C_{70} from complex mixtures of fullerenes (fullerites).[12]

Subsequently to these studies, DFT calculations for the $\mathbf{1}_2$:C_{84} complex (Fig. 2) revealed that a better energy of interaction was predicted between C_{84} and the cage than for the complex with C_{70} or C_{60}.[13] Thus, dihedral angles between the UPy moieties calculated were 134° for C_{60} and 145.1° for C_{70},[12] whereas for the C_{84} complex the dihedral angle was calculated to be 149.4°, closer to the ideal planar conformation (180°) of the UPy-dimer.

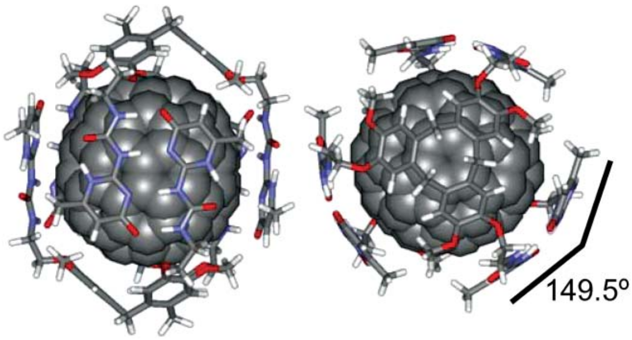


Fig. 2 Optimized model of $\mathbf{1}_2$:C_{84} complex.

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‡ Dedicated to Professor David N. Reinhoudt on the occasion of his 65th birthday.

Table 1 Association constants for $\mathbf{1}_2$:fullerene complexes

Complex	$K_{ass}(1:2\ \text{model})/M^{-2}$	$K_{ass}(1:1\ \text{model})/M^{-1}$
$\mathbf{1}_2$:C_{60}	1.93×10^6	1.82×10^3
$\mathbf{1}_2$:C_{70}	7.40×10^7	3.89×10^4
$\mathbf{1}_2$:C_{84}	2.63×10^{10}	3.70×10^5

In full agreement with these predictions, the association constant (UV-titration, tetrachloroethane, Table 1) of the $\mathbf{1}_2$:C_{84} complex was found to be one order of magnitude higher than those for the C_{60} and C_{70} complexes. In a 2 : 1 binding model the observed constant is K_3 (M^{-2}) = K_1K_2, where K_1 (M^{-1}) represents the binding of the guest with monomeric **1** whereas K_2 (M^{-1}) is the binding of this complex with another host **1** subunit. However, use of a carbamate analogue of **1** (which can not dimerize) as a model to weigh the contribution of K_1 revealed that no substantial binding with fullerenes was observed, so the binding is likely due to a partial disruption of an initial $\mathbf{1}_2$ capsule or a dimeric aggregate to accommodate the guest, in good agreement for the values calculated for a 1 : 1 binding mode.[12]

A ^{1}H NMR variable-temperature experiment (in tetrachloroethane-d_2) using receptor **1** and C_{84} displays sharp downfield NH signals for the dimer, even beyond 100 °C, indicating that this assembly is stronger that those formed with C_{60} and C_{70} (see ESI†).

In view of these results, solid-liquid extractions of fullerene mixtures (fullerite) were performed in THF, a solvent were fullerenes are poorly soluble. Fullerite composition was determined to be 65% of C_{60}, 22% of C_{70}, 5% of C_{84} and 8% of other materials. Variable concentrations of **1** were employed to optimise the selectivity for C_{84}. It was found that high receptor/fullerite ratios (*ca.* 50–60%) are better suited for a selective extraction of C_{70},[12] whereas the selectivity for C_{84} was maximised for *ca.* 5–15% receptor/fullerite ratios (Fig. 3).[14]

Indeed, the HPLC profiles (Fig. 4) indicate that beyond 10% any improvement in C_{84} extraction is accompanied by an exceedingly amount of C_{70}. It should be noted that the amount of C_{60} extracted remains constant at all ratios of extractant, indicating that this represents the inherent solubility of C_{60} in THF.

The amount of solvent (concentration) was also relevant. Indeed, better values for selectivity were achieved when the amount of solvent was reduced, as the amount of C_{60} solubilised decreased (see ESI†). Enrichment in C_{84} up to 76% was thus achieved after one single extraction, with a 75% C_{84} recovery. Thus, further extractions of the resulting C_{84}-enriched mixture did not result in any improvement of C_{84} purity due to the inherent solubilities of residual C_{60} and C_{70}. However, wash-out with some THF allowed the purity of C_{84} to rise up to 85%.

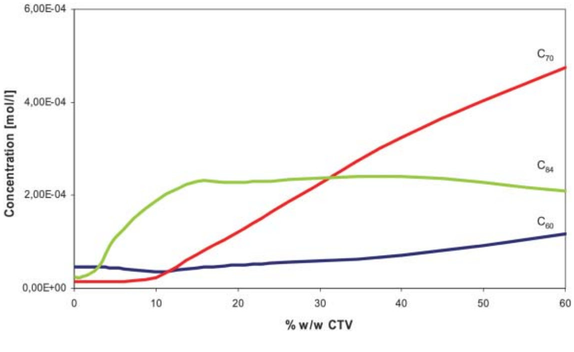

Fig. 3 Plot of concentration of fullerenes extracted against amount of receptor **1** used (w/w with respect to the solid fullerite).

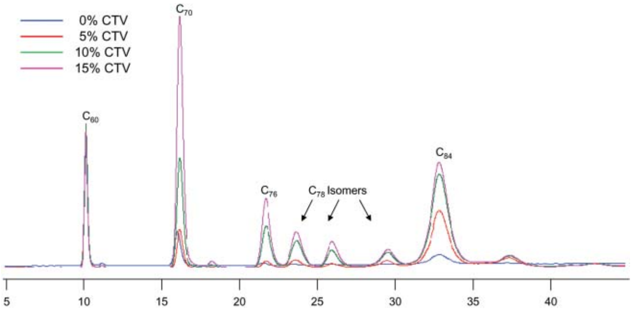

Fig. 4 HPLC profiles of extractions with different amounts of **1**. Cosmosil buckyprep-M column 4.6 × 250 mm; mobile phase: toluene–methanol (80 : 20); flow rate: 1 mL min^{-1}; T = 30 °C; detection wavelength: 290 nm.

Splitting of some signals in the NMR spectra (see ESI†) could be due to encapsulation of different C_{84} constitutional isomers as well as to the presence of diastereomeric complexes, since both the host and several C_{84} isomers are chiral. The extraction of at least two constitutional isomers was evidenced from the HPLC profiles. However, the presence of diastereoisomers in the NMR spectra was not further investigated.

In conclusion, receptor **1** has been revealed as a useful and practical tool for the selective removal of fullerenes from fullerite and fullerene mixtures derived from soot, based on a expeditious solid-liquid single extraction in THF, with high recovery efficiencies and not requiring chromatography or tedious separations. At high receptor/fullerite ratios, C_{70} is selected, whereas C_{84} enrichment is observed at low ratios. The purity of the extracted samples is only limited by the solubility of C_{60} and other fullerenes in THF, which prevents extraction of C_{84} beyond *ca.* 85% purity. A more suitable solvent, such acetonitrile,[15] would require a modified host with enhanced solubility in this solvent.[16] We are currently working in this direction, along to developing modified, longer capsules for fullerenes even higher than C_{84}.

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Notes and references

1 F. Diederich, R. Ettl, Y. Rubin, R. L. Wetthen, R. Beck, M. Álvarez, S. J. Anz, D. Sensharma, F. Wuld, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548.
2 (*a*) E. Ettl, F. Diederich and R. L. Whetten, *Nature*, 1991, **353**, 149; (*b*) F. Diederich, C. Thilgen, R. L. Whetten, E. Ettl, I. Chao and M. M. Alvarez, *Science*, 1991, **254**, 1768; (*c*) T. J. S. Dennis, T. Kai, T. Tomiyama and H. Shinohara, *Chem. Commun.*, 1998, 619.
3 For instance, current price for C_{84} is 50 US\$ mg^{-1} (SES Research, 98+% purity).
4 T. Haino, C. Fukunaga and Y. Fukazawa, *Org. Lett.*, 2006, **8**, 3545.
5 Y. Shoji, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2004, **126**, 6570.
6 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.

7 D. E. Manolopoulos and P. W. Fowler, *J. Chem. Phys.*, 1992, **96**, 7603.

8 (*a*) J. M. Hawkins, M. Nambu and A. Meyer, *J. Am. Chem. Soc.*, 1994, **116**, 7642; (*b*) J. Crassous, J. Rivera, N. S. Fender, L. H. Shu, L. Echegoyen, C. Thilgen, A. Herrmann and D. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1613; (*c*) G. W. Wang, M. Saunders, A. Khong and R. J. Cross, *J. Am. Chem. Soc.*, 2000, **122**, 3216; (*d*) R. Nuffer, A. Bartl, L. Dunsch and C. Mathis, *Synth. Met.*, 2001, **121**, 1151; (*e*) T. Wakahara, A. H. Han, Y. Niino, Y. Maeda, T. Akasaka, T. Suzuki, K. Yamamoto, M. Kako, Y. Nakadaira, K. Kobayashi and S. Nagase, *J. Mater. Chem.*, 2002, **12**, 2061; (*f*) A. D. Darwish, N. Martsinovich and R. Taylor, *Org. Biomol. Chem.*, 2004, **2**, 1364.

9 K. Shibata, Y. Kubozono, T. Kanbara, T. Hosokawa, A. Fujiwara, Y. Ito and H. Shinohara, *Appl. Phys. Lett.*, 2004, **84**, 2572.

10 (*a*) K. Harigaya, *J. Lumin.*, 1998, **76–77**, 652; (*b*) M. S. Denning, T. S. J. Dennis, M. J. Rosseinsky and H. Shinohara, *Chem. Mater.*, 2001, **13**, 4753; (*c*) E. Koudoumas, M. Konstantaki, A. Mavromanolakis, X. Michaut, S. Couris and S. Leach, *J. Phys. B*, 2001, **34**, 4983.

11 (*a*) F. B. Kooistra, V. D. Mihailetchi, L. M. Popescu, D. Kronholm, P. W. M. Blom and J. C. Hummelen, *Chem. Mater.*, 2006, **18**, 3068; (*b*) D. Anthopoulos, F. B. Kooistra, H. J. Wondergem, D. Kronholm, J. C. Hummelen and D. M. de Leeuw, *Adv. Mater.*, 2006, **18**, 1679.

12 E. Huerta, G. Metselaar, A. Fragoso, E. Santos, C. Bo and J. Mendoza, *Angew. Chem., Int. Ed.*, 2007, **46**, 202.

13 E. Santos and C. Bo, manuscript in preparation.

14 See ESI† for quantitative data on extractions, Table S4.

15 Solubility of C_{60} in THF was monitored by HPLC to be 18 μg ml^{-1}, whereas it was negligible in acetonitrile.

16 Preliminary experiments using **1** in a 4 : 1 THF–acetonitrile mixture (5% host/fullerite ratio) resulted in 85% C_{84} enrichment in a single extraction, although with a low recovery, due to the insolubility of the host in this solvent mixture.