

The self-assembly of fullerene-containing [2]pseudorotaxanes: formation of a supramolecular C₆₀ dimer

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With its unique chemical and physical properties, C₆₀ is an attractive molecule to be incorporated into molecular assemblies and supramolecular arrays. This paper reports the syntheses of a C₆₀ derivative with the macrocyclic polyether dibenzo-24-crown-8 (DB24C8) attached to the carbon sphere and of a C₆₀ adduct with a dibenzylammonium salt covalently bonded to the carbon allotrope. The C₆₀ DB24C8 conjugate forms a stable, pseudorotaxane-like 1 : 1 complex ($\Delta G^\circ = -16.6 \text{ kJ mol}^{-1}$, $T = 298 \text{ K}$, CDCl₃-CD₃CN 1 : 1) with dibenzylammonium hexafluorophosphate. Evidence for this superstructure was provided by ¹H NMR spectroscopic studies in solution and by mass spectrometric investigations in the gas phase. Equally, the C₆₀ dibenzylammonium conjugate threads through the cavity of DB24C8 to form a 1 : 1 complex with a pseudorotaxane-like geometry ($\Delta G^\circ = -23.3 \text{ kJ mol}^{-1}$, CDCl₃). Furthermore, the C₆₀ DB24C8 adduct and the C₆₀ dibenzylammonium conjugate interact with each other by means of hydrogen bonding and ion-dipole interactions to form the first supramolecular C₆₀ dimer ($\Delta G^\circ = -17.0 \text{ kJ mol}^{-1}$, CDCl₃-CD₃CN 90 : 10). In all three cases, the dibenzylammonium component is threaded through the cavity of the crown ether macrocycle. When DB24C8 is complexed to the C₆₀ dibenzylammonium conjugate, the luminescence associated with the catechol rings of the crown ether is partially quenched upon complex formation. We have profited from this special feature to monitor reversible, acid-base induced dethreading/rethreading processes.

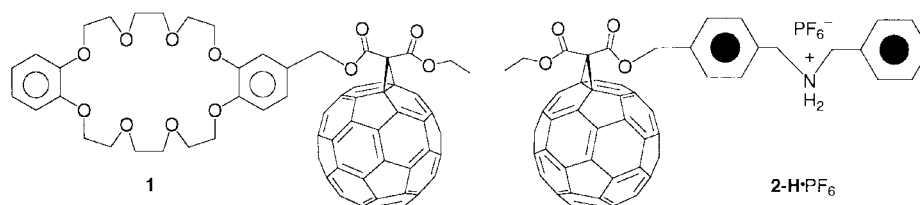
Introduction

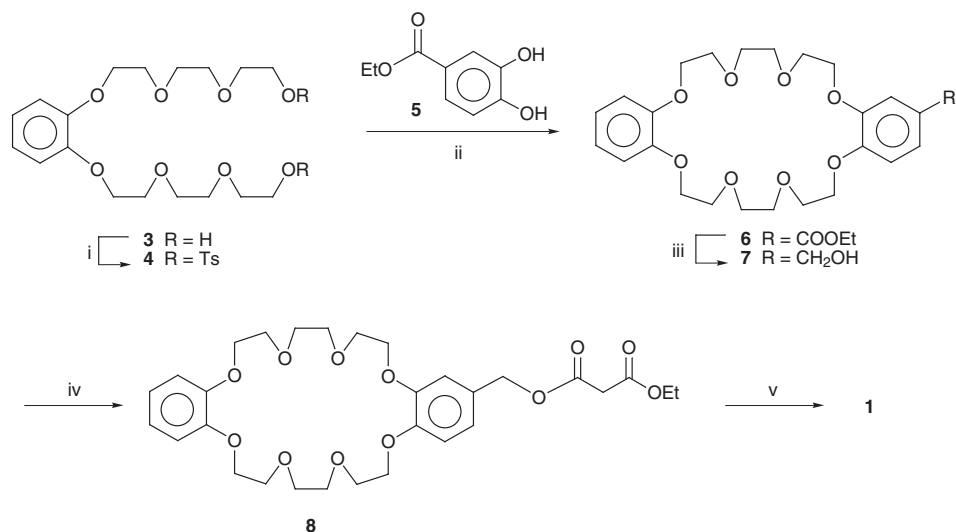
Whereas the covalent functionalisation of buckminsterfullerene, C₆₀, has seen a dramatic development,¹ the supramolecular aspects of its chemistry have not been explored to the same extent.² Supramolecular chemistry exploits non-covalent bonding interactions in order to construct large, yet ordered, molecular assemblies and supramolecular arrays³ with the potential for a wide range of real-life applications.⁴ The unique physical and chemical properties of covalent derivatives of C₆₀—such as their electronic absorption bands expanding through the whole UV/Vis spectral region,⁵ their singlet oxygen sensitising ability⁶ or their pronounced electron acceptor character⁷ make them attractive candidates to furnish functional supramolecular architectures with novel properties.^{2,8,9}

The research group of one of us (J. F. S.) discovered recently that the complexation of secondary ammonium salts (RR'NH₂⁺X⁻) by suitably sized crown ethers—such as dibenzo-24-crown-8 (DB24C8) and bis-*p*-phenylene-34-crown-10 (BPP34C10)—gives rise to a new family of complexes with pseudorotaxane-like¹⁰ geometries.¹¹ The linear ammonium ion threads through the cavity of the macrocyclic polyether; the

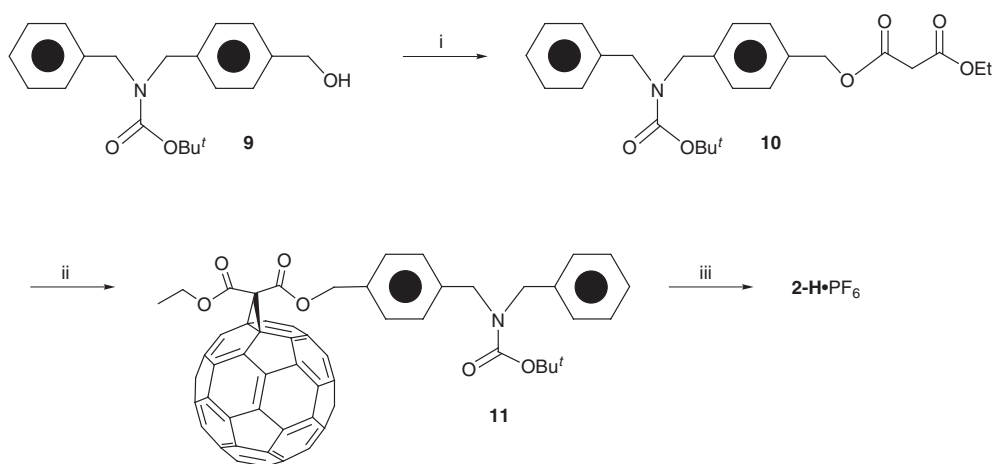
stoichiometry of the complex is determined by the size of the crown ether and the number of ammonium centres (–NH₂⁺) present in the thread-like component.¹¹ The main driving forces for formation of these superstructures are [N⁺–H···O] and [C–H···O] hydrogen bonds as well as contributions from ion-pairing and dispersive interactions.¹² These molecular recognition motifs have been exploited to harness numerous aesthetically appealing interlocked and/or threaded architectures such as [n]rotaxanes,¹³ chemically controllable molecular shuttles,¹⁴ a quadruple-stranded [5]pseudorotaxane accommodating one hexafluorophosphate counterion in the second coordination sphere of the crown ether component,¹⁵ an interwoven molecular cage,¹⁶ an artificial analogue of the photosynthetic special pair,¹⁷ and daisy chain-like oligomers.¹⁸

Here, we report the incorporation of fullerenes into both a DB24C8 macrocyclic polyether derivative¹⁹ and a secondary ammonium salt to give **1** and **2-H·PF₆**, respectively. The formation of pseudorotaxane-like complexes in solution and the gas phase is described, including the first example—to the best of our knowledge—of a supramolecular fullerene dimer.^{20,21} Furthermore, we show that the threading of a fullerene-containing diammonium salt into DB24C8 changes the luminescence properties of the catechol rings in the





Scheme 1 Synthesis of the fullerene DB24C8 conjugate **1**. i, TsCl, Et₃N, DMAP, CH₂Cl₂, 1 h, 0→20 °C, 82%; ii, K₂CO₃, LiBr (cat.), MeCN, 60 h, Δ, 56%; iii, LiAlH₄, THF, 3 h, Δ, 91%; iv, EtO₂CCH₂COCl, pyridine, CH₂Cl₂, 3 h, 0→20 °C, 53%; v, C₆₀, DBU, I₂, 12 h, 20 °C, 46%.



Scheme 2 Synthesis of the fullerene ammonium salt **2-H•PF₆**. i, EtO₂CCH₂COCl, pyridine, CH₂Cl₂, 1 h, 0→20 °C, 48%; ii, C₆₀, DBU, I₂, 10 h, 20 °C, 43%; iii, 1) CF₃COOH, CHCl₃, 12 h, 20 °C; 2) Conc. HCl, CHCl₃; 3) NH₄PF₆, H₂O–acetone, 82%.

crown ether, which could be exploited in chemical sensing or in information storage at the molecular level.

Results and discussion

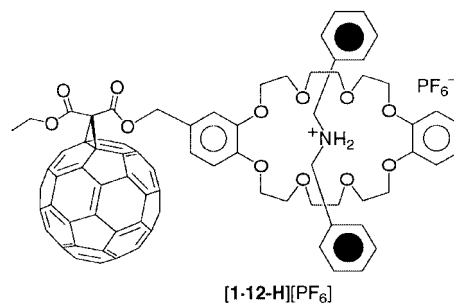
Synthesis

For the synthesis of **1** (Scheme 1), diol **3**²² was converted to the tosylate **4** using a standard procedure (toluene-*p*-sulfonyl chloride (TsCl)–Et₃N–4-(dimethylamino)pyridine (DMAP)). The crown ether **6** was obtained in 56% yield by macrocyclisation (K₂CO₃–MeCN) of **4** with ethyl 3,4-dihydroxybenzoate (**5**) under semi-high dilution conditions. Reduction with LiAlH₄ produced benzyl alcohol **7** which was reacted with ethyl malonyl chloride in the presence of pyridine to provide the malonate-appended crown **8**. Modified Bingel reaction^{23,24} (1,8-diazabicyclo[5.4.0]undec-7-ene (1,5-5) (DBU), I₂) of C₆₀ with **8** finally afforded methanofullerene **1** in 46% yield.

The preparation of the fullerene-containing ammonium salt **2-H•PF₆** started with the reaction of the previously described benzyl alcohol **9**²⁵ with ethyl malonyl chloride to provide malonate **10** (Scheme 2). Bingel reaction (DBU–I₂) of **10** with C₆₀ afforded the methanofullerene **11** which was deprotected (CF₃COOH–CH₂Cl₂), protonated (HCl) and subjected to ion exchange (NH₄PF₆–H₂O–acetone) to yield **2-H•PF₆** (Scheme 2).

¹H NMR complexation studies

In a first study, we investigated the ability of the fullerene crown ether conjugate **1** to form a [2]pseudorotaxane-like complex with dibenzylammonium hexafluorophosphate (**12-H•PF₆**). This salt, despite being highly soluble in MeOH, Me₂CO and MeCN, is virtually insoluble in CHCl₃ and CH₂Cl₂. Upon addition of **1**, it becomes soluble in CH₂Cl₂ and CHCl₃ solutions, which provides a first evidence for complex formation.^{11a}



The ¹H NMR spectrum (300 MHz, 298 K) of a 1 : 1 mixture of **1** and **12-H•PF₆** in CDCl₃ showed very broad signals and displayed multiple resonances compared with the spectra of the free species. The complicated pattern seems to indicate that

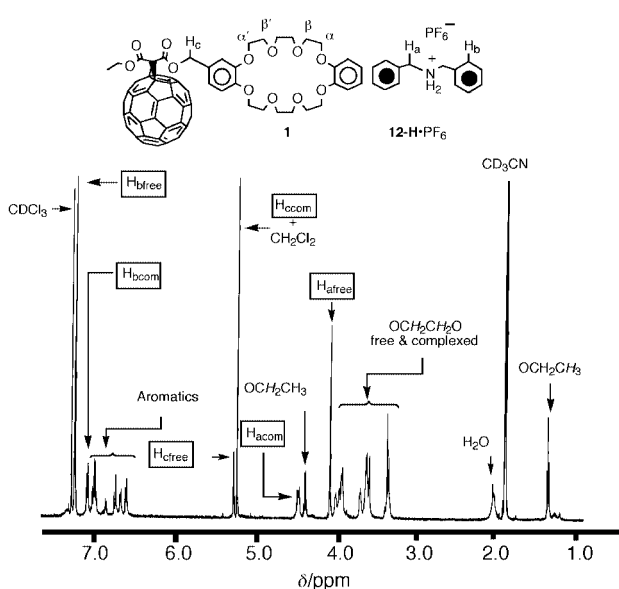


Fig. 1 ^1H NMR spectrum (500 MHz, 298 K, CDCl_3 – CD_3CN 1:1) of a 1:1 mixture of the crown ether fullerene conjugate **1** and the secondary ammonium salt **12-H**· PF_6^- ; $c = 3.8$ mM.

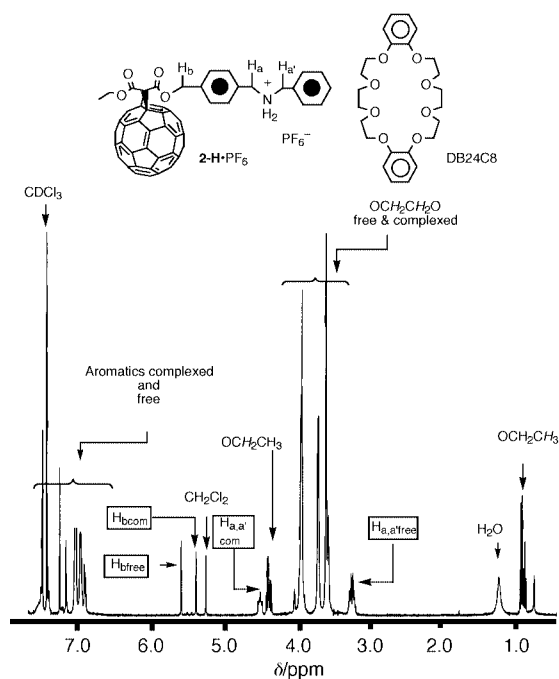


Fig. 2 ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of a 1:1 mixture of DB24C8 and the fullerene ammonium salt conjugate **2-H**· PF_6^- , $c = 3.8$ mM.

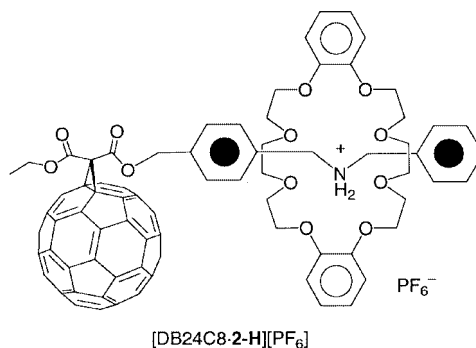
complexation is indeed taking place. Nevertheless, the broadness of the resonances does not allow for precise analysis of the process of complex formation. The broad nature of the signals in the ^1H NMR spectrum in CDCl_3 could be attributed to some kind of aggregation.

Upon addition of a more protic solvent, such as CD_3CN or CD_3COCD_3 , a sharpening of the resonances is observed. The ^1H NMR spectrum (500 MHz, 298 K) of a 1:1 mixture of **1** and **12-H**· PF_6^- ($c = 3.8$ mM) in CDCl_3 – CD_3CN 1:1 displays three sets of resonances which correspond to the two free components and the 1:1 complex **[1·12-H]**· PF_6^- , respectively (Fig. 1). Apparently, host–guest exchange is slow on the ^1H NMR time scale at room temperature.^{11a} Integration of the signals for the complexed species proves the formation of a 1:1 complex and evaluation of the signal intensities of the three

species in equilibrium affords the association constant $K_a = 820$ M^{-1} and the binding free energy $\Delta G^\circ = -16.6$ kJ mol^{-1} .

The multiplet at $\delta = 4.60$ ppm corresponds to the CH_2 protons (H_{acom} , Fig. 1) of the complexed ammonium salt and is the most diagnostic signal²⁶ for complex formation. The pseudorotaxane geometry of **[1·12-H]**· PF_6^- was confirmed by NOE spectroscopy.^{11a} Irradiation of the signals of the crown ether OCH_2 protons—probably the β and β' protons (Fig. 1)—enhances the intensities of the resonances assigned to the aromatic protons H_{bcom} and the benzylic protons H_{acom} belonging to complexed **12-H**· PF_6^- . These results are indicative of the threading of the latter component through the crown ether cavity of **1**, since examinations of space filling models show that the protons H_{bcom} and H_{acom} and the crown ether OCH_2 protons come in close spatial proximity in a pseudorotaxane-like complex. For the complex between DB24C8 and **12-H**· PF_6^- , the presumed co-conformation of the components has been supported by X-ray crystallographic studies.^{11a}

Next, the complexation of the fullerene ammonium salt conjugate **2-H**· PF_6^- with DB24C8 was investigated. Again, the ammonium salt is only slightly soluble in solvents such as CH_2Cl_2 and CHCl_3 , but is readily solubilised upon addition of DB24C8. The ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of a 1:1 mixture of **2-H**· PF_6^- and DB24C8 ($c = 3.8$ mM; Fig. 2) shows three sets of resonances, two for the free components and one for the complex, in agreement with slow host–guest exchange. The association constant for the formed 1:1 complex **[DB24C8·2-H]**· PF_6^- in CDCl_3 was calculated to be $K_a = 12500$ M^{-1} ($\Delta G^\circ = -23.3$ kJ mol^{-1}) and is of similar magnitude to that reported for the 1:1 complex formed between DB24C8 and **12-H**· PF_6^- ($K_a = 27000$ M^{-1}) in that solvent.^{11a} The ^1H NMR spectrum resembles the one recorded for the 1:1 mixture of **1** and **12-H**· PF_6^- (Fig. 1) and displays the diagnostic signal for the CH_2N protons of the complexed ammonium salt as a multiplet at $\delta = 4.62$ ppm.



Finally, the complexation between the two fullerene derivatives **1** and **2-H**· PF_6^- was studied. Again, the fullerene-conjugated ammonium salt **2-H**· PF_6^- becomes readily soluble in solvents such as CH_2Cl_2 and CHCl_3 upon addition of the crown ether **1**. The ^1H NMR spectrum (300 MHz, 298 K) in CDCl_3 showed a complicated pattern with broad resonances, indicative of aggregation, and a precipitate was observed to form within a few minutes. Upon addition of a more polar solvent such as CD_3COCD_3 and/or CD_3CN , the solubility increased and the resonances sharpened. The ^1H NMR spectrum (500 MHz, CDCl_3 – CD_3CN 90:10, 298 K) of a 1:1 mixture of **1** and **2-H**· PF_6^- ($c = 1.5$ mM; Fig. 3) displayed three sets of resonances which could be readily assigned to the individual components and the 1:1 complex **[1·2-H]**· PF_6^- , respectively. The association constant was determined as $K_a = 970$ M^{-1} ($\Delta G^\circ = -17.0$ kJ mol^{-1}). The diagnostic, strongly downfield shifted resonance for the CH_2N protons of complexed **2-H**· PF_6^- appears as a broad multiplet at $\delta = 4.58$ ppm. The topology of this first example of a supramolecular fullerene dimer was studied by

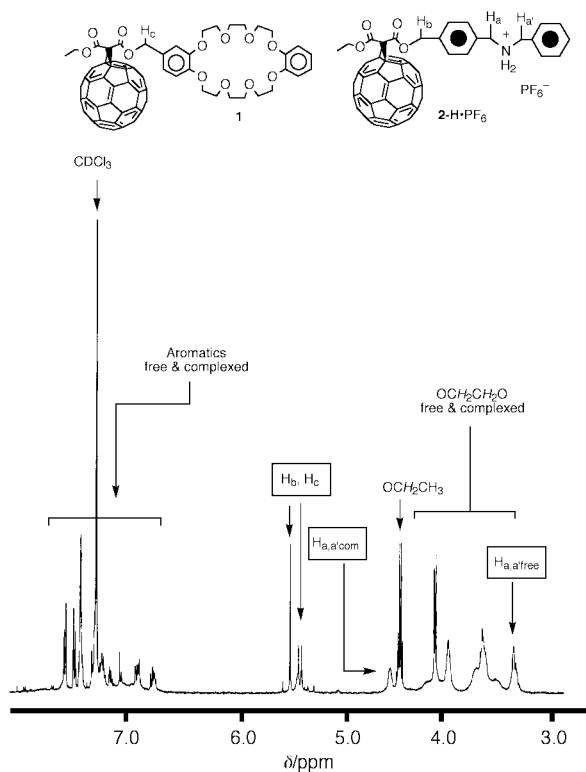
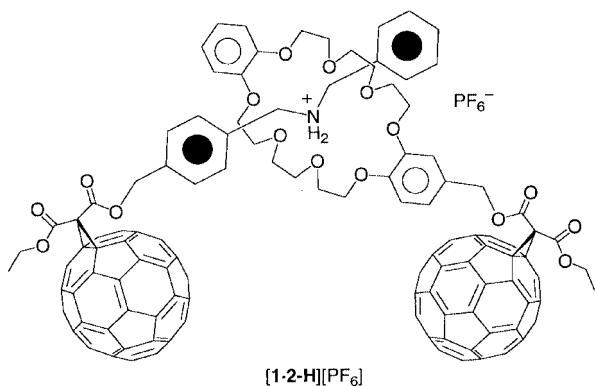


Fig. 3 ^1H NMR spectrum (500 MHz, 298 K, CDCl_3 - CD_3CN 9:1) of a 1:1 mixture of the fullerene conjugates **1** and **2-H**· PF_6 , $c = 1.5$ nm.



molecular modelling²⁷ which suggested a centre-to-centre distance between the two carbon spheres of *ca.* 20 Å (Fig. 4).

Mass spectrometric studies

The formation of the 1:1 complexes $[\mathbf{1}\cdot\mathbf{2-H}][\text{PF}_6]$, $[\text{DB24C8}\cdot\mathbf{2-H}][\text{PF}_6]$ and $[\mathbf{1}\cdot\mathbf{2-H}][\text{PF}_6]$ was also evidenced in the gas phase by matrix assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectrometry in the positive ion mode. The matrix in each case was 2,5-dihydroxybenzoic acid (2,5-DHB). The spectrum recorded from a 1:1 mixture of the fullerene crown ether conjugate **1** and ammonium salt **2-H**· PF_6 displayed an intense peak at m/z 1655 (Fig. 5) which corresponds to the supramolecular ion $[\mathbf{1}\cdot\mathbf{2-H}\cdot\text{PF}_6]^+$. The base peak is detected at m/z 1511 which can be assigned to the 1:1 complex after loss of the PF_6^- counterion.

The detection of the two other supramolecular complexes by MALDI-TOF mass spectrometry was similarly successful. In the spectrum obtained from a 1:1 mixture of DB24C8 and the fullerene ammonium salt conjugate **2-H**· PF_6 , the base peak is observed at m/z 1511 which corresponds to the supramolecular ion of the 1:1 complex minus the PF_6^- counterion, *i.e.* $[\text{DB24C8}\cdot\mathbf{2-H}]^+$ (Fig. 6). A peak of less intensity—at m/z

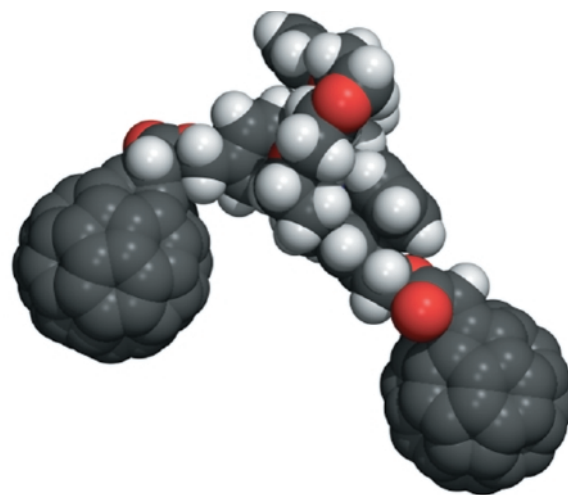


Fig. 4 Space-filling representation of the geometry-optimised supramolecular fullerene dimer $[\mathbf{1}\cdot\mathbf{2-H}][\text{PF}_6]$. In the molecular mechanics calculations, the ethoxycarbonyl groups have been substituted by hydrogens for computational ease.

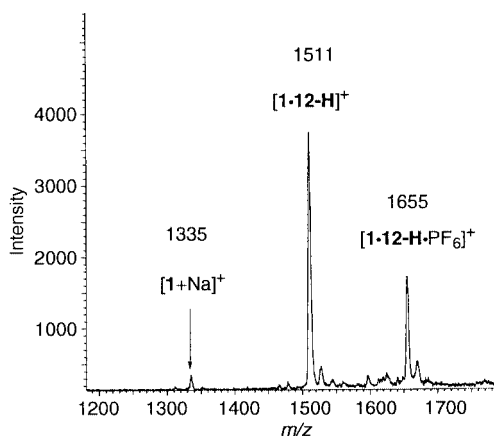


Fig. 5 MALDI-TOF mass spectrum of a 1:1 mixture of the fullerene crown ether conjugate **1** and **2-H**· PF_6 ; matrix: 2,5-DHB.

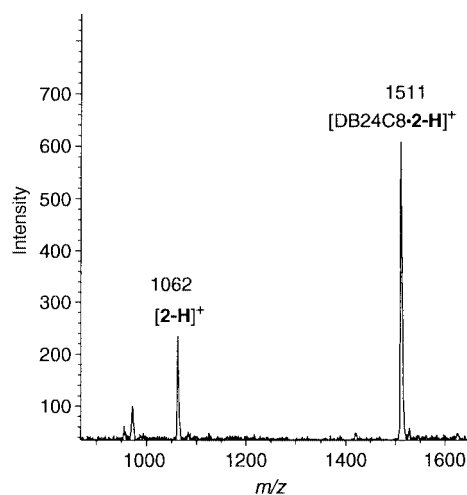
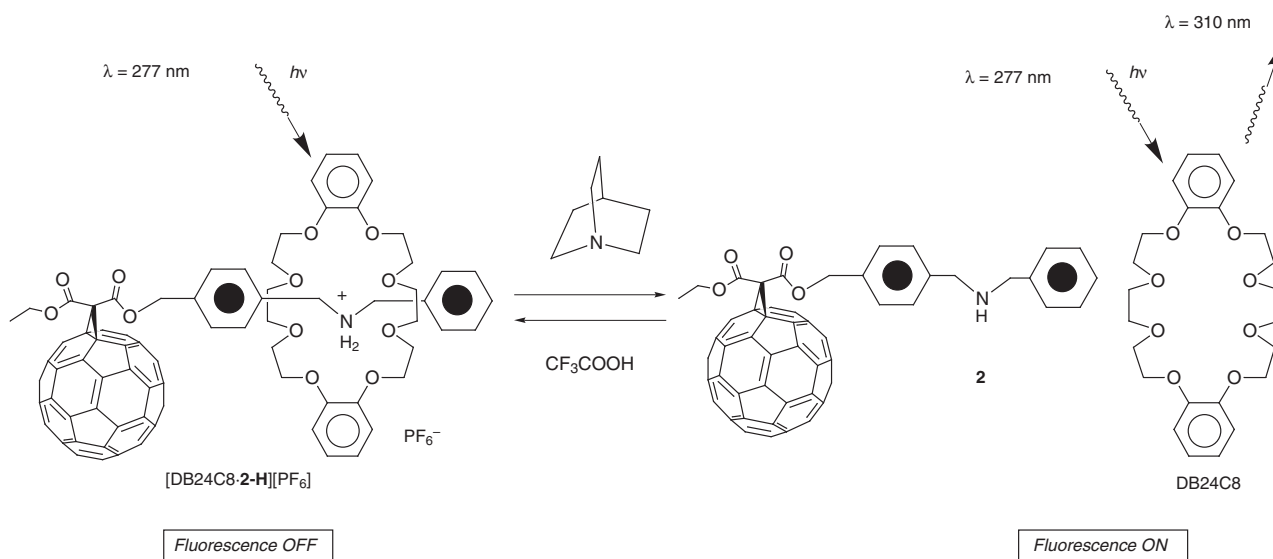


Fig. 6 MALDI-TOF mass spectrum of a 1:1 mixture of DB24C8 and the fullerene ammonium salt conjugate **2-H**· PF_6 ; matrix: 2,5-DHB.

1062—can be assigned to the molecular ion of the fullerene ammonium salt conjugate minus the PF_6^- counterion.

Furthermore, the MALDI-TOF mass spectrum of a 1:1 mixture of the two fullerene conjugates **1** and **2-H**· PF_6 displays a strong peak at $m/z = 2373$ which corresponds to the supramolecular ion minus the PF_6^- counterion (Fig. 7). The base peak is observed at $m/z = 1335$ and can be assigned to the



Scheme 3 A reversible acid–base controlled de-/rethreading process. The two states can be monitored by the on/off-switching of the fluorescence of the crown ether component.

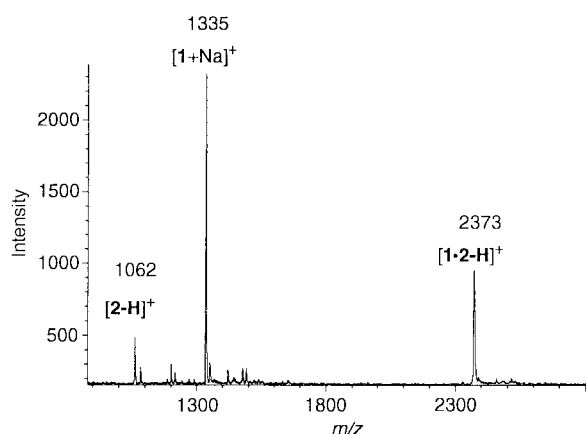


Fig. 7 MALDI-TOF mass spectrum of a 1:1 mixture of the fullerene conjugates **1** and **2-H·PF₆**; matrix: 2,5-DHB.

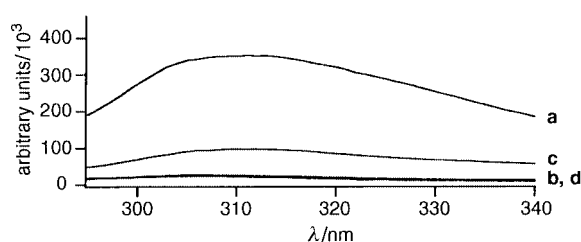


Fig. 8 Fluorescence spectra ($\lambda_{\text{exc}} = 277 \text{ nm}$, CH_2Cl_2) of (a) a solution of pristine DB24C8; (b) a solution of DB24C8 after the addition of 1 equiv. **2-H·PF₆**; (c) solution (b) after adding 1.5 equiv. of quinuclidine; (d) solution (c) after adding 1.75 equiv. of CF_3COOH .

sodium complex of **1**. A smaller peak at $m/z = 1062$ corresponds to the molecular ion of the fullerene ammonium conjugate after loss of the PF_6^- counterion.

Fluorescence studies

We made a series of interesting observations when the complexation between DB24C8 and the fullerene-containing ammonium salt **2-H·PF₆** was investigated by luminescence studies. Preliminary results are reported here.

It is known that the catechol rings in DB24C8 exhibit an intense short-lived fluorescence at $\lambda_{\text{max}} = 310 \text{ nm}$ when irradiated at $\lambda_{\text{exc}} = 277 \text{ nm}$.²⁸ A very large decrease in intensity of this luminescence was observed when the fullerene ammo-

onium salt conjugate **2-H·PF₆** was added to a CH_2Cl_2 solution of DB24C8 (Fig. 8). Since **2-H·PF₆** features a strong absorption at $\lambda = 277 \text{ nm}$, this decrease can be attributed, at least partially, to the fact that the fullerene component is absorbing some of the photons previously employed to excite the catechol units in DB24C8.

Subsequent experimentation suggested that some of the decrease in luminescence intensity also originates from either energy or electron transfer from the photoexcited DB24C8 donor to the fullerene acceptor in the supramolecular complex **[DB24C8·2-H][PF₆]**.^{8f,9d,29} The 1:1 complex in CH_2Cl_2 was treated with the non-nucleophilic base quinuclidine with the expectation that it would deprotonate the $-\text{NH}_2^+$ centre, thereby disrupting the noncovalent bonding interactions that initially brought the components together and, hence, promoting (Scheme 3) the dethreading of the linear component. When 1.5 equivalents of quinuclidine were added, around one fourth of the initial fluorescence intensity was recovered (Fig. 8). This result seems to indicate that the [2]pseudo-rotaxane **[DB24C8·2-H][PF₆]** undergoes a disassembly process after the deprotonation of the $-\text{NH}_2^+$ centre and, hence, the luminescence of the catechol rings is partially restored. The total recovery of the DB24C8 luminescence is not possible since after dethreading, the C_{60} unit in amine **2** is still absorbing strongly at $\lambda_{\text{exc}} = 277 \text{ nm}$. Addition of 1.75 equivalents of trifluoroacetic acid results again in the complete disappearance of the fluorescence band at $\lambda_{\text{max}} = 310 \text{ nm}$. This observation suggests that the $-\text{NH}_2^+$ centre is regenerated and rethreading (Scheme 3) of the linear component through the cavity of DB24C8 is taking place, thus rendering the assembly/disassembly process reversible.

Although the difference in signal intensity between the two states—“on” and “off”—is relatively small,³⁰ the observation that the photophysical properties of the 1:1 complex differ significantly from those of the individual species—and from those of the corresponding supramolecular systems lacking the C_{60} moiety—is of significance and further investigations on the nature of the luminescence quenching in this supramolecular switching system are undertaken.

Electrochemical studies

The redox properties of the fullerene conjugates and their complexes were studied by cyclic voltammetry (CV) at room temperature in CH_2Cl_2 –MeCN 1:1 or in pure CH_2Cl_2 (+0.1 M Bu_4NPF_6) and potentials were measured against the ferrocene/ferrocinium (Fc/Fc^+) couple as internal reference (Table 1).^{7a}

Table 1 Redox parameters of the fullerene adducts and their complexes^a

Compound	Solvent	$E^1_{1/2}$ (red.)	$E^2_{1/2}$ (red.)	$E^3_{1/2}$ (red.)
1	CH ₂ Cl ₂ -MeCN 1:1	-1.0 (80)	-1.41 (90)	
[1 · 12-H][PF ₆]	CH ₂ Cl ₂ -MeCN 1:1	-1.0 (82)	-1.41 (90)	
11	CH ₂ Cl ₂	-1.07 (78)	-1.46 (58)	-1.92 (83)
2-H ·PF ₆	CH ₂ Cl ₂	-1.06 (91)	-1.43 (103) ^b	-1.92 (75)
[DB24C8· 2-H][PF ₆]	CH ₂ Cl ₂	-1.03 (68)	-1.43 (58) ^b	-1.90 (81)
[1 · 2-H][PF ₆]	CH ₂ Cl ₂	-1.07 (140)	-1.48 (150)	-1.91

^a The values are given in V vs. Fc/Fc⁺; ΔE values in mV are in parentheses; solvent contains 0.1 M Bu₄NPF₆. ^b The presence of a shoulder at -1.58 V makes it difficult to exactly determine the value of $E^2_{1/2}$.

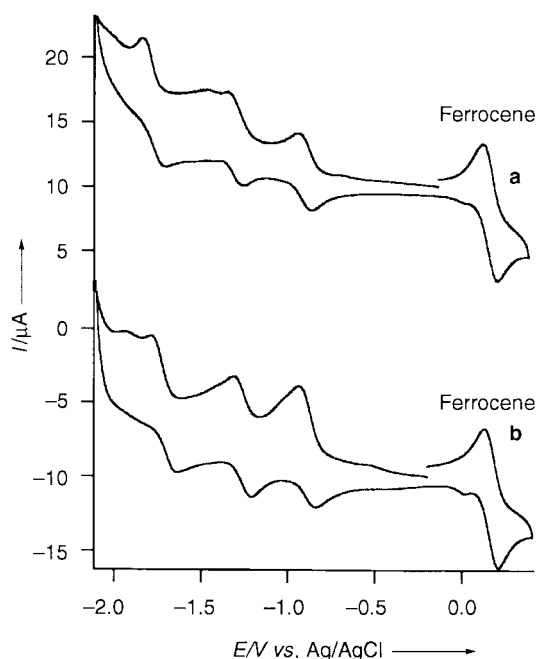


Fig. 9 Cyclovoltammograms in CH₂Cl₂ (+0.1 M Bu₄NPF₆) of (a) **2-H**·PF₆ and (b) [DB24C8·**2-H**][PF₆].

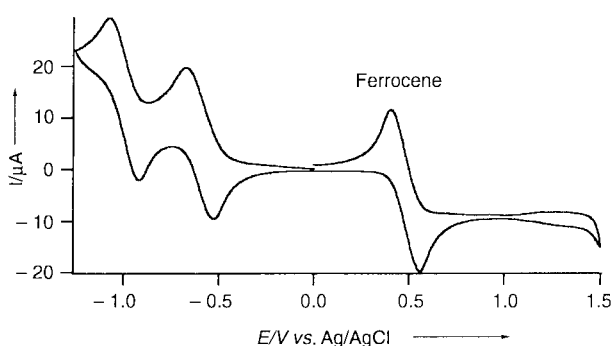


Fig. 10 Cyclovoltammogram of the supramolecular dimer [**1**·**2-H**][PF₆] in CH₂Cl₂ (+0.1 M Bu₄NPF₆).

For both free and complexed fullerene derivatives, two or three, mostly reversible C₆₀-centred reduction waves were observed at potentials similar to those measured previously for other methano[60]fullerenes.^{21b,31} The comparison between the redox properties of free and complexed fullerene conjugates revealed that complexation does not significantly influence the reduction potentials.

The CV of **2-H**·PF₆ (Fig. 9) shows a quasi-reversible first one-electron reduction wave at $E^1_{1/2} = -1.06$ V. This wave exhibits a shoulder which could be indicative of some irreversible chemical process taking place after one-electron reduction. The second reduction wave becomes chemically irreversible and it clearly shows an even larger shoulder at $E = -1.58$ V. This shoulder might arise from the formation

of a different fullerene-containing species—by means of an irreversible chemical process occurring after reduction. Furthermore, it was observed that after the first one-electron reduction a film starts to precipitate on the electrode making the monitoring of subsequent redox processes more difficult. The CV of the 1:1 mixture of the DB24C8 and **2-H**·PF₆ gave basically the same results.

The two first reduction waves in the CV of the solution of the supramolecular dimer [**1**·**2-H**][PF₆] are slightly broadened (Fig. 10), which seems to indicate that each wave corresponds to a two-electron transfer process involving reduction of both fullerene moieties in the complex. No evidence for possible electronic interactions between the two fullerenes within the supramolecular dimer was obtained, which can be explained by the large spatial distance between the two carbon spheres in the complex, as disclosed by the molecular modelling studies. This result is in agreement with electrochemical studies on covalent fullerene dimers.^{21b,31f}

Conclusions

The new methanofullerenes **1** and **2-H**·PF₆ feature molecular recognition motifs suitable for the construction of pseudorotaxane-like supramolecular architectures. In aprotic solvents, fullerene crown ether conjugate **1** forms a 1:1 complex with the dibenzylammonium salt **12-H**·PF₆ and the fullerene ammonium salt conjugate **2-H**·PF₆ complexes with DB24C8. Finally, **1** and **2-H**·PF₆ undergo association to form the first supramolecular C₆₀ dimer. The pseudorotaxane-like architectures of these complexes and their association strengths were derived from ¹H NMR spectroscopic measurements; furthermore, MALDI-TOF mass spectra revealed the high stability of these supramolecular species in the gas phase. Threading of the fullerene ammonium salt conjugate **2-H**·PF₆ into DB24C8 changes the luminescence properties of the catechol moieties in the crown ether and this property can be used to monitor the pH-dependent, reversible formation (on/off-switching) of the pseudorotaxane-like complex. By describing the construction of supramolecular fullerene materials whose properties can be tuned by external stimuli, this paper provides yet another example for the promising technological potential³² of the rapidly emerging field of supramolecular fullerene chemistry.

Experimental

General

Reagents and solvents were purchased reagent-grade and used without further purification, except for THF which was distilled in the presence of Na. Fullerene soot extract was purchased from MER Corporation, Tucson, Arizona (AZ) 85706, USA. All reactions were performed in standard glassware. Evaporation and concentration *in vacuo* were done at water aspirator pressure, and compounds were dried at 10⁻² Torr. Column chromatography (CC): SiO₂ 60 (230–400 mesh, 0.040–0.063 mm) from E. Merck. TLC glass plates coated with SiO₂ 60 F₂₅₄ from E. Merck; visualisation by UV light. UV/Vis

spectra: Varian Cary-5 spectrophotometer. Melting points: Büchi Melting Point B-540, uncorrected. IR spectra: Perkin-Elmer; 1600-FTIR. NMR Spectra: Bruker AM 500 and Varian Gemini 300 or 200 spectrometers at 298 K, with solvent peaks as reference. FABMS: VG ZAB 2SEQ instrument, 3-nitrobenzyl alcohol as matrix; MALDI-TOF-MS: measured with reflectron detection in the positive or negative ion mode, acceleration voltage 15–20 kV, on a Bruker REFLEX spectrometer; matrices are 2,5-dihydroxybenzoic acid (DBH, 0.1 M in MeCN–EtOH–H₂O 50:45:5), α -cyano-4-hydroxycinnamic acid (CCA, 0.1 M in MeCN–EtOH–H₂O 50:45:5) or anthracene-1,8,9-triol (dithranol, 0.05 M in CHCl₃–MeOH 1:1). Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. Compounds **3** and **9** were synthesised according to refs. 22 and 25, respectively.

Electrochemical studies

A 3 mm glassy carbon electrode was used as the working electrode, while a Pt wire served as the counter electrode. An aq. Ag/AgCl electrode, separated by a *Vycor* tip, was used as the reference. In every run, ferrocene (Fc) was added as an internal potential reference, and all the values reported in Table 1 are relative to the Fc/Fc⁺ couple. Typical scan rates were 100 mV s⁻¹, and the potentiostat used was an EG&G PAR model 263A.

Fluorescence studies

Fluorescence studies were performed with solutions (~10⁻⁵ M) of the fluorescent component DB24C8 to which was added sequentially 1 equiv. of **2-H**·PF₆, 1.5 equiv. of quinuclidine and 1.75 equiv. of CF₃COOH. Excitation occurred at $\lambda_{\text{exc}} = 277$ nm in a fluorescence spectrometer (Spex 1860) equipped with a 0.22 m double-grating monochromator and a 450 W xenon lamp with a band pass of 3.4 nm.

1,2-Phenylenebis(oxyethylenoxyethylenoxyethylene) ditosylate (4)

To **3** (9.0 g, 24 mmol), Et₃N (10.1 g, 100 mmol) and a catalytic amount of DMAP in CH₂Cl₂ (100 ml) at 0 °C under N₂ was added dropwise TsCl (11.5 g, 60 mmol) in CH₂Cl₂ (200 ml) and the solution was stirred at 0 °C for 1 h, then warmed to 20 °C. Filtration and concentration of the filtrate *in vacuo* left an oil which was taken up in CH₂Cl₂ and washed with 0.1 M HCl (2 × 200 ml) and sat. aq. NaCl solution (2 × 200 ml). Drying (MgSO₄) and evaporation *in vacuo*, followed by column chromatography (SiO₂, CH₂Cl₂, then CH₂Cl₂–MeOH 99:1) yielded **4** (13.46 g, 82%) as a colourless oil [Found: C, 56.42; H, 6.22. Calc. for C₃₂H₄₂O₁₂S₂ (682.81): C, 56.29; H, 6.20%]; ν_{max} (KBr)/cm⁻¹ 2923, 2869, 1592, 1600, 1446, 1358, 1169, 1123, 915, 761, 653, 546; δ_{H} (200 MHz, CDCl₃) 2.42 (6 H, s), 3.59–3.61 (4 H, m), 3.65–3.79 (8 H, m), 3.81–3.84 (4 H, m), 4.11–4.18 (8 H, m), 6.91 (4 H, s), 7.33 (4 H, “d”, *J* 8.1), 7.79 (4 H, “d”, *J* 8.1); δ_{C} (50 MHz, CDCl₃) 19.11, 51.10, 66.28, 66.43, 66.91, 67.42, 68.37, 112.59, 119.35, 125.63, 127.54, 130.68, 142.55, 146.71; *m/z* (FABMS) 682 (M⁺, 100%).

Ethyl 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b,n*][1,4,7,10,13,16,19,22]octaoxacyclotetrasilicose-2-carboxylate (6)

A solution of **5** (1.62 g, 9.0 mmol), K₂CO₃ (5.04 g, 36 mmol) and a catalytic amount of LiBr in MeCN (1 l) was heated to reflux under N₂ for 1 h. A solution of **4** (6.14 g, 9.0 mmol) in MeCN (500 ml) was added dropwise over 12 h and the mixture was heated to reflux for 48 h. Filtration and concentration of the filtrate *in vacuo* left an oil which was taken up in CH₂Cl₂ (200 ml) and washed with 0.1 M HCl (2 × 200 ml) and sat. aq. NaCl solution (200 ml). Drying (MgSO₄) and evaporation *in vacuo* followed by column chromatography (SiO₂, CH₂Cl₂–

MeOH 99:1, then CH₂Cl₂–MeOH 98:2) afforded **6** (2.62 g, 56%) as a white solid: mp 79.2–79.5 °C [Found: C, 62.11; H, 6.96. Calc. for C₂₇H₃₆O₁₀ (520.58): C, 62.30; H, 6.97%]; ν_{max} (KBr)/cm⁻¹ 3461, 1923, 1707, 1592, 1500, 1269, 1246, 1200, 1123, 731; δ_{H} (200 MHz, CDCl₃) 1.37 (3 H, t, *J* 7.0), 3.79–3.86 (8 H, m), 3.90–3.98 (8 H, m), 4.13–4.24 (8 H, m), 4.34 (2 H, q, *J* 7.0), 6.85 (1 H, d, *J* 8.3), 6.86–6.90 (4 H, m), 7.54 (1 H, d, *J* 2.0), 7.65 (1 H, dd, *J* 2.0, 8.3); δ_{C} (50 MHz, CDCl₃) 11.87, 51.04, 58.34, 66.88, 67.01, 67.10, 67.23, 67.39, 67.54, 68.88, 68.94, 69.04, 109.70, 111.73, 112.05, 119.09, 120.90, 121.51, 126.01, 126.04, 145.95, 146.64, 150.55, 164.07; *m/z* (FABMS) 475 ([M – OEt]⁺, 100), 520 (M⁺, 77), 543 ([M + Na]⁺, 11%).

6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b,n*]-[1,4,7,10,13,16,19,22]octaoxacyclotetrasilicose-2-ylmethanol (7)

LiAlH₄ (1 M in THF) (12.1 ml) was added under N₂ to a solution of **6** (1.26 g, 2.4 mmol) in THF (200 ml). The mixture was stirred for 1 h at 20 °C, then heated to reflux for 2 h. After cooling, H₂O was added dropwise (**very carefully!**) to destroy the excess of LiAlH₄. The suspension was washed with CH₂Cl₂ (3 × 100 ml), the combined organic phases were washed by sat. aq. NaHCO₃ solution (100 ml) and sat. aq. NaCl solution (100 ml). Drying (MgSO₄) and evaporation *in vacuo* yielded **7** (1.05 g, 91%) as a white powder: mp 90.9–91.2 °C; ν_{max} (KBr)/cm⁻¹ 3431, 2923, 2854, 1584, 1511, 1454, 1427, 1254, 1127, 1100, 942, 727; δ_{H} (200 MHz, CDCl₃) 3.83 (8 H, s), 3.85–3.93 (8 H, m), 4.12–4.17 (8 H, m), 4.57 (2 H, s), 6.83–6.90 (7 H, m); δ_{C} (50 MHz, CDCl₃) 23.11, 62.56, 66.97, 67.13, 67.48, 68.46, 110.65, 111.60, 111.79, 117.54, 119.10, 126.01, 132.14, 146.68; *m/z* (FABMS) 461 ([M – OH]⁺, 87), 478 (M⁺, 100), 501 ([M + Na]⁺, 37%); *m/z* (HR-FABMS) 478.2204 (M⁺, [C₂₅H₃₄O₉]⁺; calc. 478.2203).

1-(6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b,n*]-[1,4,7,10,13,16,19,22]octaoxacyclotetrasilicose-2-ylmethyl) 3-ethyl propane-1,3-dioate (8)

To **7** (915 mg, 2 mmol) and C₅H₅N (0.72 ml, 2 mmol) in CH₂Cl₂ (50 ml) was added at 0 °C under N₂ ethyl malonyl chloride (430 mg, 3 mmol) and the solution was stirred for 1 h at 0 °C and for 2 h at 20 °C. The mixture was washed with sat. aq. NH₄Cl solution (2 × 100 ml), H₂O (100 ml) and sat. aq. NaCl solution (2 × 50 ml). Drying (MgSO₄) and evaporation *in vacuo*, followed by column chromatography (SiO₂, CH₂Cl₂–MeOH 99:1) afforded **8** (620 mg, 53%) as a white powder: mp 68.8–69.3 °C [Found: C, 61.01; H, 6.77. Calc. for C₃₀H₄₀O₁₂ (592.64): C, 60.80; H, 6.80%]; ν_{max} (KBr)/cm⁻¹ 2946, 2261, 1731, 1592, 1515, 1446, 1369, 1325, 1253, 1130, 731; δ_{H} (200 MHz, CDCl₃) 1.26 (3 H, t, *J* 7.3), 3.41 (2 H, s), 3.78 (8 H, s), 3.85–3.96 (8 H, m), 4.15–4.22 (10 H, m), 5.11 (2 H, s), 6.87–6.90 (7 H, m); δ_{C} (50 MHz, CDCl₃) 13.61, 21.93, 25.17, 41.20, 61.11, 66.72, 68.98, 69.07, 69.42, 69.52, 113.23, 113.71, 114.02, 121.04, 121.42, 124.63, 127.93, 148.50, 148.56, 148.76, 161.49, 166.09; *m/z* (FABMS) 461 ([M – OCOCH₂CO₂Et]⁺, 100), 592 (M⁺, 99), 615 ([M + Na]⁺, 47%).

1-(6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b,n*]-[1,4,7,10,13,16,19,22]octaoxacyclotetrasilicose-2-ylmethyl) 3-ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (1)

DBU (402 mg, 2.7 mmol) was added to a solution of **8** (314 mg, 0.53 mmol), C₆₀ (382 mg, 0.53 mmol) and I₂ (140 mg, 0.53 mmol) in PhMe (500 ml) and the mixture was stirred for 12 h under N₂. Filtration through a plug (SiO₂) eluting first with PhMe until all the unreacted C₆₀ had been collected and then with CH₂Cl₂–MeOH 97:3, followed by column chromatography (CH₂Cl₂–MeOH 99:1) gave **1** (319 mg, 46%) as a glassy purple solid: mp >250 °C; ν_{max} (KBr)/cm⁻¹ 3455, 1739, 1683, 1455, 1405, 1161, 1100, 694, 517; λ_{max} (CH₂Cl₂)/nm (ε/dm³ mol⁻¹ cm⁻¹) 256 (110000), 326 (42000), 408 (sh, 3500),

426 (3400), 477 (1600), 686 (320); δ_{H} (200 MHz, CDCl_3) 1.40 (3 H, t, J 7.0), 3.84 (8 H, br s), 3.85–3.93 (8 H, m), 4.10–4.20 (8 H, m), 4.52 (2 H, q, J 7.0), 5.45 (2 H, s), 6.84–7.09 (7 H, m); δ_{C} (125 MHz, CDCl_3) 14.10, 22.63, 31.57, 52.10, 63.45, 68.96, 69.37, 69.41, 69.48, 69.52, 69.81, 69.96, 71.31, 71.37, 71.54, 113.43, 114.05, 114.95, 121.45, 122.77, 125.28, 127.68, 128.21, 129.02, 140.85, 140.93, 141.81, 141.85, 142.15, 142.18, 142.92, 142.98, 143.04, 143.81, 143.86, 144.46, 144.58, 144.63, 144.64, 144.66, 144.84, 145.01, 145.03, 145.12, 145.13, 145.20, 145.23, 145.28, 148.87, 148.92, 149.49, 163.46, 163.50; m/z (FABMS) 720 (C_{60}^+ , 100), 1311 (M^+ , 49), 1333 ($[\text{M} + \text{Na}]^+$, 37%); m/z (HR-FABMS) 1310.2371 (M^+ , $[\text{C}_{90}\text{H}_{38}\text{O}_{12}]^+$; calc. 1310.2363).

1-([4-((*tert*-Butyl)oxy)carbonyl]([phenyl)methyl]amino)methyl]phenyl)methyl) 3-ethyl propane-1,3-dioate (10)

Ethyl malonyl chloride (1.5 g, 10 mmol) was added to a solution of **9** (1.63 g, 5 mmol) and $\text{C}_5\text{H}_5\text{N}$ (0.79 g, 10 mmol) in CH_2Cl_2 (100 ml) at 0 °C and the mixture was stirred under N_2 for 1 h. The solution was washed with sat. aq. NH_4Cl solution (2 × 200 ml) and H_2O (2 × 200 ml), the organic phase was dried (MgSO_4) and evaporated *in vacuo*. Column chromatography (SiO_2 , hexane–EtOAc 1:1) provided **10** (1.05 g, 48%) as a colourless oil [Found: C, 68.03; H, 7.25; N, 3.14. Calc. for $\text{C}_{25}\text{H}_{31}\text{NO}_6$ (441.52): C, 68.01; H, 7.08; N, 3.17%]; ν_{max} (KBr)/ cm^{-1} 2978, 1744, 1689, 1455, 1405, 1361, 1156, 1033, 883, 700; δ_{H} (200 MHz, CDCl_3) 1.27 (3 H, t, J 7.0), 1.51 (9 H, s), 3.44 (2 H, s), 4.20 (2 H, q, J 7.0), 4.27–4.42 (4 H, br m), 5.20 (2 H, s), 7.25–7.37 (9 H, m); δ_{C} (50 MHz, CDCl_3) 11.55, 25.96, 39.17, 46.53, 59.13, 64.50, 77.76, 124.97, 125.66, 126.04, 126.24, 132.01, 135.60, 136.11, 153.69, 164.13; m/z (FABMS) 340 ($[\text{M} - \text{CO}_2\text{Bu}]^+$, 35), 386 ($[\text{M} - \text{Bu}]^+$, 23), 440 (M^+ , 5%).

1-([4-((*tert*-Butyl)oxy)carbonyl]([phenyl)methyl]amino)methyl]phenyl)methyl) 3-ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (11)

DBU (0.7 mg, 4.6 mmol) was added to a solution of **10** (204 mg, 0.46 mmol), C_{60} (500 mg, 0.47 mmol) and I_2 (162 mg, 0.46 mmol) in PhMe (500 ml) and the mixture was stirred for 10 h at 20 °C under N_2 . Filtration through a plug (SiO_2) using first PhMe as the eluent to isolate unreacted C_{60} and then CH_2Cl_2 –MeOH 90:10, followed by column chromatography (SiO_2 , CH_2Cl_2) yielded **11** (232 mg, 43%) as a glassy solid: mp >250 °C; ν_{max} (KBr)/ cm^{-1} 2978, 1739, 1689, 1450, 1400, 1355, 1228, 1156, 694, 522; λ_{max} (CH_2Cl_2)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 258 (255900), 326 (79000), 403 (sh, 4600), 413 (sh, 3600), 426 (3500), 484 (2070), 624 (sh, 400), 688 (230); δ_{H} (200 MHz, CDCl_3) 1.40 (3 H, t, J 7.0), 1.52 (9 H, s), 4.37–4.42 (4 H, br m), 4.48 (2 H, q, J 7.0), 5.54 (2 H, s), 7.26–7.37 (7 H, m), 7.49 (2 H, “d”, J 7.9); δ_{C} (125 MHz, CDCl_3) 14.11, 28.42, 63.42, 68.58, 71.46, 80.17, 80.32, 127.28, 127.66, 127.96, 128.18, 128.25, 128.54, 129.30, 133.62, 137.85, 138.75, 139.26, 140.86, 140.90, 141.80, 142.14, 142.16, 142.31, 142.91, 142.96, 142.97, 143.03, 143.05, 143.82, 143.84, 144.47, 144.51, 144.57, 144.63, 144.76, 144.83, 145.03, 145.05, 145.12, 145.14, 145.19, 145.21, 155.87, 163.37, 163.61; m/z (MALDI-TOFMS) 1159 (M^+), 1103 ($[\text{M} - \text{Bu}]^+$).

1-([4-([([phenyl)methyl]ammonio)methyl]phenyl)methyl] 3-ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate hexafluorophosphate (2-H·PF₆)

A solution of **11** (200 mg, 0.17 mmol) and CF_3COOH (0.4 ml, 3.4 mmol) in CHCl_3 (30 ml) was stirred under N_2 at 20 °C for 12 h. After evaporation *in vacuo*, the residue was taken up into CH_2Cl_2 (200 ml) and washed with 6 M NaOH (200 ml). The aq. phase was washed with CH_2Cl_2 (2 × 100 ml) and the combined organic layers were dried (MgSO_4) and evaporated *in vacuo* to yield the corresponding amine which was dissolved in CHCl_3 (20 ml). Conc aq. HCl solution was added to reach pH < 2, the

solvent was removed *in vacuo* and the resultant solid suspended in Me_2CO (250 ml). Sat. aq. NH_4PF_6 solution was added to the suspension until a clear solution formed. Evaporation of the solvent Me_2CO *in vacuo*, filtration of the resulting suspension, and washing with copious amounts of H_2O yielded **2-H·PF₆** (170 mg, 82%) as a brown solid: mp >250 °C; ν_{max} (KBr)/ cm^{-1} 3522, 3222, 2944, 1739, 1600, 1456, 1428, 1233, 839, 556, 522; λ_{max} (CH_2Cl_2)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 258 (102500), 326 (34000), 404 (sh, 2900), 414 (sh, 2400), 426 (2300), 478 (1600), 687 (430); δ_{H} (200 MHz, CDCl_3 – CD_3CN 1:1) 1.12–1.27 (3 H, br m), 3.97 (4 H, br m), 4.41 (2 H, br m), 5.42 (2 H, br s), 7.29–7.50 (9 H, br m); δ_{C} (125 MHz, CDCl_3 – CD_3CN 1:1) 12.80, 23.08, 50.42, 50.90, 58.15, 63.10, 67.61, 70.97, 128.69, 128.99, 129.16, 129.37, 129.76, 135.86, 138.23, 138.63, 140.38, 140.45, 141.21, 141.33, 141.61, 141.67, 142.39, 142.48, 142.50, 142.51, 142.55, 142.57, 143.28, 143.34, 143.90, 144.02, 144.09, 144.11, 144.17, 144.35, 144.52, 144.57, 144.60, 144.66, 144.69, 144.75, 162.71, 162.73; m/z (MALDI-TOFMS) 1060, $[\text{M} - \text{PF}_6]^+$.

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Paper 9/03687C