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Synthesis of 18π annulenic fluorofullerenes from tertiary carbanions: size matters!

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A range of tertiary carbanions *X*CH(CO_2Et)$_2$ of differing sizes have been reacted with $C_{60}F_{18}$ to assess the steric effect of *X* on the position of nucleophilic substitution. For *X* = CO_2Et, NO_2, P(O)(OMe)$_2$, SO_2CH_2Ph, the all *trans* annulenes (trannulenes) were obtained as a result of extended S_N2' (*i.e.* S_N2'') substitution; in the case of the phosphorus compound, with reduced amounts of base (DBU) dephosphonylation of one or more P(O)(OMe)$_2$ groups by hydrogen occurred. Trannulene formation did not occur for *X* = F, CN due to the smaller size of the nucleophile, and in the latter case substitution was shown to take place by an S_N2' mechanism, resulting in the addend being adjacent to a fluorine addend. Trannulenes (*X* = CO_2Et, Br, Cl) exhibited reversible one-electron reductions at potentials (−0.02 to −0.09 V) significantly more positive than for [60]fullerene. Trannulene (*X* = NO_2) exhibited an irreversible one-electron reduction (0.08 V); the irreversibility may be associated with fluorine loss. Conformational isomerism at temperatures below 298 K was observed for all trannulene derivatives as a result of eclipsing addend–addend interactions. Minimum energy conformations with a rotational energy barrier of 12–15 kcal mol^{-1} were observed when these interactions are calculated using molecular mechanics.

Introduction

Recently we reported the preparation of the first all-*trans* 18π annulenic fluorofullerene (named trannulene) *via* a triple nucleophilic substitution of diethyl bromomalonate carbanion in $C_{60}F_{18}$(Fig. 1, X = Br, R′ = Et).[1] This serendipitous discovery arose because instead of formation of the expected methanofullerene, an extended S_N2'-derived nucleophilic substitution (S_N2'') by the bromomalonate carbanion takes place in $C_{60}F_{18}$ at a remote (δ) position relative to the departing fluoride anion, giving the tris-substitution product (Scheme 1).

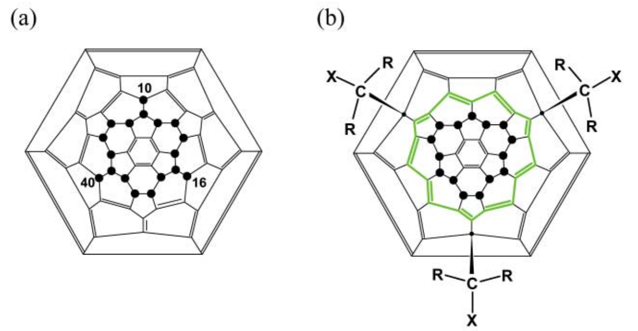
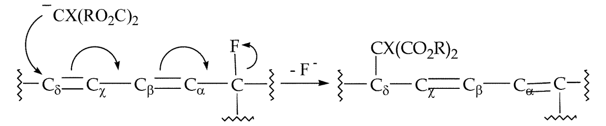


Fig. 1 Schlegel diagrams of (a) $C_{60}F_{18}$ (● = F), in which the outermost fluorines (attached to carbons 10, 16 and 40) are nucleophilically displaced; and (b) the general structure of [18]trannulenes (18π annulene shown in green) (R = CO_2R', X = electron withdrawing group, R′ = Me, Et. ● = F.



Scheme 1 Generalisation of the nucleophilic attack of the α-halomalonate carbanion with $C_{60}F_{18}$ (X = Br, Cl; R = Me, Et).

Semi-empirical calculations however revealed that trannulation of $C_{60}F_{18}$ will occur only if the incipient carbanion is of sufficient steric bulk.[2] Further work was undertaken to determine some aspects of the size boundary, using compounds with X = Br, R′ = Me; X = Cl, R′ = Et (Fig. 1b),[3] however these compounds still afforded the corresponding trannulenes. The presence of oxide functions (ethers) in the fluorinated part of the cage also did not affect trannulene formation.[3]

Three features are characteristic of trannulenes. First they have a brilliant emerald-green colour. Secondly, they tend not to show the parent ion in EI mass spectrometry, but rather the $C_{60}F_{15}^+$ fragmentation ion at 1005 amu. Thirdly, the ^{19}F NMR spectra show three peaks in a 1 : 2 : 2 ratio near δ_F −137 and −144/−144 (coincident or nearly so).

The present work was undertaken with two aspects in mind. First we wished to investigate the trannulation of $C_{60}F_{18}$ by using a series of tertiary carbanions in which both the steric bulk and the geometrical molecular arrangement close to the tertiary nucleophilic centre are altered. This will provide further evidence as to whether steric bulk of the nucleophile is the predominant factor in trannulene formation. Secondly, we wished to examine the effect of the substituents on the spectroscopic and electrochemical properties of the trannulenes.

The underlying interest in the physical properties of these compounds is their potential for the preparation of multi-component donor–acceptor assemblies, and molecular electronic devices. Relative to [60]fullerene, the fundamental advantages of trannulenes lie in their improved chromophoric features, and greater electron-acceptor properties. Strong visible light absorption, with a maximum *ca.* 660–670 nm, renders them good light-harvesting building blocks. Indeed an initial

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Table 1 Products of reaction of carbon acids with $C_{60}F_{18}$

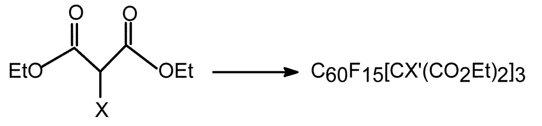
Reactant	X	Product	X′	Yield (%)
1a	F	**2**^{a,d}	NA	—
1b	CN	**3a/3b**^{a,c}	NA	—
1c	$COCH_2CH_2Ph$	$^{b,\,c\,or\,d}$	NA	—
1d	CO_2Et	**4**^{d}	CO_2Et	29^{c}
1e	NO_2	**5**^{d}	NO_2	33^{d}
1f	$P(O)(OMe)_2$	**6**^{d}	H	14^{c}
1g	SO_2CH_2Ph	**7**^{c}	SO_2CH_2Ph	Trace^{c}

[a] Reaction afforded product other than trannulene [b] No product was isolated [c] Reagents and conditions: (i) tertiary carbon acid (1.6 equiv.), $C_{60}F_{18}$ (1.0 equiv.), DBU (1.5 equiv.), toluene [d] Reagents and conditions: (i) tertiary carbon acid (1.0 equiv.), $C_{60}F_{18}$ (1.0 equiv.), DBU (0.9 equiv.), toluene

foray into a trannulene-extended tetrathiafulvalene tetrad has proved encouraging with an energetically low lying (0.54 eV) and long-lived charge-separated state (870 ns), generated *via* a rapid intramolecular electron-transfer process.[4]

Results and discussion

The tertiary carbon acids (**1a**–**g**, Scheme 2) were chosen for this study. Diethyl fluoromalonate (**1a**) has a single electron-withdrawing atom attached to the tertiary carbon centre, and provides a direct comparison with the bromo- and chloro-analogues, shown previously to afford trannulene derivatives. Electron withdrawal by the cyano group in diethyl cyanomalonate (**1b**) should similarly aid trannulene formation, but on the other hand its linearity produces little steric bulk at the tertiary nucleophilic centre, and similar in fact to the fluorine substituent. Thus compounds **1a** and **1b** would presumably react in a similar fashion.



1a X = -F
1b X = -CN
1c X = $-COCH_2CH_2Ph$
1d X = $-CO_2Et$
1e X = $-NO_2$
1f X = $-P(O)(OMe)_2$
1g X = $-SO_2CH_2Ph$

Scheme 2 Tertiary carbon acids utilised in the reaction with $C_{60}F_{18}$.

The trigonal planar geometry of the keto function of compound **1c** confers a significant increase in steric bulk compared with compounds **1a** and **1b**. However the presence of keto–enol tautomers[5] could provide unique substitution patterns. By contrast the trigonal planar ester function of **1d** prevents enolisation[5,6] and provides another stepwise increase in steric bulk over **1c**. Compounds **1e**, **1f** and **1g** provide yet further stepwise increases in both the atomic radius of atoms adjacent to the nucleophilic centre, the steric bulk of atoms surrounding the nucleophilic centre and the geometry of the substituent (trigonal planar for the nitro substituent in **1e**; tetrahedral for the phosphonate and sulfonate in **1f** and **1g**).

Table 1 summarises the products derived from the reaction of compounds **1a**–**g** with $C_{60}F_{18}$ under Bingel conditions. Each reaction will be discussed in detail.

Compound 2

HPLC (high pressure liquid chromatography) analysis of the products from reaction of $C_{60}F_{18}$, **1a** and DBU (see Experimental section) revealed a peak at 8.2 min (4.7 ml min^{-1}), a large amount of unreacted $C_{60}F_{18}$ (38 min) and a host of minor products. Although the 7.4 min fraction was only present in minor amounts, mass spectrometric analysis (Fig. 2) revealed a molecular ion at *m*/*z* 1220 corresponding to the monoaddition product $C_{60}F_{17}[CF(CO_2Et)_2]$ (**2**). The fragment ion at *m*/*z* 1201 most likely results from the loss of fluorine attached to the addend. The base peak at *m*/*z* 1043 corresponds to the loss of the entire methano addend resulting in the formation of the stable $C_{60}F_{17}^+$cation. Altering the reaction conditions (*i.e.* increasing the amount of **1a** and base to 1.6 and 1.5 equiv. respectively) produced a dramatic increase in black precipitate.

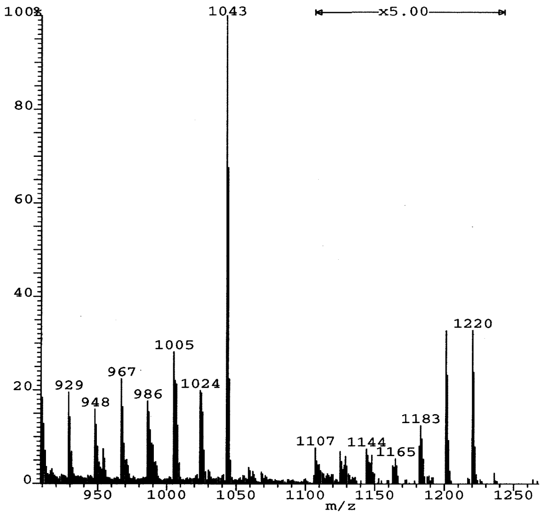


Fig. 2 EI mass spectrum (70 eV) for compound **2**.

HPLC analysis revealed a decrease in recovered $C_{60}F_{18}$ but no change in the yield of **2**. This result deviates from previous experiments using halomalonate precursors, whereby the diethyl chloro- and bromomalonate analogues afford the corresponding trannulenes as the major product.[2,3]

Compounds 3a and 3b

HPLC analysis of products from reaction of $C_{60}F_{18}$ with **1b** and DBU (see Experimental section) revealed two major peaks at 6.4 (13%) and 12.7 min (25%) accompanied by a minor amount of unreacted $C_{60}F_{18}$. The mass spectra (Fig. 3a,b) exhibited molecular ions at *m*/*z* 1227 and 1392, corresponding to mono- $C_{60}F_{17}[CCN(CO_2Et)_2]$ and bisaddition ($C_{60}F_{16}[CCN(CO_2Et)_2]_2$, products, **3a** and **3b**, respectively. Compound **3a** exhibited a base peak at *m*/*z*1043 corresponding to the formation of $C_{60}F_{17}^+$resulting from the loss of the addend (*cf.* fragmentation of compound **2**). Compound **3b** revealed fragment ions at *m*/*z* 1208 and 1024, corresponding to the loss of one and two addends respectively, giving in the latter case, $C_{60}F_{16}^+$. ^1H NMR analysis of both **3a** and **3b** revealed broad AX coupled systems corresponding to the ethyl ester resonances.

The ^{19}F NMR spectrum of **3a** comprises eleven fluorine resonances, seven of which are of single intensity, and two each of double and triple intensity (Fig. 4). Thus a total of seventeen fluorines are present, showing **3a** to be non-symmetrical. Comparison with the ^{19}F NMR spectrum of the corresponding bromo monoadduct (*i.e.* $C_{60}F_{17}[CBr(CO_2Et)_2]$) revealed significant differences. Most notably the NMR spectrum of the bromo compound comprised a distinct downfield resonance (δ −107.2) corresponding to one of the outermost fluorines. Such a resonance is not observed in the ^{19}F NMR spectrum of **3a** in which the most downfield resonance is a double intensity peak at −130.1 ppm. Such a considerable difference in chemical shifts of these outermost fluorines indicates a different substitution pattern. A 2D F–F COSY experiment acquired in both d_8-toluene and $CDCl_3$ yielded the assignments of **3a** shown in Table 2.

Table 2 Chemical shifts and peak assignments of the F–F COSY spectrum of **3a** (d_8 toluene)

Chemical Shift (δ_F)	Fluorine Type	Connectivities
−130.1	A_1/A_2	B_1, B_2, C_1, C_4, C_5, C_6
−136.1	C_2/C_3	D_2. D_3, E
−136.5	$C_4/C_5/C_6$	B_1, B_2, D_4, D_5/D_6
−136.7	C_1	B_1, D_1
−140.4	D_1	C_1, D_2
−141.1	D_3	C_3, D_4
−142.0	D_4	C_4, D_3
−142.7	$D_5/D_6/E$	C_2/C_3, C_5/C_6
−145.8	D_2	D_1, C_2
−157.5	B_2	A_2, C_4/C_5
−157.7	B_1	A_1, C_1, C_6

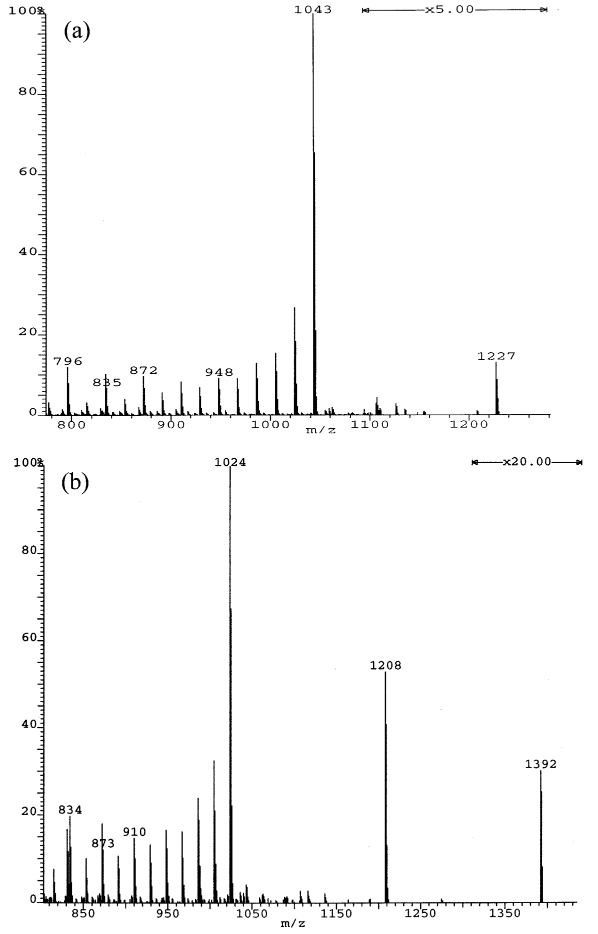


Fig. 3 EI mass spectra (70 eV) for compounds (a) **3a** and (b) **3b**.

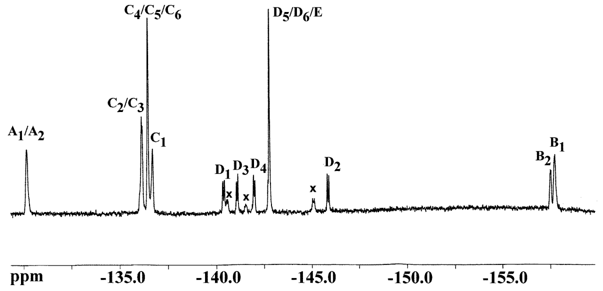


Fig. 4 ^{19}F NMR (376 MHz, d_8-toluene) spectrum of compound **3**.

Three regiochemical possibilities arise for **3a** as follows: (i) direct substitution of one of the outermost fluorines (*i.e.* either fluorine 10, 16, 40 in Fig. 1); (ii) substitution at the β-position relative to the departing fluorine; (iii) substitution at the δ-position relative to the departing fluorine (Scheme 1).

Increasing the amounts of **1b** and base relative to $C_{60}F_{18}$ was found not to afford a corresponding trannulene derivative. In addition to **3a** exhibiting a unique ^{19}F NMR spectrum when compared to a known δ–substituted monoadduct (*i.e.* $C_{60}F_{17}[CBr(CO_2Et)_2]$), substitution of the carbanion of **1b** at the δ-position is unlikely. Direct S_N2 substitution is not sterically possible, leaving as the only alternative S_N2' substitution of **3a** at the β-position relative to the outgoing fluorine (Fig. 5). Such a deviation in the substitution process previously observed for diethyl chloro and bromomalonate is due to the reduced steric bulk of the cyano subsituent, so that substitution at the β-position becomes favourable. We assume that the substitution pattern of compound **2** would also be in the β-position due to its comparable steric bulk around the tertiary nucleophilic centre.

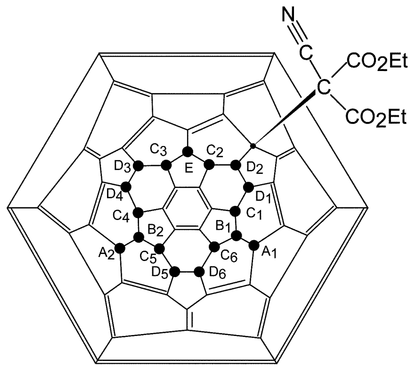


Fig. 5 Schlegel diagram of $C_{60}F_{17}[CCN(CO_2Et)_2]$ **3a**.

Use of the keto ester 1c

No discernable product was obtained using the keto diester **1c** in the presence of $C_{60}F_{18}$ and DBU. The presence of keto–enol equilibria is presumed to be responsible for this.

Compound 4

Treatment of a toluene solution of **1d** and $C_{60}F_{18}$ with base afforded the desired trannulene **4** in moderate yield (29%) after HPLC purification (Table 1). The EI mass spectrum of **4** showed a molecular ion (M^+) at *m*/*z* 1698 and fragment ions at *m*/*z* 1467 and 1236 corresponding to the loss of one and two methane tricarboxylate addends respectively. The base peak at *m*/*z* 1005 corresponds to the $C_{60}F_{15}^+$ cation. The ^{1}H NMR spectrum of **4** comprised an AX coupled system [δ 1.47 (t, J = 7.1 Hz), 4.50 (br q, J = 7.1 Hz)] corresponding to the ethyl ester of the methanetricarboxylate moiety. The ^{19}F NMR spectrum of **4** (Fig. 6a) showed three resonances (1 : 2 : 2 intensity), indicative of C_{3v} symmetry, as observed in previous trannulene derivatives.[1–3] It contrasts with that of $C_{60}F_{18}$ by the

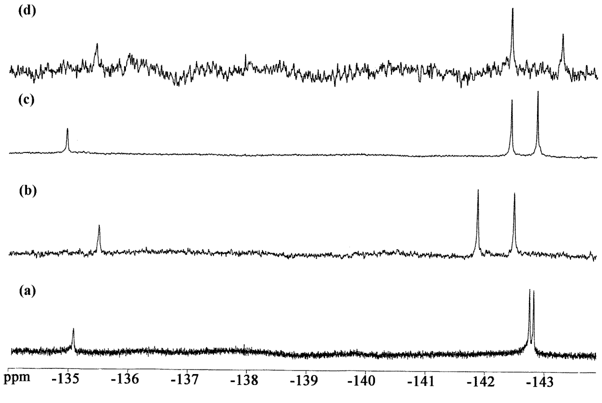


Fig. 6 ^{19}F NMR spectra of compounds (a) **4**, (b) **5**, (c) **6** and (d) **7** at 298 K.

notable absence of the most upfield resonance (*ca.* −158 ppm) which is associated with the fluorine attached to a fullerene sp^3 carbon surrounded by three fluorinated sp^3 carbons (see Fig. 1a).[7] This fluorine resonance exhibits a downfield shift (from *ca.* −158 to *ca.* −142 ppm) due to the loss of the neighbouring (conjugatively electron *donating*) fluorine atoms.[8]

Compound 5

The highest yield of a trannulene product was obtained using the commercially available diethyl nitromalonate (**1e**). Equimolar amounts of **1e**, $C_{60}F_{18}$ and base, gave the trannulene **5** in 33% yield. EI mass spectrometric analysis showed only a peak at *m*/*z* 720 due to C_{60}^+. MALDI-TOF revealed an extremely weak fragment ion at 1574 corresponding to $[M - NO_2]^+$. Stronger fragment ions at *m*/*z* 1415, 1323 and 1166 correspond to $C_{60}F_{15}[C(CO_2Et)_2NO_2]_2^+$, $C_{60}F_{15}[C(CO_2Et)_2]_2^+$, and $C_{60}F_{15}[C(CO_2Et)_2]^+$ respectively. No peak corresponding to $C_{60}F_{15}^+$was observed in the positive mode, however negative mode revealed $[C_{60}F_{15}]^-$ (*m*/*z* 1005) as the base peak.

The ^{1}H NMR spectrum of **5** comprised an AX coupled system [δ 1.57 (t, J = 7.3 Hz), 4.67 (br q, J = 7.3 Hz)] associated with the ethyl ester of the diethyl nitromalonate moiety. The presence of the nitro function causes a downfield shift of the methylene resonance compared with those found in the corresponding ethyl ester (compound **4**, δ 4.50) and bromo trannulenes (δ 4.13).[1–3] The effect of the nitro group on the trannulene structure is more significant in the ^{19}F NMR spectrum (Fig. 6b), which comprises three resonances at δ −142.5, −141.9 and −135.5. The fluorines in closest proximity to the site of functionalisation (set C in Fig. 7) exhibit a downfield shift of over 2 ppm compared with the corresponding fluorines of compound **4**; likewise set B fluorines exhibit a downfield (but smaller) shift (*ca.*1.7 ppm). By contrast the fluorines that are further away from the functional group (set A, Fig. 7) are shifted relatively upfield.

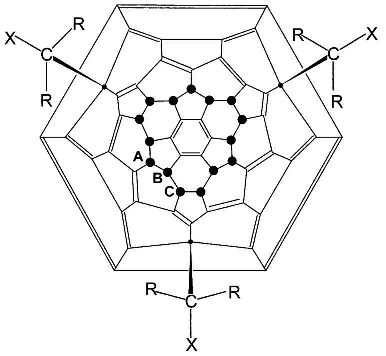


Fig. 7 Schlegel diagram (R = CO_2Et, X = CO_2Et, NO_2, $P(O)(OMe)_2$, SO_2CH_2Ph; ● = F) showing three sets of fluorines labelled A, B, C, in C_{3v}-symmetrical [18]trannulenes.

Compound 6

An unexpected result arose from the reaction of the corresponding carbanion of the phosphonate diester **1f** (1.0 equiv.) with $C_{60}F_{18}$ (1.0 equiv.). Upon addition of base (0.9 equiv.), the solution changed colour from the lemon yellow of $C_{60}F_{18}$ to the characteristic emerald-green of a trannulene. HPLC purification of the emerald-green solution in toluene afforded a major peak at 7.6 min with a minor (emerald-green) fraction eluting at 8.0 min. The MALDI-TOF spectra of neither fraction showed a molecular ion corresponding to a phosphonate-containing trannulene. Both exhibited a base peak in the negative mode corresponding to $[C_{60}F_{15}]^-$ and a minor fragment ion at 1163 attributed to $C_{60}F_{15}[C(CO_2Et)_2]^-$.

^{1}H NMR analysis of **6** (7.6 min fraction) revealed the absence of bis-methoxy resonances δ 3.82 and δ 3.85 (for **1f**) associated with the phosphonate ester; suggestive of dephosphonylation. The lack of a ^{31}P resonance confirmed the loss of the dimethyl phosphonate moiety. A 1 D NOE difference experiment of **6** using a long pulse delay revealed an NOE from a singlet resonance (3 H, δ 4.08) to the ABX_3 multiplet of methylene protons (12 H, δ 4.55) associated with the malonate functionality. Thus the three phosphonate moieties have been replaced by three hydrogen substituents. The ^{19}F NMR spectrum of **5** comprised a resolved set of three fluorine resonances at δ_F −142.9, −141.9 and −135.5 (Fig. 6c).

A possible mechanism for the formation of **6** from the tertiary carbon acid **1f** is shown in Scheme 3. The first step is presumed to be nucleophilic attack of the fullerene carbon δ to the departing fluorine *via* **8** to form the phosphonate-containing trannulene **9**. Dephosphonylation of quaternary phosphonates using potassium fluoride in triglyme was reported by Thanappan and Burton.[9] Since each nucleophilic addition of **1f** to $C_{60}F_{18}$ produces an equimolar amount of fluoride, the fluoride is able to attack the pentavalent phosphorus centre to produce a strong P–F bond (**11**). Protonation of **10** by the conjugate acid of DBU affords **6**. The low observed yields compared to **4** and **5** can be explained by the presence of excess DBU as a consequence of the protonation of **10**.

Consistent with this explanation is the fact that when the amount of base is reduced (0.5 equivalents compared with one equivalent of $C_{60}F_{18}$ and **1f**) the yield of the 8.0 min fraction rises sharply. ^{1}H NMR of the 8.0 min fraction revealed a complex multiplet (δ 4.58) corresponding to the methylene resonances of the ethyl ester. At least four unique resonances in the methyl region (δ 1.5–1.6) confirmed the presence of several products; a doublet (δ 4.18, J = 11.3 Hz) is consistent with one or two phosphonate moieties, whilst a singlet at δ 4.06 revealed the dephosphorylation of at least one of them. ^{19}F NMR analysis revealed the presence of at least three trannulene products, with one set of resonances corresponding to compound **6**. Thus reducing the amount of base present in the reaction system is a critical factor in the formation of **6** *via* **9**.

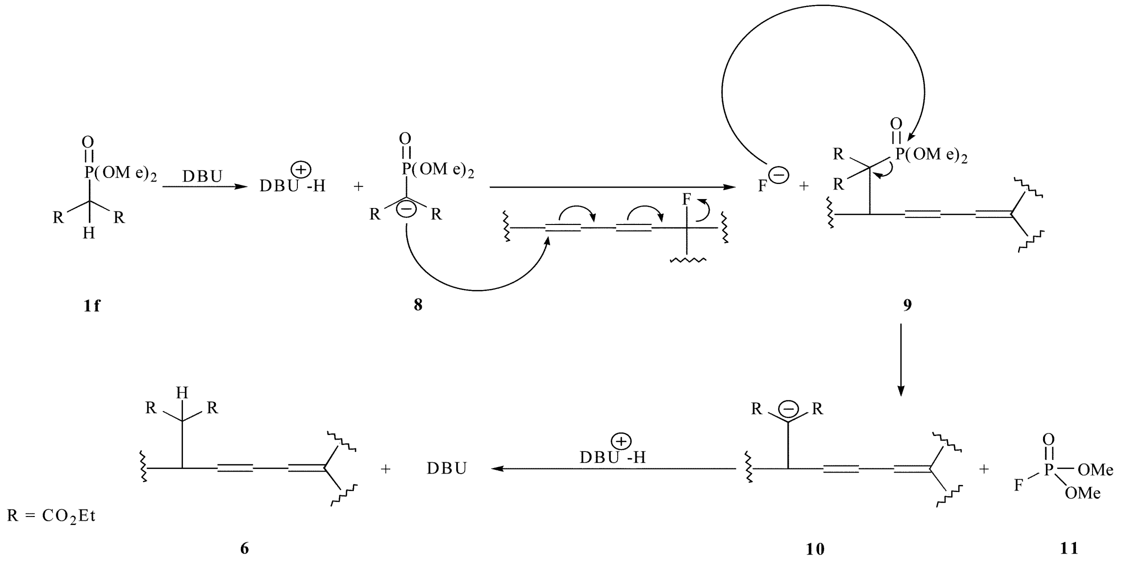
Compound 7

Upon addition of base to a toluene solution of $C_{60}F_{18}$ and **1g**, a colour change from lemon-yellow to pale emerald-green was accompanied by formation of a large amount of black precipitate. HPLC purification revealed only trace amounts of the corresponding trannulene **7**. The MALDI-TOF spectrum afforded peaks at *m*/*z* 1481, 1323 and 1163 corresponding to $[C_{60}F_{15}[C(CO_2Et)_2]_3]^+$, $[C_{60}F_{15}[C(CO_2Et)_2]_2]^+$ and $C_{60}F_{15}[C(CO_2Et)_2]^+$ respectively. No $[C_{60}F_{15}]^+$ was observed in the positive mode, however negative mode afforded *m*/*z* 1005 $[C_{60}F_{15}]^-$ exclusively. In contrast to the reaction of **1f** with $C_{60}F_{18}$ and DBU, no desulfonylation was observed, confirmed by the presence of the benzylsulfonate function in the ^{1}H NMR spectra.

The methylene resonances associated with the ethyl ester afforded an ABX_3 coupled system [δ 1.35 (t, 18 H, J = 7.1 Hz), 4.34 (qd, 12 H, J = 7.1, 1.1 Hz)] rather than a broad quartet in previous (room temperature) examples. The ^{19}F NMR spectrum of **7** (Fig. 6d) exhibited three fluorine resonances (δ −135.5, −142.4, −143.3) characteristic of trannulation. The presence of the sulfonate group causes an upfield shift of the fluorines close to the site of functionalisation (*i.e.* set B and C in Fig. 7).

Electrochemistry

Cyclic voltammetry of **4** displayed two reduction peaks, denoted as I and II (E_p)(Fig. 8). Peak I was found to be reversible ($E_{1/2}$ = −0.09 V) and corresponds to a one-electron transfer, whereas peak II was irreversible (E_p = −0.70 V). When the scan potential is reversed after peak II, also peak I becomes less reversible (*i.e.* the corresponding anodic-to-cathodic peak current ratio is significantly less than one). Furthermore, a broad anodic peak (peak A at *ca.* 1.5 V) appears as the result of



Scheme 3 Conjectured mechanism for dephosphonylation of compound **1f**.

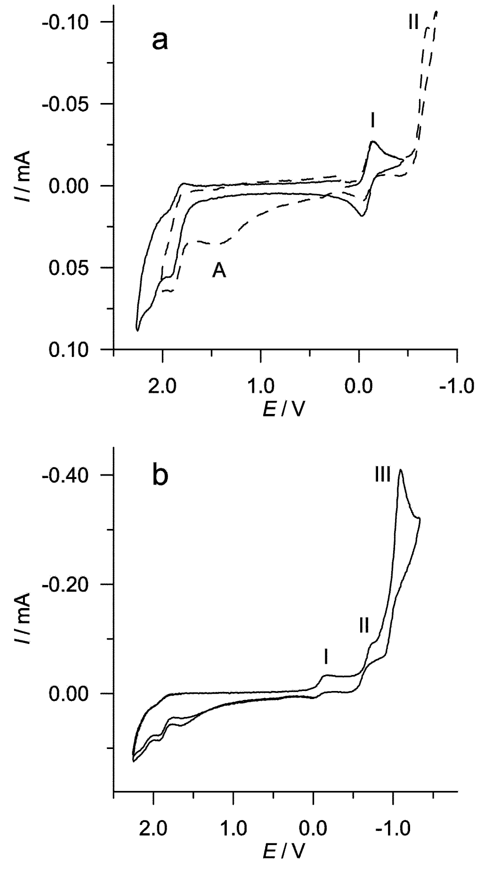


Fig. 8 Cyclic voltammetric curves for a 0.5 mM solution of **4**, 0.05 M tetrabutylammonium tetrafluoroborate, tetrachloroethane solution. Scan rate: 0.5 V s^{-1}. Working electrode: Pt disc (62 µm radius). T = 25 °C; (a) negative switching potential: −0.45 V (——) and −0.85 V (- - -); (b) negative switching potential: −1.33 V.

II and is attributed to the oxidation of a follow-up product of the latter irreversible reduction (electrochemical–chemical – EC-mechanism[10]).

At more negative potentials, an unresolved multi-electron irreversible peak is observed (peak III $E_p = -1.08$ V; Fig. 8b). This corresponds to the exchange of a much larger charge than in previous processes (*i.e. ca.* 20 times compared with peak I based on convolutive analysis[9]). The CV behaviour of **4** was investigated at scan rates up to 100 V s^{-1} without any significant change of the CV pattern, suggesting that the peak at −1.08 V is probably associated with fast follow-up catalytic reactions coupled to the charge-transfer processes.†

In the region of positive potentials, two oxidation peaks are observed, the first (reversible) with $E_{1/2}$ = 1.85 V and the second (irreversible) with E_p = 2.15 V (at 0.5 V s^{-1}). By comparison with the one-electron reversible reduction peak, the reversible anodic process at 1.85 V should correspond to the exchange of two electrons.

Similar electrochemical behaviour was observed for compounds **12** and **13** (Table 3). Slight differences in the $E_{1/2}$ values were observed, while the irreversible multi-electron reduction peak remained unchanged. By contrast, significantly different behaviour was observed for compound **5** (Fig. 9). The first one-electron peak I, occurring at 0.08 V, was irreversible at scan rates up to 10 V s^{-1}. Reversibility of this peak was only obtained at scan rates greater than 10 V s^{-1} (Fig. 9, inset). Assuming that the irreversibility is due to the occurrence of a first-order follow-up reaction (EC mechanism), a kinetic rate

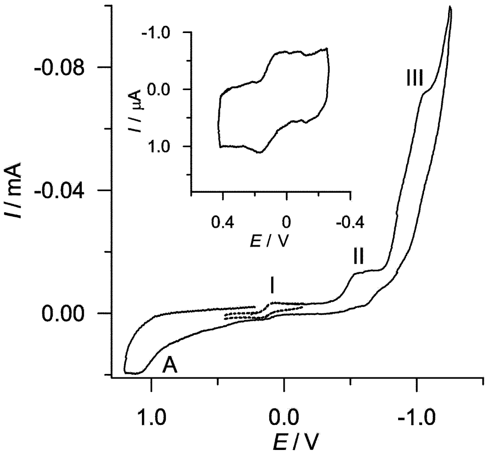


Fig. 9 Cyclic voltammetric curves for a 0.5 mM solution of **5**, 0.05 M tetrabutylammonium tetrafluoroborate, tetrachloroethane solution. Scan rate: 0.5 V s^{-1}. Working electrode: Pt disc (62 µm radius); (inset) scan rate: 10 V s^{-1}. Working electrode: Pt disc (12 µm radius). T = 25 °C.

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† Similar multielectron irreversible reduction processes were also observed in other polyfluorinated fullerenes *e.g.* $C_{60}F_{48}$, $C_{60}F_{36}$[11] investigated under the same conditions used in this work. This would suggest that the fluorine atoms may be involved in the mechanism of the reactions coupled to the electron transfer processes, analogous to the catalytic process observed in $C_{60}F_{18}$.[12]

Table 3 Electronic absorption and electrochemical data for trannulenes $C_{60}F_{15}[C(CO_2Et)_2X]_3$, in tetrachloroethane at 25 °C

Compound	X	λ/nm (10^3 ε/M^{-1} cm^{-1})						$E_{1/2}$/V
4	CO_2Et	666 (9.1)	617[a] (5.5)	438 (8.7)	397 (24.4)	339 (24.7)	279 (23.7)	−0.09
5	NO_2	660 (7.3)	613 (4.9)	434 (8.8)	396 (24.0)	315[a] (23.5)	278[a] (30.7)	0.08
12	Br	665 (7.7)	618[a] (4.9)	437 (8.8)	397 (24.0)	335 (25.0)	276 (33.2)	−0.03
13	Cl	663 (7.9)	617 (5.4)	435 (10.8)	395 (25.4)	332[a] (31.4)	278[a] (41.5)	−0.02

[a] Shoulder.

constant of *ca.* 10 s^{-1} was estimated by digital simulation of the CV curves. Furthermore a significant shift of the irreversible reduction peak II (E_p = −0.56 V) and of the irreversible oxidation peak A (E_p = 1.10 V) in the reverse scan was observed (Fig. 9). The multi-electron peak III (E_p = −1.08 V) largely replicated that of the previous species in compounds **4**, **12** and **13**, and is analogously attributed to an electro-catalytic reduction process likely involving fluorine loss.

Spectroelectrochemical experiments were carried out in order to further characterize the radical anions generated by the first one-electron reduction of the above species. Fig. 10b shows the absorption spectrum obtained for a 3 mM solution of **4** in tetrachloroethane after *in-situ* bulk reduction at −0.45 V, corresponding to the first reversible one-electron reduction of **4**.

After electrolysis, the intense absorption bands at 666 and 397 nm disappeared while those at 617, 438 and 339 nm greatly diminished. The most interesting feature of the absorption spectrum of $\mathbf{4}^{\bullet-}$ is however the appearance of the intense and broad band in the NIR region, centred at 952 nm. Analogous to C_{60} and several of its derivatives, the NIR triplet–triplet transition represents the fingerprint of the fullerene-centred radical anion and was recently used for the identification of the charge-separated state generated by photoexcitation of a trannulene-based photoactive dyad.[4] Similar spectral changes were observed for **5**, **12** and **13**.

In line with the observed 170 mV positive shifts of the first reduction in **5** with respect to **4**, the NIR absorption band was also shifted in the former to 989 nm (Fig. 10c). The pristine absorption spectra were recovered in the case of **4**, **11** and **13** upon re-oxidation of the electrolysed solutions. In the case of **5**, by contrast, and in line with the irreversible CV behaviour, the original spectrum was not recovered.

Dynamic behaviour of trannulenes as observed by NMR

A previous variable temperature NMR study on a trannulene derivative (X = Br, **12**)[1] revealed broadening of the ethyl ester resonances at temperatures below 298 K. This unusual feature was shown to be reversible, an observation also observed for compounds **4**–**7**. Fig. 11 illustrates the methylene region of **4** at various temperatures. At 298 K a single methylene quartet (δ 4.50) is observed (Fig. 11a). As the temperature is lowered the methylene quartet broadens significantly (Figs. 11b,c) and moves downfield (δ 4.76, Fig. 11d). At 213 K (Fig. 11e) other minor signals (δ 5.17, δ 4.21 and δ 3.38) appear in the spectrum at chemical shifts unique to the methylene quartet at 298 K, and three major signals are also present. The reversibility of this variable temperature behaviour is indicative of conformational isomerism. Although the addends comprise a number of bonds that could contribute to various conformations, restricted rotation of the carbon–carbon bond connecting the addend to the fluorofullerene core (Fig. 12b) would most likely induce significant perturbations in chemical shifts. Molecular mechanics calculations (pcff forcefield)[13] were performed on compound **12** (a crystal structure being available)[1] in order to evaluate the relationship of the potential energy and the dihedral angle (Φ) of the addends relative to each other. Due to the flexible nature of the addends, calculations were performed with the positions of the addend atoms fixed. The dihedral angle of a single addend–fluorofullerene carbon bond was rotated at 15 degree intervals and an optimisation calculation performed.

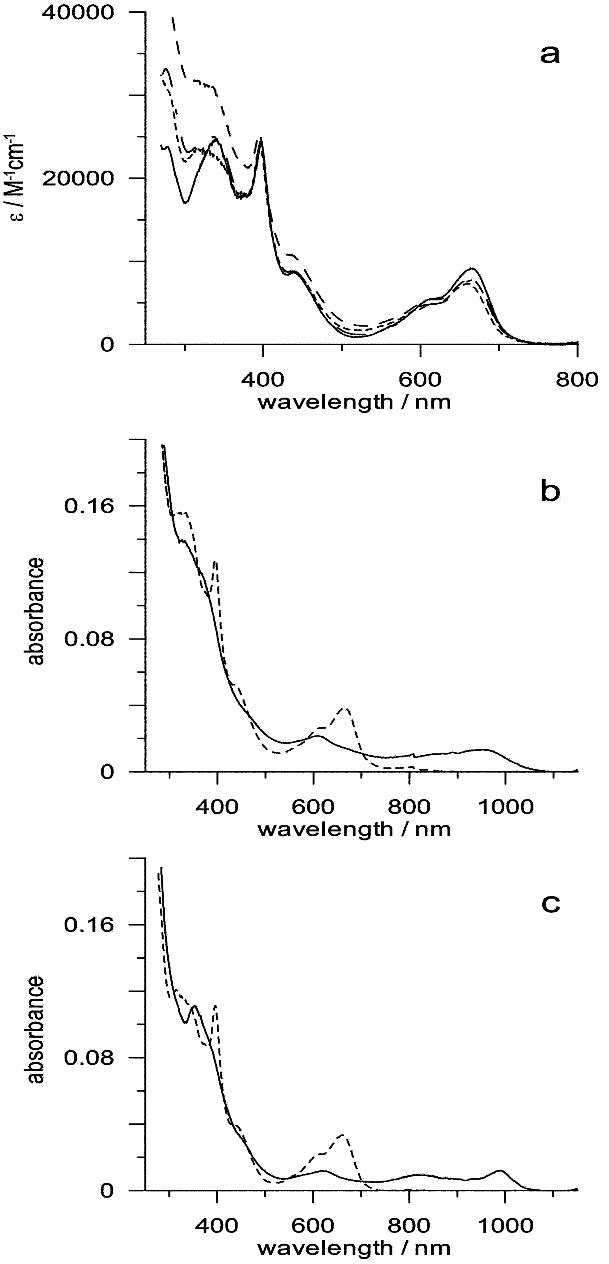

Fig. 10 UV-Vis electronic absorption spectra in tetrachloroethane soluions, 25 °C for (a) compounds 4 (——), **5** (- - -), **12** (-··-) and **13** (---); (b) UV-Vis-NIR spectra of $\mathbf{4}^{\bullet-}$(——) and **4** (---); (c) UV-Vis-NIR spectra of $\mathbf{5}^{\bullet-}$ (——) and **5** (---).

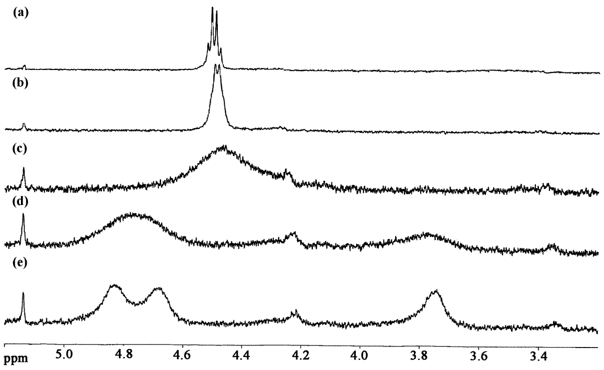

Fig. 11 ^{1}H NMR (500 MHz, CD_2Cl_2–$CDCl_3$) spectra of the methylene region of compound **4** at (a) 298 K, (b) 283 K, (c) 243 K, (d) 213 K and (e) at 205 K.

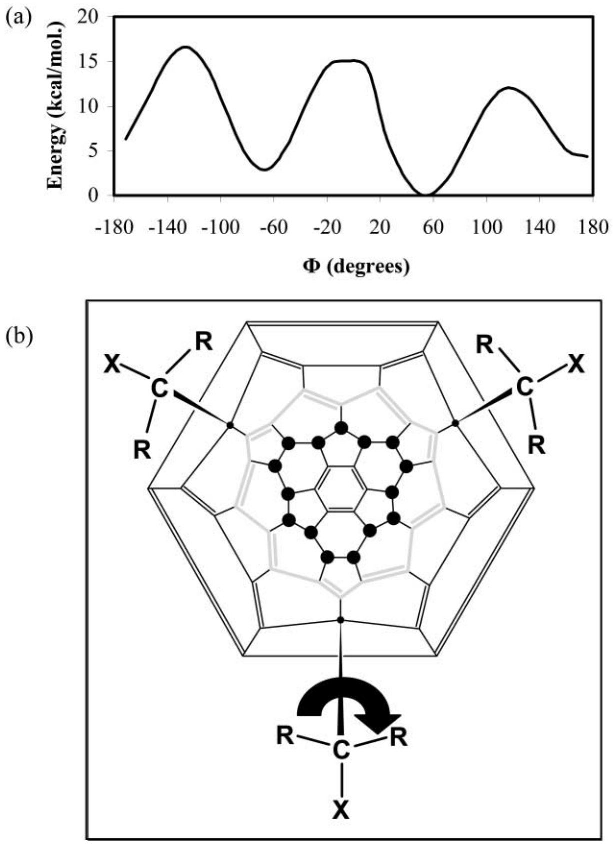

Fig. 12 (a) Calculated potential energy profile (pcff) as a function of dihedral angle of the C–C bond between the addend and the fluorofullerene. (b) Schlegel diagram of **12** (R = CO_2Et; X = Br) illustrating the rotation of the addend–fluorofullerene C–C bond.

Fig. 12a illustrates the energy profile of **12** as a function of *Φ*. The lowest energy minimum was found to correspond to the starting crystal structure. Two other energy minima were found at dihedral angles resulting from a 120° and 240° rotation from the starting crystal structure conformation. The corresponding three energy maxima resulted from a 60° rotation from an energy minima. Inspection of the conformations adopted at the respective energy maxima and minima revealed the potential energy of a conformation reaches a maximum when eclipsing interactions (at dihedral angles of −125° and −6°) of the ethyl ester addends occurs. The lower energy maximum conformation (at dihedral angle 131°) corresponds to an eclipsing interaction between the bromo and ethyl ester substituents. Thus, the mimimum energy conformations correspond to such conformations whereby these eclipsing interactions are minimised (at dihedral angles 4°, 55° and −65°).

The three most stable conformers are very similar in energy (3–4 kcal mol^{-1}) with a rotational energy barrier *ca.* 12–15 kcal mol^{-1}between each minimum energy conformation. With no restrictions imposed on each of the respective conformations, a molecular mechanics optimisation produces a conformation identical to the starting crystal structure. This confirms that the crystal structure is a true energy minimum and the rotational energy barrier is small enough for conformations to interchange until the respective minimum is established. A rotational energy barrier of 12–15 kcal mol^{-1} for **12** was found to be significantly smaller than conformers found in a pyrrolidinofullerene–calix[4]arene[14] derivative (15–20 kcal mol^{-1}). The smaller rotational energy barrier is reflected in the lower conformer coalescence temperature of **12** (298 K) compared with that (393 K) for the pyrrolidinofullerene–calix[4]arene derivative.

Conclusions

We have demonstrated the synthetic versatility of trannulene-formation beyond chloro- and bromomalonate carbanion additions to $C_{60}F_{18}$. This provides a range of novel trannulenes comprising functions amenable for further chemical manipulation. The steric bulk of the tertiary carbanion was confirmed to be the predominant factor in trannulation with the fluoro- and cyano- functions being sterically insufficient for S_N2'' subsitution. In the case of carbanion additions of diethyl cyanomalonate (**1b**) the first/second example of an S_N2' subsitution was observed giving the corresponding monoadduct $C_{60}F_{17}$-$[CCN(CO_2Et)_2]$.

All trannulenes exhibit a one-electron reduction potential anodically shifted by nearly one volt compared withg C_{60}. The nitro function of compound **5** causes an irreversibility, arising most likely from fluorine loss.

We have also demonstrated that trannnulene derivatives exhibit conformational isomerism arising most likely from the C–C bond connecting the addends to the fluorofullerene nucleus. At 298 K the addends rotate with relative freedom, the conformational freedom being reduced markedly at temperatures below 298 K due to eclipsing addend–addend interactions. Possibilities of utilising these restricted conformations in a functional sense such as molecular propellers and switches will be investigated in due course.

Experimental

Toluene was distilled from sodium benzophenone ketyl. Other sovents used were purchased from Aldrich. All reactions were performed in standard glassware under an inert atmosphere of argon. Evaporation and concentration *in vacuo* utilised water-aspirator pressure, and compounds were dried at 10^{-1} Torr. Flash column chromatography was performed using silica 60 (230–400 mesh, 0.040–0.063 mm, Aldrich). MALDI-TOF spectra were recorded on a Kratos Kompact MALDI IV (Kratos Inc.) mass spectrometer in positive and negative ion modes using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile as matrix.

Electrospray mass spectra were recorded on a Bruker FT-MS APEX-III. ^{1}H, ^{19}F and ^{13}C NMR spectra were acquired at 500, 376.5 and 75 MHz, respectively. ^{19}F NMR spectra used either $CDCl_3$ or d_8-toluene as solvent. HPLC separations employed a 10 × 250 mm Cosmosil Buckyprep column operated at a flow rate of either 4.7 or 2.0 mL min^{-1} using toluene as eluent.

Electrochemical instrumentation and measurements

The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Viton O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck flask containing the solvent were obtained by spherical joints also fitted with Viton O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically 1.0 to 2.0 × 10^{-5} mbar. The working electrode consisted either of a Pt disc ultramicroelectrode (r = 62 or 12 µm) sealed in glass. The counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm.

Potentials were measured with the ferrocene standard and are referred to saturated calomel electrode (SCE). $E_{1/2}$ values correspond to $(E_{pc} + E_{pa})/2$ from CV. For irreversible peaks, the peak potential, E_p, is given, measured at 0.5 V s^{-1}. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple. The temperature dependence of the ferrocinium–ferrocene couple standard potential was measured with respect to SCE by a non-isothermal arrangement.

Voltammograms were recorded with a AMEL Model 552 potentiostat or a custom-made fast potentiostat controlled by either an AMEL Model 568 or ELCHEMA Model FG-206F function generator. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda RL6 CS thermostat. The DigiSim 3.03 software by Bioanalytical Systems Inc., or the Antigona software developed by Dr L. Mottier (http://www.ciam.unibo.it/electrochem.html/), were used for the simulation of the CV curves. The latter program was also used for the acquisition of the CV curves and their convolutive analysis.

The spectroelectrochemical experiments were carried out using a quartz OTTLE cell with a 0.03 cm path length. Temperature control was achieved by a special cell holder with quartz windows, in which two nitrogen fluxes (one at room temperature and the other at low temperature) are regulated by two needle valves. All the spectra have been recorded by a Varian Cary 5 spectrophotometer.

Preparation of $C_{60}F_{18}$

Most of the $C_{60}F_{18}$used in this study was prepared by fluorinating [60]fullerene with K_2PtF_6[15] and was supplemented by material obtained by fluorinating with a mixture of MnF_3–K_2NiF_6, (a lower yield process). Fuller details together with relative and absolute yields, and description of the large-scale HPLC purification process will be described elsewhere.[16]

Preparation of addends

Compounds **1a**, **1d** and **1e** were obtained from Aldrich, and **1b** was prepared by reaction of the enolate of ethyl cyanoacetate with ethyl chloroformate.[17] Compound **1c** was prepared by reaction of the enolate of diethyl malonate with 3-phenylpropionyl chloride,[18] and **1f** was prepared by reaction of the enolate of ethyl dimethylphosphonoacetate with ethyl chloroformate.[9]

Diethyl 2-(2-phenylmethanesulfonyl)malonate (1g)

A suspension of NaH (0.209 g, 5.21 mmol, 60% dispersion in oil) was added to a solution of diethyl malonate (0.696 g, 4.35 mmol) in DMF (5 mL) at −20 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 30 min. The reaction mixture was then recooled to −20 °C and 2-phenylmethanesulfonyl chloride (0.995 g, 5.22 mmol) was added. The reaction mixture was allowed to warm to room temperature, stirred for a further 3 h, then quenched with saturated ammonium chloride (20 mL), diluted with DCM (200 mL) and washed with saturated ammonium chloride (20 mL), and brine (3 × 20 mL) to neutrality. The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*.

Flash column chromatography (silica gel), eluting with DCM : petroleum spirit (80 : 20) provided the desired product (0.408 g, 30%) as a pale yellow solid. ^1H NMR: δ 1.31 (t, 6 H, J 6.9 Hz), 4.30 (q, 4 H, J 6.9 Hz), 4.71 (s, 2 H), 4.72 (s, 1 H), 7.40 (m, 5 H). ^{13}C NMR δ 13.8, 58.8, 63.4, 70.6, 126.0, 128.9, 129.3, 131.4, 161.2. MS(ES): m/z 337.0721 $[M + Na]^+$.

Preparation of Trannulenes

Compound 2. Treatment of a toluene solution of equimolar amounts of $C_{60}F_{18}$ (3.0 mg, 2.82 µmol) and **1a** (0.8 mg, 4.52 µmol) with DBU (0.6 mg, 4.24 µmol) at room temperature produced a lemon yellow solution which gradually turned light brown with the formation of large amounts of black precipitate. The reaction mixture was stirred for a further 10 min and filtered. HPLC (4.7 mL min^{-1}) afforded fractions at 8.2 min and 38.0 min ($C_{60}F_{18}$). Concentration of fractions gave trace amounts of **2** and recovered $C_{60}F_{18}$ (1.0 mg). MS(EI): m/z 1220 $[M]^+$, 1201 $[M - F]^+$, 1043 $[C_{60}F_{17}]^+$ (100%).

Compounds 3a/3b. Using **1b** under similar reaction conditions to the reaction of **1a** and $C_{60}F_{18}$ with base, gave a pale yellow–brown solution with only a minimal amount of black precipitate. DBU (1.5 mg, 10.2 µmol) was added to a solution of $C_{60}F_{18}$ (12.0 mg, 11.30 µmol) and **1b** (2.1 mg, 11.30 µmol) in toluene at room temperature. The solution changed colour from lemon yellow to light brown. The reaction mixture was stirred for a further 10 min and filtered. HPLC (flow rate 4.7 mL min^{-1}) gave fractions at 6.4 min, 12.7 min and 38.0 min ($C_{60}F_{18}$). Concentration of these fractions afforded **3b** (2.0 mg, 13%), **3a** (4.0 mg, 25%) and $C_{60}F_{18}$ (2.0 mg) respectively.

3a: UV/vis (DCM): 343 nm, 442, 505. ^1H NMR: δ 4.42 (br q, 4 H), 1.45 (br t, 6 H, J 7.3 Hz). ^{19}F NMR (d_8-toluene): δ −157.7 (m, 1 F), −157.5 (m, 1 F), −145.9 (d, 1 F, J 30.1 Hz), −142.7 (m, 3 F), −142.0 (d, J 26.4 Hz, 1 F), −141.1 (d, J 26.4 Hz, 1 F), −140.4 (d, J 30.1 Hz, 1 F), −136.7 (br s, 1 F), −136.45 (br s, 3 F), −136.15 (br s, 2 F), −130.15 (br s, 2 F). MS(EI): 1227 $[M]^+$, 1043 $[C_{60}F_{17}]^+$ (100%).

3b: UV/vis (DCM): 344 nm, 444, 513. ^1H NMR: δ 4.41 (br m, 8 H), 1.43 (br t, 6 H, J7.3 Hz), 1.41 (br t, 6 H, J 7.3 Hz). MS(EI): 1392 $[M]^+$, 1208 $[C_{60}F_{16}[CCN(CO_2Et)_2]]^+$, 1024 $[C_{60}F_{16}]^+$ (100%).

Compound 4. DBU (1.9 mg, 12.7 µmol) was added to a solution of $C_{60}F_{18}$ (15.0 mg, 14.1 µmol) and **1d** (3.3 mg, 14.1 µmol) in toluene at room temperature. The solution changed colour from lemon-yellow to emerald-green. The reaction mixture was stirred for a further 10 min and filtered. HPLC (2.0 mL min^{-1}) gave a single fraction at 7.7 min. Concentration of the toluene solution gave the product as a green solid (7.0 mg, 29%). UV/vis [DCM, (ε)]: 440(3690) nm, 614(2590), 666(3760). ^1H NMR: δ 1.47 (t, 27 H, J 7.1 Hz), 4.50 (br q, H, J 7.1 Hz). ^{19}F NMR: δ −144.24 (s, 6 F), −144.23 (s, 6 F), −136.7 (s, 3 F). MS(EI): m/z 1698 $[M]^+$, 1467 $[C_{60}F_{15}[C(CO_2Et)_3]_2]^+$, 1236 $[C_{60}F_{15}$-$[C(CO_2Et)_3]]^+$, 1005 $[C_{60}F_{15}]^+$ (100%).

Compound 5. DBU (0.8 mg, 5.08 µmol) was added to a solution of $C_{60}F_{18}$ (6.0 mg, 5.65 µmol) and **1e** (1.2 mg, 5.65 µmol) in toluene at room temperature. The solution changed colour from lemon-yellow to emerald-green. The reaction mixture was stirred for a further 10 min and filtered. HPLC (4.7 mL min^{-1}) gave fractions at 3.2 min and 38.0 min. Concentration of the toluene solution provided the desired product as a green solid (3.0 mg, 33%) and recovered $C_{60}F_{18}$ (1.0 mg). UV/vis (DCM): 435 nm, 609, 659. ^1H NMR: δ 1.57 (t, 18 H, J 7.3 Hz), 4.67 (br q, 12 H, J 7.3 Hz). ^{19}F NMR: δ −142.5 (s, 6 F), −141.9 (s, 6 F), −135.5 (s, 3 F). MALDI-TOF (+ve ion mode): m/z 1574 $[M - NO_2]^+$, 1415 $[C_{60}F_{15}[C(CO_2Et)_2NO_2]_2]^+$, 1323

$[C_{60}F_{15}[C(CO_2Et)_2]_2]^+$, 1166 $[C_{60}F_{15}[C(CO_2Et)_2]]^+$, 1005 (−ve mode only, $[C_{60}F_{15}]^-$).

Compound 6. DBU (0.6 mg, 4.24 µmol) was added to a solution of $C_{60}F_{18}$ (5.0 mg, 4.71 µmol) and **1f** (1.3 mg, 4.71 µmol) in toluene at room temperature. The solution changed colour from lemon yellow to emerald green. The reaction mixture was stirred for a further 10 min and filtered. HPLC (flow rate 2.0 mL min^{-1}) gave fractions at 7.6 min and 8.0 min. UV/vis (DCM): 392 nm, 443 (sh), 613, 666. ^{1}H NMR: δ 4.55 (m, AB part of ABX_3 spin system, 12 H, *J* 10.4, 7.2 Hz), 4.08 (s, 3 H), 1.53 (t, 18 H, *J* 7.3 Hz). ^{19}F NMR: δ −142.9 (s, F), −141.9 (s, F), −135.5 (s, F). MALDI-TOF (−ve ion mode): *m*/*z* 1163 $[C_{60}F_{15}[C(CO_2Et)_2]]^-$, 1007 $[C_{60}F_{15}]^-$ (100%).

Compound 7. DBU (0.6 mg, 4.24 µmol) was added to a solution of $C_{60}F_{18}$ (3.0 mg, 2.82 µmol) and **1g** (1.4 mg, 4.52 µmol) in toluene at room temperature. The solution changed colour from lemon-yellow to a pale green. The reaction mixture was stirred for a further 10 min and filtered. HPLC (flow rate 2.0 mL min^{-1}) afforded a major fraction at 7.7 min. Concentration of the toluene solution provided trace amounts of the product as a green solid. UV/vis (DCM): ^{1}H NMR: δ 1.35 (t, 18 H, *J* 7.1 Hz), 4.34 (qd, 1 H, *J* 7.1, 1.1 Hz), 4.75 (s, 6 H), 7.41 (m, 15 H), 7.47 (m, 6 H); ^{19}F NMR: δ −143.3 (s, 6 F), −142.4 (s, 6 F), −135.5 (s, 3 F). MALDI-TOF (+ve ion mode): *m*/*z* 1481 $[C_{60}F_{15}[C(CO_2Et)_2]_3 + H]^+$, 1323 $[C_{60}F_{15}[C(CO_2Et)_2]_2]^+$, 1163 $[C_{60}F_{15}[C(CO_2Et)_2]]^+$, 1005 (−ve mode only, $[C_{60}F_{15}]^-$).

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