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Design and synthesis of multi-component 18π annulenic fluorofullerene ensembles suitable for donor–acceptor applications

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A series of trannulene (all-*trans* annulene) derivatives of [60]fullerene have been prepared by reacting $C_{60}F_{18}$ with methanetricarboxylate esters that incorporate a range of photoactive functions. All the compounds have the intense emerald-green colour of fullerene trannulenes, characterised by strong bands at *ca.* 612 and 667 nm. Single crystal X-ray studies show that the packing varies with the nature of the addend, attributable to differing steric effects. UV/vis absorption spectra display transitions of the respective fullerene and addend models, indicating absence of electronic interactions between them in the ground state. These now provide an extensive series for testing photoactive (light-harvesting) properties, with the exceptional properties of having strong visible light absorption. Their exceptional stability is attributed to the 18π aromatic circuit, inability to undergo nucleophilic substitution without disrupting this circuit, and a curved cage region that is shielded to reagents by the three bulky addends.

Introduction

The design and successful construction of nanoscale molecular devices that transduce light energy into useful chemical work with high efficiency is a major goal of the physical and chemical sciences. Photosynthesis achieves this goal by a complex series of energy-absorbing and electron-transfer events resulting in the production of cellular fuel in the form of adenosine triphosphate. There is now widespread interest in mimicking the basic processes of photosynthesis by linking moieties that can, upon photoexcitation, transfer and store energy/electrons.[1,2]

With the advent of fullerenes, a new energy/electron-accepting functionality became available. This three-dimensional molecule exhibits many characteristics amenable for the construction of artificial photovoltaic devices.[1–3] However, saturation of one or more of the fullerene carbon–carbon double bonds as a consequence of derivatisation usually results in a reduction in electron affinity of the carbon cage.[4] By contrast the strong fluorine electron withdrawal results in *enhancement* of the electron affinity (values for $C_{60}F_{18}$ and $C_{60}F_{36}$ are *ca.* 3.10 and 3.48 eV compared with 2.67 eV for C_{60})[5] thus improving the fullerene suitability for photovoltaic applications.

Of the fluorofullerenes available, the recent discovery of the family of trannulenes comprising an 18π annulene in the all-*trans* configuration, provided a new opportunity for the design of organic-based photovoltaic devices.[3,6] Trannulenes have high electron affinities enabling them to stabilise charged entities more effectively than conventional fullerene derivatives. Additionally trannulenes have rich visible absorptions attributed to the diatropic 18π annulene substructure.[3,6,7] Coupled with a mild preparative methodology producing radial three-dimensional architectures, these molecules could be a useful molecular building block for tailor-made components for optoelectronics, molecular-scale logic gates and sensor design. Preliminary electron-transfer investigations of an extended tetrathiafulvalene trannulene dyad confirmed the ability of these remarkable molecules to accept a charged-entity and store the photoexcitation energy in a long-lived charge-separated state.[6a]

We now describe the preparation of many multi-component trannulenes (Fig. 1), incorporating a range of photoactive functionalities.

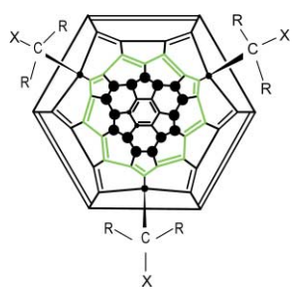

Fig. 1 Schlegel diagram of [18]trannulenes (18π annulene shown in green) (R = CO_2R', X = electron withdrawing group. ● = F).

Results and discussion

A. Preparation of trannulenes incorporating photoactive functions using bromomalonate

We reported recently that trannulation of $C_{60}F_{18}$ can be achieved using tertiary Michael donors if the steric bulk of the carbon nucleophile was sufficient to effect the required substitution process (Scheme 1),[6b] which takes place threefold.

Preliminary investigations revealed the use of bromo- and chloromalonate esters provided the necessary bulk to produce trannulation.[3] Trannulene formation requires direct reaction of the corresponding tertiary Michael donor with $C_{60}F_{18}$ in the presence of base, rather than the *in situ* generation of the corresponding halomalonate ion, due to the markedly different rates

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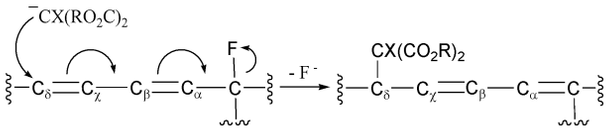
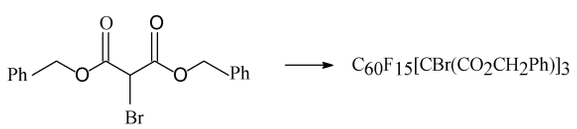


Scheme 1 Generalisation of nucleophilic attack of the α-halomalonate carbanion on $C_{60}F_{18}$ (X = EWG; R = Me, Et).

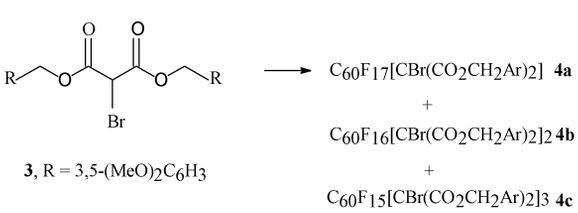
of deprotonation of the malonate ester *vs.* the reaction of DBU with $C_{60}F_{18}$.[8]

Therefore, substitution of one or both ester groups with suitable photoactive motifs would provide an initial avenue for the investigation of the photophysical and electrochemical properties of trannulene-based arrays. Trannulene formation using equimolar amounts of dibenzyl bromomalonate (**1**) and $C_{60}F_{18}$ in the presence of base proved encouraging, with the formation of (**2**). Typical spectroscopic characteristics for trannulenes were observed using MALDI-TOF and ^{19}F NMR *i.e.* intense base peak at 1005 amu (negative mode) corresponding to the stable $[C_{60}F_{15}]^-$ anion; the presence of three singlet resonances in 1 : 2 : 2 ratio (see Experimental) confirming C_{3v} symmetry. The ^{1}H NMR spectrum of **2** comprised a multiplet corresponding to aromatic protons [δ 7.43 (m, 30 H)], and an AB coupled spin system assigned to the benzylic protons [δ 5.45 (d, 6 H, J 12 Hz), 5.49 (d, 6 H, J 12 Hz)]. The induction of diastereotopicity observed for the benzylic protons is a consequence of the restricted rotation of the C–C bond connecting the bromomalonato addend to the trannulene sphere.[6b] In the case of trannulenes comprising the diethyl bromomalonato function, the conformers coalesce at room temperature. However no coalescence was observed for **2** up to 313 K, indicative of the greater energy barrier of the respective conformers due to the increased steric bulk of the benzyl esters.



1 **2**

As a result of this initial success, the stepwise preparations of stronger electron-donating functions were undertaken (Scheme 2). Reaction of equimolar amounts of the corresponding bromomalonate of the 3,5-dimethoxybenzyl ester (**3**) with $C_{60}F_{18}$ afforded trace amounts of the corresponding trannulene (**4c**) and associated bis-substitution adduct (**4b**); the corresponding mono-substitution product (**4a**) being the major derivative. Increasing the amount of **3** and base provided the desired trannulene in 32% yield (Table 1). The stepwise increase in the steric bulk of the dimethoxy functions is assumed to be responsible for the differences in stoichiometry required. This effect from the 3,5-dimethoxybenzyl substituents was apparent in both the ^{1}H and ^{19}F NMR spectra of **4c**, which exhibited reversible dynamic processes associated with the restricted rotation of the malonato addend, though complete coalescence of these conformers was not observed.



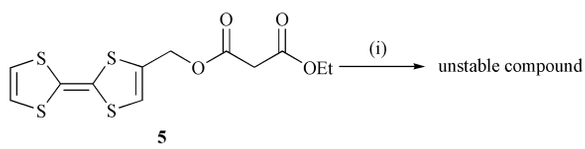
Scheme 2 *Reagents and conditions:* See Table 1.

Tetrathiafulvalene (TTF)–fullerene-based arrays are promising candidates for the preparation of photovoltaic devices due to their ability to store photoexcitation energy in the form of a long-lived charge-separated state.[9] We therefore investigated the synthesis of a trannulene covalently-tethered to a TTF moiety *via* the formation of the corresponding bromomalonate. Although the preparation of the TTF malonate (**5**) was straightforward, the instability of the corresponding bromomalonate precluded further utilisation (Scheme 3). Substituted nitromalonate esters were also considered, however their electrochemical instability also precluded their utilisation.[6b]

Table 1 Products of reaction of **3** with $C_{60}F_{18}$

Reactant	Conditions	Product	Yield
3	[a]	**4a**	34
3	[a]	**4b**	Trace
3	[a]	**4c**	Trace
3	[b]	**4c**	32

[a] **3** (1.0 equiv.), DBU (1.0 equiv.), $C_{60}F_{18}$.(1.0 equiv.) [b] **3** (1.6 equiv.), DBU (1.3 equiv.), $C_{60}F_{18}$.(1.0 equiv.).

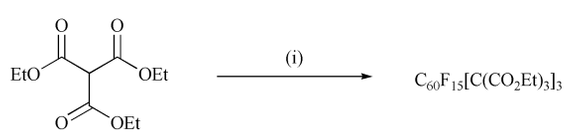


5

Scheme 3 *Reagents and conditions:* (i) DBU (1.0 equiv.), CBr_4 (1.1 equiv.), −78 °C, THF.

B. Use of methanetricarboxylates for the preparation of photoactive trannulenes

(i) Preparation of methanetricarboxylates. Methanetricarboxylate esters proved to be an attractive alternative to the use of substituted halomalonate and nitromalonate functions. By virtue of their low pK_a, high nucleophilicity, absence of keto–enol equilibria,[10] and sufficient steric bulk, they satisfy all the requirements for an expedient tertiary Michael donor for trannulation of the $C_{60}F_{18}$ cage. Previous investigations using the commercially available triethyl methanetricarboxylate (**6**) in the presence of $C_{60}F_{18}$ and DBU afforded the desired trannulene **7** in moderate yield (Scheme 4).[6]



6 **7**

Scheme 4 *Reagents and conditions*: (i) $C_{60}F_{18}$ (1.0 equiv.), DBU (0.9 equiv.), toluene, 29%.

The preparation of larger amounts of **7** allowed the acquisition of the first ^{13}C NMR spectrum of a trannulene. For comparative purposes we show first the spectrum for $C_{60}F_{18}$ (Fig. 2), comprising three singlets (each 2 C) at δ 151.76, 149.46, and 148.01, two 1 C singlets at δ 147.69 and 141.64, a 2 C doublet at δ 143.63, J 24.1 Hz and two 2 C multiplets at δ 135.21 (J 13 Hz) and 131.92 (J 9 Hz).

The spectrum of **7** shows marked differences from that for $C_{60}F_{18}$. The spectrum comprises four singlets at δ 150.9, 147.15, 146.8 and 131.7, a singlet at δ 163.05, a doublet at δ 135.03 and multiplets at δ 148.2 and 131.04 (no integration available).

In order to aid assignment of the NMR spectra, *ab initio* calculations of the absolute nuclear shieldings were performed for C_{60}, $C_{60}F_{18}$ and for a model $C_{60}F_{15}H_3$ trannulene structure in which the bulky methanetricarboxylate groups are formally replaced by H atoms.[7] The calculations were carried out at the Restricted Hartree–Fock optimal geometries (RHF/STO-3G for C_{60} and $C_{60}F_{18}$, RHF/6-31G** for $C_{60}F_{15}H_3$), using coupled Hartree–Fock theory with a 6-31G** basis, in the CTOCD-PZ2

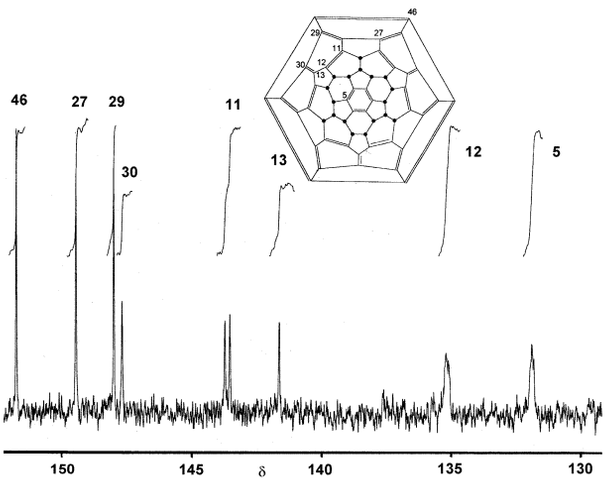


Fig. 2 ^{13}C NMR spectrum of $C_{60}F_{18}$ with calculated assignment of the resonances.

formulation,[11] as implemented in the SYSMO program.[12] Absolute shieldings σ were converted to a ^{13}C chemical shift scale by aligning the computed shielding for C_{60} (31.6 ppm) to the experimental chemical shift with respect to the TMS reference (δ 142.7), leading to a conversion formula: $\delta = 174.3 - (\sigma/\text{ppm})$.

The computed patterns of chemical shifts in the sp^2 region have a wider spread than the experimental spectra, but show a good overall resemblance to them and should be sufficiently accurate for the purpose of assignment. The computed spectrum for $C_{60}F_{18}$ (with atom numbering as in Fig. 2) has δ 151.8 (C46), 147.0 (C27), 144.1 (C29), 142.6 (C30), 135.2 (C11), 135.0 (C13), 126.4 (C12), 126.2 (C5), leading to the assignment of the experimental spectrum given in Fig. 2. Confidence in this assignment is increased by the fact that the computed spectrum reproduces the sequence of 1 C and 2 C lines, and is compatible with the experimental distinction between centres with three sp^2 neighbours (singlets in the experimental spectrum) and centres geminal to a fluorine atom (doublet/multiplet). In this assignment, the C5 signal for the carbon of the isolated hexagonal ring of $C_{60}F_{18}$ is shifted 3.5 ppm upfield from that in benzene itself.

The computed spectrum of the $C_{60}F_{15}H_3$ model trannulene has (with atom numbering as in Fig. 4) δ 165.4 (C13), 148.9 (C11), 144.4 (C46), 143.9 (C12), 140.4 (C29), 133.9 (C10), 122.9 (C27), 117.5 (C5), leading to the assignment of the experimental spectrum given in Fig. 3a. The shift of the 1 C singlet for C13 is well reproduced by the calculation, although the experimental multiplet structure at δ 148.2, 147.2 indicates that the closely spaced lines for C12 and C46 in the computed model spectrum are in reverse order. The C5 signal for the carbon of the isolated hexagonal cycle is shifted only slightly from its position in $C_{60}F_{18}$; those carbons of the trannulene circuit that are common to $C_{60}F_{18}$ and $C_{60}F_{15}H_3$ are moved downfield in the latter, by shifts that range from 7.5 ppm (C11) to 23.4 ppm (C13).

Compound **7** crystallises from a chloroform solution as emerald green plates. The X-ray crystal structure shows almost identical structural morphology compared with that of the trannulene derived from diethyl bromomalonate ($C_{60}F_{15}[CBr(CO_2Et)_2]_3$).[3a] However, deviations in the packing arrangement of **7** are observed compared with $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (Fig. 5). The triclinic crystal of **7** reveals the flattened aromatic faces of each molecule exist in a parallel arrangement relative to each other within the crystal cell (Fig. 5a). Other features reveal the intermolecular dihedral angle is virtually zero enabling the observed alternate arrangement of each molecule. This alternate packing arrangement was not observed for the monoclinic crystal of $C_{60}F_{15}[CBr(CO_2Et)_3]_3$ (Fig. 5b), due probably to the bulky bromo substituent disrupting the packing arrangement.

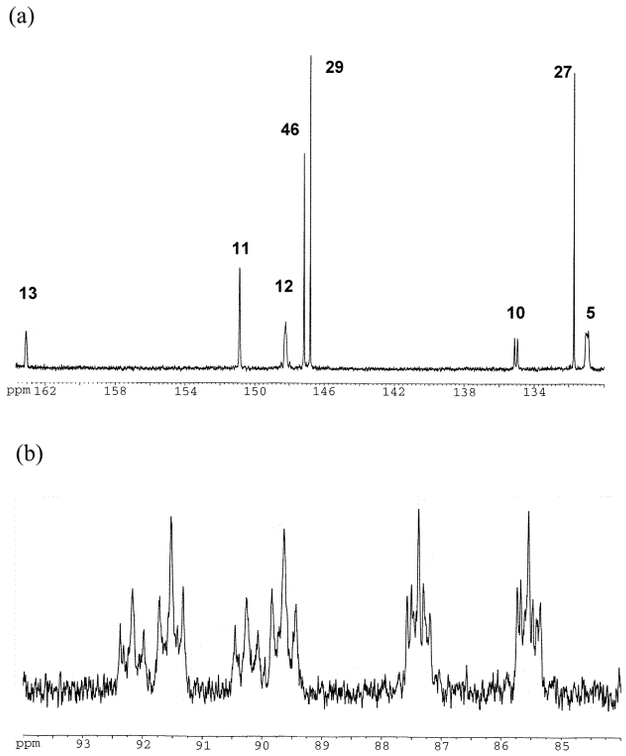


Fig. 3 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **7** showing (a) sp^2 C=C region (assigned according to *ab initio* calculation), and (b) fluorinated sp^3 C–F region with 6 : 6 : 3 peak intensity ratio.

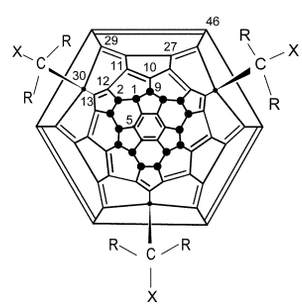


Fig. 4 Trannulene Schlegel diagram showing (lowest locant) numbering for peak identification

From this encouraging result, the preparation of trannulenes tethered to photoactive moieties **8a**–**h** (Chart 1) *via* the methanetricarboxylate reactive function was undertaken. Alcohols **8a**–**c** were commercially available whereas **8d** was prepared *via* the methylation of methyl fluorene-9-carboxylate, followed by reduction using lithium aluminium hydride. Compound **8e** was prepared by initial formylation followed by reduction of the corresponding aldehyde.[14] The corresponding π-extended TTF alcohol (**8f**) was prepared by a modified method reported by Martín *et al.* (Scheme 5).[15] Protection of the commercially available 2-hydroxymethyl-9,10-anthraquinone (**9**), followed by a double Wittig–Horner addition of the 1,3-dithiol phosphonate ester (**10**) afforded the *O*-protected, π-extended TTF (**11**). Treatment of **11** under acid conditions afforded the desired π-extended TTF alcohol **8f** in 94% yield.

The preparation of the ferrocenyl alcohol (**8g**) involved initial Wittig addition of the corresponding ylide of (ferrocenylmethyl)triphenylphosphonium iodide (**12**) with *p*-bromomethylbenzaldehyde to form the ferrocenyl stilbene **13a/b** as a mixture of *cis*/*trans* isomers (Scheme 6). Hydrolysis using barium carbonate furnished the ferrocenyl alcohol (**8g**, 36% overall) as the pure *trans* isomer. 3-Perylenemethanol (**8h**) was prepared *via* Vilsmier formylation of perylene,[16a] followed by reduction of 3-formylperylene to the desired alcohol.[16b]

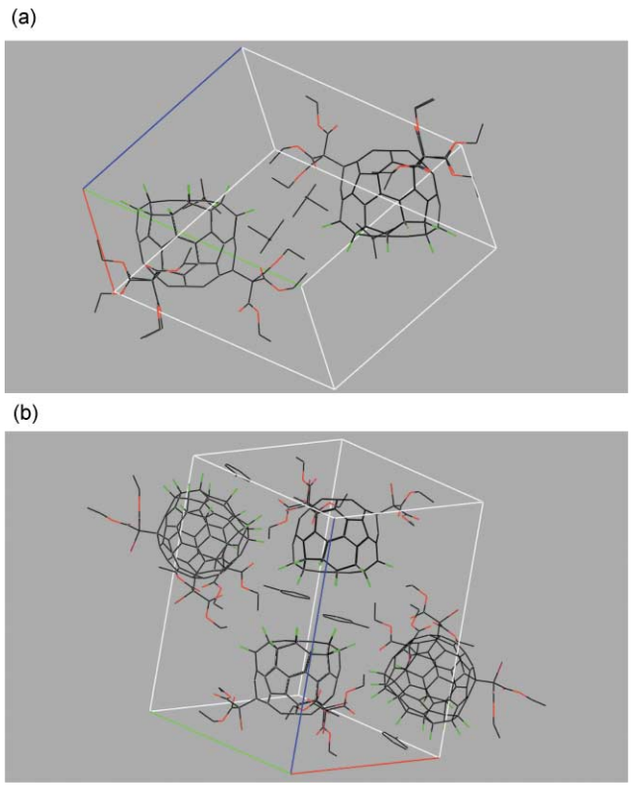


Fig. 5 X-Ray crystal structures revealing the molecular packing arrangements of (a) compound **7** (triclinic, $CHCl_3$ solvate) and (b) $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (monoclinic, toluene solvate). Hydrogens have been omitted for clarity.

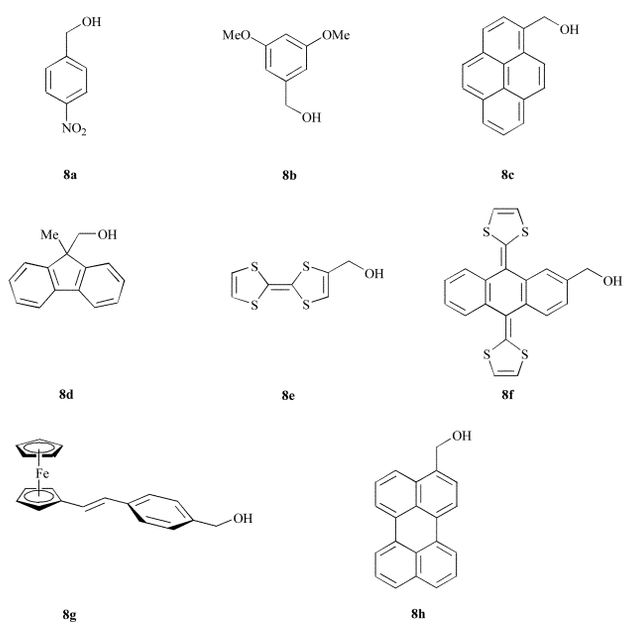
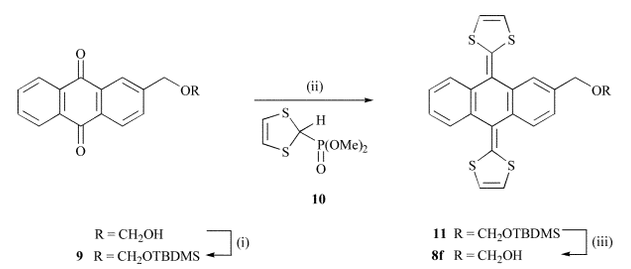


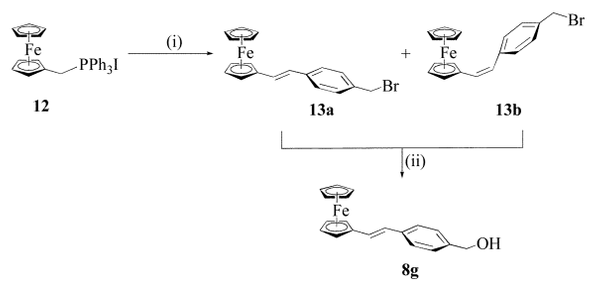
Chart 1



Scheme 5 *Reagents and conditions*: (i) TBDMS-Cl, imidazole, DMF, 79%; (ii) *n*-butyl lithium, −78 °C, THF, 61%; (iii) H^+, THF, 94%.

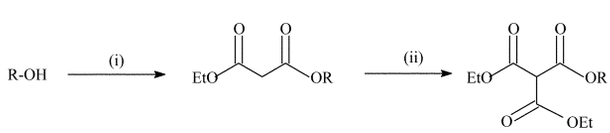
Table 2 Products of reaction of **15a**–**g** with $C_{60}F_{18}$ in toluene

Reactant	Reagent ratio; ester : $C_{60}F_{18}$: DBU	Product	Yield (%)
15a	1.0 : 1.0 : 1.0	**16a**	41
15b	1.6 : 1.0 : 1.3	**16b**	34
15c	1.6 : 1.0 : 1.3	**16c**	28
15d	1.6 : 1.0 : 1.3	**16d**	33
15e	1.5 : 1.0 : 1.0	**16e**	28
15f	1.8 : 1.0 : 1.7	**16f**	See ref. 6*a*
15g	1.6 : 1.0 : 1.3	**16g**	28
15h	2.0 : 1.0 : 1.7	**16h**	Trace



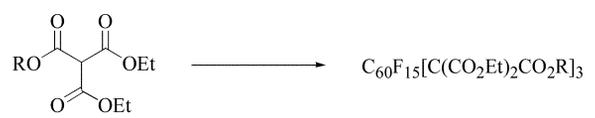
Scheme 6 *Reagents and conditions*: (i) *n*-butyllithium, 4-bromomethylbenzaldehyde, −78 °C, THF; (ii) $BaCO_3$, acetone : water (9 : 1), 36%.

The respective methanetricarboxylate esters (**15a**–**h**) were prepared by initial formation of α-carbanion of the malonate esters (**14a**–**h**) followed by quenching with ethyl chloroformate (Scheme 7). Purification of **15a**–**h** proved troublesome due to similar polarities with their corresponding malonate precursors. Methanetricarboxylate esters with small, polar functional groups can be easily purified *via* base extraction of the crude mixture followed by re-acidification of the alkaline aqueous phase. However the motifs used in the current methanetricarboxylate series were too hydrophobic for this technique. Compounds **15a**–**h** were eventually purified using a combination of a long flash column and HPLC.

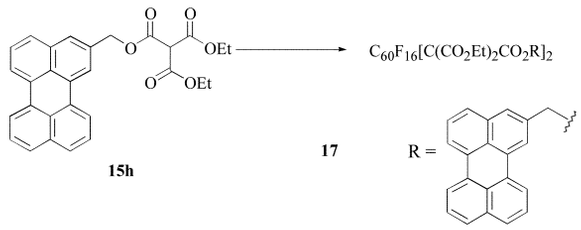


Scheme 7 *Reagents and conditions*: (i) EtO_2CCH_2COCl, pyridine, 0 °C, DCM; (ii) 1. NaH, 2. EtO_2CCl, 0 °C, DMF.

(ii) Preparation of trannulenes from methanetricarboxylates 15a–h. Table 2 and Scheme 8 summarise the trannulenes prepared using the corresponding methanetricarboxylates (**15a**–**h**). The amount of methanetricarboxylate required for trannulation was greater, as the steric bulk of the substituent in close proximity to the carbanionic centre becomes larger (*cf*. ref. 6), for example, the formation of **16f** from **15f** required 1.8 equiv. whereas the less sterically demanding methanetricarboxylate **15a** only required an equimolar equivalent relative to $C_{60}F_{18}$ to furnish **16a**. One notable exception was the attempted trannulene formation from **15h**. An extremely low yield of the trannulene derivative (**16h**) resulted, the major product being the corresponding bisadduct (**17**, Scheme 9). Despite varying the conditions, a satisfactory yield of **16h** was unobtainable. This was attributed to the sterically demanding perylene function.

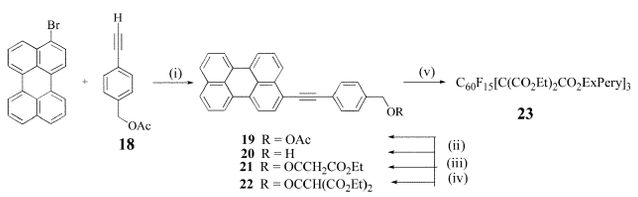


Scheme 8 *Reagents and conditions:* See Table 2 for details.



Scheme 9 *Reagents and conditions:* $C_{60}F_{18}$ (1.0 equiv.), DBU (0.9 equiv.), toluene.

This steric barrier was overcome *via* the incorporation of a rigid phenylacetylene bridge between the perylene nucleus and the methanetricarboxylate function (Scheme 10). Palladium-catalysed coupling of 3-bromoperylene with the substituted phenylacetylene (**18**) afforded **19** in 46% yield. Acetyl deprotection of **19** to afford **20**, followed by malonate formation furnished **21**. Methanetricarboxylate **22** was isolated from a mixture comprising the starting material **21** using HPLC purification.



Scheme 10 *Reagents and conditions:* (i) *N*-bromosuccinimide, DMF; (ii) $Pd[PPh_3]_4$, CuI, trimethylsilylacetylene, piperidine, THF, Δ; (iii) TBAF, THF, −78 °C; (iv) $Pd[PPh_3]_4$, CuI, piperidine, THF; (v) K_2CO_3, THF/MeOH, (v) $C_{60}F_{18}$ (1.0 equiv.), DBU (1.3 equiv.), toluene, 31%.

Treatment of **22** and $C_{60}F_{18}$ with base afforded the desired trannulene **23** in 31% yield after HPLC purification.

C. Dynamic behaviour of trannulenes as observed by NMR

A previous variable-temperature ^{1}H NMR study on a trannulene derivative ($C_{60}F_{15}[CBr(CO_2Et)_2]_3$) revealed broadening of the ethyl ester resonances at temperatures below 298 K.[6b] This unusual feature was shown to be reversible, an observation also observed for compounds **16a**–**g** and **23**. An increase in the conformational restriction of the C–C bond connecting the addend to the trannulene nucleus was observed in trannulenes exhibiting an increase in lateral steric bulk. This is illustrated in the ^{19}F NMR spectra (Fig. 6) of trannulenes **16b** and **16f**.

For trannulenes where the steric bulk is transduced longitudinally from the site of attachment, as is the case in **16g** and **23**, the presence of conformational isomerism in the ^{19}F NMR spectra is not observed. However, as lateral steric size is increased, the presence of conformers becomes apparent. The most extreme example is the ^{19}F NMR of **16f** (Fig. 6d), where the presence of three extended tetrathiafulvalenyl rings induce significant lateral steric bulk, resulting in the observation of approximately four conformers at 298 K.

D. Electronic absorption spectra

The ground-state absorption spectra of trannulenes **16a**–**g**, **23** display transitions that can be assigned to the trannulene and to substituents respectively. Figs. 7a–e show the spectra of **16c**,**d**,**f**,**g** and **23** compared to those of the respective models compounds **15c**,**d**,**f**,**g** and **22**. All fullerene-centred diagnostic bands of trannulenes are observed in the dyads[3,6] together with those of models compounds and no shift of such bands were observed in the dyads with respect to models (Table 3), indicating the absence of any electronic interaction between the two moieties.

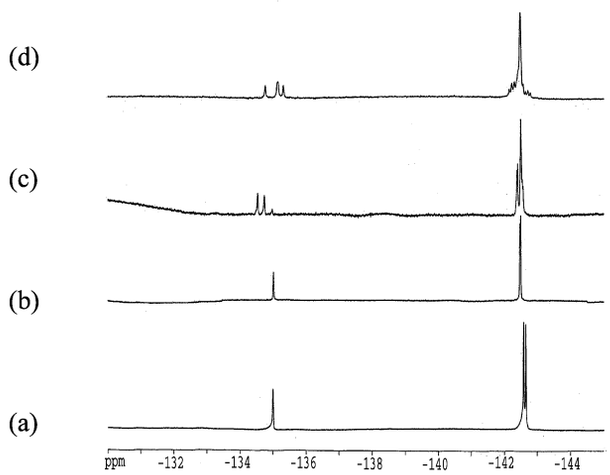


Fig. 6 ^{19}F NMR ($CDCl_3$) spectra of compounds (a) **16g**, (b) **23**, (c) **16b** and (d) **16f** at 298 K.

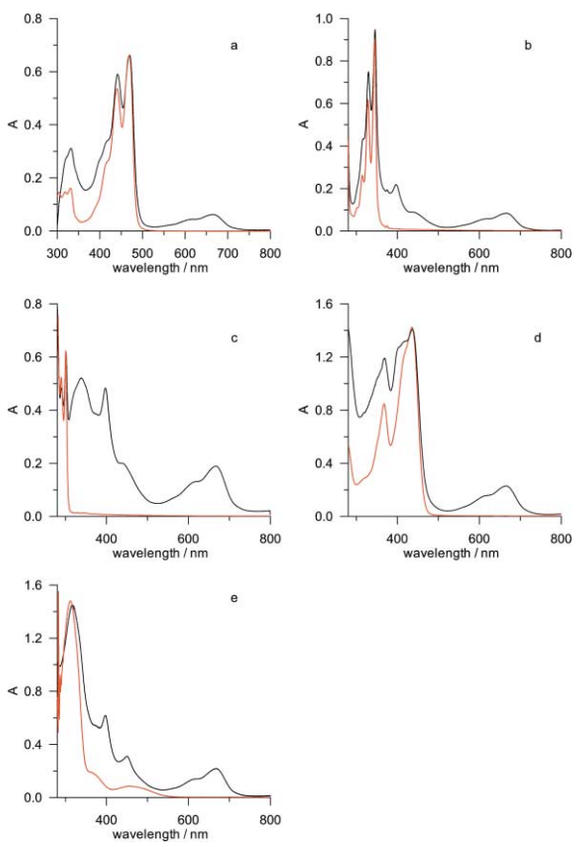


Fig. 7 Electronic absorption spectra of CH_2Cl_2 solutions of trannulenes **16c**,**d**,**f**,**g**, **23** and related model compounds **15c**,**d**,**f**,**g**, **22**. (a) **23** (black line) and **22** (red line); (b) **16c** (black line) and **15c** (red line); (c) **16d** (black line) and **15d** (red line); (d) **16f** (black line) and **15f** (red line) (e) **16g** (black line) and **15g** (red line), all at 25 °C.

E. Stability of the trannulenes

The trannulenes derived from $C_{60}F_{18}$ are more stable towards storage than any other fullerene that we have encountered. In contrast to other fluorofullerenes, they are even resistant to standing overnight in aqueous acetone. We attribute this exceptional stability to three factors: (i) the increased aromaticity arising from the presence of the 18π annulene chain, (ii) inability to nucleophilically substitute any of the fluorines by either the S_N2' or extended S_N2' (S_N2'') mechanisms without disrupting the annulene chain, and (iii) shielding from attacking reagents of the curved portion of the cage by the three bulky addends.

Table 3 Electronic absorption for trannulenes and precursors in dichloromethane at 25 °C

Compound	λ_{max}/nm						
16a	667	612	438	397	338		
16b	667	612	397	280			
16c	666	612	440	396	344	328	314
15c					344	328	314
16d	667	615	397	301	290	258	
15d				300	289	258	
16e	667	613		318	309		
16f	666	616	436	368	262		
15f			436	368	262		
16g	667	612	450	397	320		
15g			462	366	312		
16h	663	610	469	441	332	304	
15h			468	440	330	304	
22	668	611	472	442		333	305
23						332	304

Conclusions

In summary, we have described a simple and efficient method for the preparation of a series of novel, multi-component photoactive systems based on the trannulene structure, and having strong visible light absorption. The simple reaction of methanetricarboxylate anions with $C_{60}F_{18}$ demonstrates the versatility of this methodology enabling the attachment of a plethora of functions tailored for specific applications. Photophysical investigations of these trannulene derivatives are currently underway, and the most promising compounds will be synthesised in large (*ca.* 400 mg) quantities, the minimum required for testing in light-harvesting applications.

Experimental

Toluene was distilled from sodium benzophenone ketyl. Other solvents 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.

Preparation of addends

Normal work up involved DCM addition, washing (brine), drying ($MgSO_4$) and concentration (*in vacuo*).

Compound **1** was prepared according to the method of Cossement *et al.*[17]

Bis-(3,5-dimethoxybenzyl) malonate

Malonyl dichloride (145 μL, 1.49 mmol) was added to a solution of 3,5-dimethoxybenzyl alcohol (0.500 g, 2.98 mmol) and pyridine (239 μL, 2.96 mmol) in DCM (5 mL) at 0 °C. The reaction was stirred at 0 °C for 2 h. then at RT for a further 4 h. Normal work up and flash column chromatography (silica gel), eluting with DCM : EtOH (99 : 1) gave the product (0.310 g, 52%) as a white solid.

^{1}H NMR ($CDCl_3$): δ 3.36 (s, 2 H), 3.70 (s, 12 H), 5.05 (s, 4 H), 6.34 (bt, 2 H), 6.41 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 41.5, 55.3, 67.1, 100.3, 105.8, 137.4, 160.9, 166.2. MS(EI): *m*/*z* 404 $[M]^+$.

Compound 3

DBU (100 μL, 0.668 mmol) was added to a solution of bis-(3,5-dimethoxybenzyl) malonate (0.300 g, 0.743 mmol) in THF (50 mL) at room temperature and stirred for one hour. The reaction mixture was then cooled to −78 °C and a solution of carbon tetrabromide (0.222 g, 0.668 mmol) in THF (5 mL) was added and the reaction mixture was stirred at −78 °C for a further 2 h. The reaction mixture was quenched (1% HCl, 5 mL) and allowed to warm to RT. Normal work up and flash column chromatography (silica gel), eluting with DCM : petroleum spirit (80 : 20) gave **3** (0.252 g, 70%) as a white solid.

^{1}H NMR ($CDCl_3$): δ 3.70 (s, 12 H), 4.88 (s, 1 H), 5.10 (s, 4 H), 6.35 (bt, 2 H), 6.46 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 42.1, 55.3, 68.4, 100.4, 105.7, 136.6, 160.9, 164.2. MS(EI): *m*/*z* 482 $[M]^{+\ 79}$Br, 484 $[M]^{+\ 81}$Br.

Compound 11

n-Butyllithium (1.78 mL, 1.6 M, 2.84 mmol) was added dropwise to a solution of dimethyl 1,3-dithiol-2-ylphosphonate (0.602 g, 2.84 mmol) in THF (10 mL) at −78 °C and stirred for 1 h. A solution of 2-(*tert*-butyldimethylsilanyloxymethyl)-anthraquinone (0.500 g, 1.42 mmol) in THF (5 mL) was added dropwise to the reaction mixture and stirred at −78 °C for a further 1 h. The reaction mixture was allowed to warm to RT and stirred overnight. Normal work up and flash column chromatography (silica gel), eluting with DCM : petroleum spirit (1 : 1) provided the desired product (0.287 g, 39%) as a bright yellow solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.11 (s, 6 H), 0.95 (s, 9 H), 4.77 (s, 2 H), 6.27 (s, 4 H), 7.28 (m, 2 H), 7.64 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −4.8, 18.9, 26.4, 65.3, 117.0, 117.2, 122.5, 123.5, 124.7, 124.8, 124.9, 125.8, 134.1, 135.3, 135.4, 139.3. MS(EI): *m*/*z* 524 (M^+, 100%), 393 (M − OTBMS, 50%), 196 (25%).

Compound 8e

5% HCl (15 mL) was added to a solution of (9,10-bis-[1,3]-dithiol-2-ylidene-9,10-dihydroanthracen-2-ylmethoxy)-*tert*-butyldimethylsilane (0.167 g, 0.319 mmol) in THF (20 mL) and stirred at RT overnight. Normal work up and flash column chromatography (silica gel), eluting with EtOAc : petroleum spirit (1 : 1), followed by EtOAc provided the desired product (0.123 g, 94%) as a bright yellow solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.65 (bt, 1 H, *J* 6 Hz), 4.71 (d, 2 H, *J* 6 Hz), 6.20 (s, 4 H), 7.28 (m, 2 H), 7.64 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 65.4, 117.0, 117.1, 117.2, 122.0, 123.6, 124.5, 124.9, 125.1, 126.0, 134.9, 135.3, 135.5, 135.7, 135.8, 138.9. MS(EI): *m*/*z* 410 (M^+, 100%).

Compound 8g

n-Butyllithium (1.17 mL, 1.6 M, 1.87 mmol) was added to a suspension of (ferrocenylmethyl)triphenylphosphonium iodide (1.00 g, 1.69 mmol) in THF (30 mL) at −78 °C and stirred for 1 h. A solution of *p*-bromomethylbenzaldehyde (0.338 g, 1.69 mmol) in THF (5 mL) was added dropwise to the reaction mixture and stirred at −78 °C for a further 1 h. The reaction mixture was allowed to warm to RT and stirred overnight. Normal work-up and flash column chromatography (silica gel), eluting with DCM : petroleum spirit (1 : 1) provided the desired product (0.300 g, 46%) as a bright orange oil. This material was used directly for the hydrolysis. Barium carbonate (0.309 g, 1.57 mmol) was added to the solution of 1-ferrocenyl-2-(*para*-bromomethylphenyl)ethylene (0.300 g, 0.783 mmol) in acetone : water (9 : 1, 50 mL) at RT. The reaction mixture was stirred for 3 days, then filtered. Normal work-up and flash column

chromatography (silica gel), eluting initially with DCM : petroleum spirit (1 : 1), followed by DCM provided the desired product (0.192 g, 36%) as a bright orange solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.57 (t, 1 H, *J* 6 Hz), 4.12 (s, 5 H), 4.27 (m, 2 H), 4.44 (m, 2 H), 4.66 (d, 2 H, *J* 6 Hz), 6.77 (d, 1 H, *J* 16 Hz), 6.87 (d, 1 H, *J* 16 Hz), 7.31 (d, 2 H, *J* 8 Hz), 7.41 (d, 2 H, *J* 8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 65.2, 66.9, 69.1, 69.2, 83.2, 125.5, 125.9, 127.1, 127.4, 137.4, 139.3. MS(ES): *m*/*z* 318.0673 (M^+) (calculated 318.1976 for $C_{19}H_{18}OFe$).

Compound 19

Tetrakis(triphenylphosphine)palladium(0) (0.022 g, 19.2 μmol) and copper(I) iodide (0.002 g, 9.6 μmol) were loaded into a Schlenck flask and thoroughly evacuated *in vacuo*. The flask was then placed under an argon atmosphere and THF (5 mL) was added. Solutions of 3-bromoperylene (0.317 g, 0.96 mmol) in THF (10 mL) and piperidine (20 mL) were added sequentially and the reaction mixture was stirred at RT for 30 min. A solution of 4-ethynylbenzyl acetate (0.200 g, 1.15 mmol) in THF (5 mL) was added and the reaction mixture was heated to reflux for 2 h. followed by stirring at RT overnight. The reaction mixture was concentrated *in vacuo*. Flash column chromatography (silica gel), eluting with DCM : petroleum spirit (1 : 3) gave starting material (0.038 g, 12%) and the desired product (0.188 g, 46%; 53% based on recovered starting material) as bright yellow/orange solids.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 2.16 (s, 3 H), 5.16 (s, 2 H), 7.40 (d, 2 H, *J* 7.9 Hz), 7.48 (m, 2 H), 7.57 (dd, 1 H; *J* 8.2, 0.7 Hz), 7.66 (d, 2 H, *J* 7.9 Hz), 7.69 (m, 2 H), 7.70 (d, 1 H, *J* 7.9 Hz), 8.10 (d, 1 H, *J* 8.0 Hz), 8.14 (dd, 1 H, *J* 7.7, 1.0 Hz), 8.17 (dd, 1 H, *J* 7.7, 1.0 Hz), 8.20 (dd, 1 H, *J* 7.7, 1.0 Hz), 8.25 (dd, 1 H, *J* 7.7, 1.0 Hz). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 20.9, 65.9, 88.6, 94.9, 119.6, 120.0, 120.6, 120.7, 120.9, 123.4, 126.0, 126.5, 126.6, 127.2, 128.0, 128.3, 128.4, 128.5, 129.9, 130.6, 130.9, 131.0, 131.4, 131.7, 131.9, 134.5, 134.6, 136.1, 170.8. MS(EI): *m*/*z* 424 $[M]^+$, 365 $[M - OAc]^+$.

Compound 20

K_2CO_3 (0.611 g, 4.4 mmol) was added to a solution of **19** (0.188 g, 0.44 mmol) in THF/MeOH (20 mL; 1 : 1) and stirred at room temperature for 3 h. Normal work-up and flash column chromatography (silica gel), eluting with DCM : petroleum spirit (1 : 1) followed by DCM provided trace amounts of starting material and **20** (0.157 g, 93%) as a bright yellow/orange solid. MS(EI): *m*/*z* 380 $[M]^+$, 368 $[M - OH]^+$.

General procedure for the preparation of malonate esters

Ethyl 3-chloro-3-oxo-propanoate (1.5 equiv.) was added to a solution of the corresponding alcohol (1.0 equiv.) and pyridine (1.0–1.5 equiv.) in dichloromethane (10 mL) 0 °C. The reaction was stirred at 0 °C for 2 h, then at room temperature for a further 4 h. This was followed by normal work up.

Compound 5

Using 4-(hydroxymethyl)tetrathiafulvalene (0.120 g, 0.513 mmol), pyridine (62 μL, 0.769 mmol) and ethyl 3-chloro-3-oxo-propanoate (102 μL, 0.769 mmol) gave **5** (0.090 g, 50%) as a bright yellow oil after flash column chromatography (silica gel, DCM).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (t, 3 H, *J* 7.2 Hz), 3.39 (s, 2 H), 4.21 (q, 2 H, *J* 7.2 Hz), 4.85 (s, 2 H), 6.28 (s, 2 H), 6.34 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.5, 41.7, 61.9, 62.1, 119.4 (2 C), 119.5, 120.3, 130.6, 166.4, 166.5. MS(EI): *m*/*z* 348 $[M]^+$.

Compound 14a

Using 4-nitrobenzyl alcohol (0.500 g, 3.27 mmol), pyridine (553 μL, 4.90 mmol) and ethyl 3-chloro-3-oxo-propanoate (629 μL, 4.90 mmol) gave **14a** (0.598 g, 68%) as a colourless oil after flash column chromatography (silica gel, DCM).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, 3 H, *J* 7.2 Hz), 3.48 (s, 2H), 4.19 (q, 2 H, *J* 7.2 Hz), 5.23 (s, 2 H), 7.49 (d, 2 H, *J* 9 Hz), 8.21 (d, 2 H, *J* 9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 41.4, 61.9, 66.4, 124.1 (2 C), 128.6 (3 C), 142.4, 166.0, 166.1. MS(EI): *m*/*z* 267 $[M]^+$.

Compound 14b

Using 3,5-dimethoxybenzyl alcohol (1.00 g, 5.95 mmol), pyridine (721 μL, 8.93 mmol) and ethyl 3-chloro-3-oxo-propanoate (1.18 mL, 8.93 mmol) gave **14b** (1.68 g, 71%) as a colourless oil after flash column chromatography (silica gel, DCM).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (t, 3 H, *J* 7.2 Hz), 3.41 (s, 2 H), 3.76 (s, 6 H), 4.22 (q, 2 H, *J* 7.2 Hz), 5.09 (s, 2 H), 6.39 (t, 1 H, *J* 2.1 Hz), 6.47 (d, 2 H, *J* 2.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 41.4, 61.9, 66.4, 124.1 (2 × C), 128.6 (3 C), 142.4, 166.0, 166.1. MS(ES): *m*/*z* 305.09968 $[M + Na]^+$.

Compound 14c

Using 1-pyrenemethanol (0.500 g, 0.22 mmol), pyridine (365 μL, 3.23 mmol) and ethyl 3-chloro-3-oxo-propanoate (414 μL, 3.23 mmol) gave **14c** (0.598 g, 80%) as a colourless solid after flash column chromatography [silica gel, DCM : petroleum spirit (80 : 20)].

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (t, 3H, *J* 7.2 Hz), 3.43 (s, 2 H), 4.14 (q, 2 H, *J* 7.2 Hz), 5.88 (s, 2 H), 8.08 (m, 5 H), 8.22 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 41.6, 61.6, 65.7, 122.7, 124.5, 124.8, 125.5, 125.6, 126.1, 127.3 (2 C), 127.8, 127.9, 128.0, 128.2, 129.5, 130.6, 131.1, 131.8, 166.4, 166.6. MS(ES): *m*/*z* 369.11034 $[M + Na]^+$.

Compound 14d

Using **8d** (0.120 g, 0.57 mmol), pyridine (97 μL, 0.86 mmol) and ethyl 3-chloro-3-oxo-propanoate (108 μL, 0.86 mmol) gave **14d** (0.151 g, 82%) as a colourless oil after flash column chromatography [silica gel, DCM : petroleum spirit (80 : 20)].

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (t, 3 H, *J* 7.2 Hz), 1.53 (s, 3 H), 3.37 (s, 2 H), 4.19 (q, 2 H, *J* 7.2 Hz), 4.26 (s, 2 H), 7.33 (m, 4 H), 7.48 (d, 2 H, *J* 7.2 Hz), 7.73 (d, 2 H, *J* 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 21.5, 41.6, 49.9, 61.5, 71.1, 120.1, 123.8, 127.3, 127.8, 140.0, 148.6, 166.3, 166.6. MS(EI): *m*/*z* 324 $[M]^+$.

Compound 14f

Using **8f** (0.150 g, 0.366 mmol), pyridine (45 μL, 0.549 mmol) and ethyl 3-chloro-3-oxo-propanoate (75 μL, 0.549 mmol) gave **14f** (1.19 g, 71%) as a yellow solid after flash column chromatography [silica gel, DCM : petroleum spirit (50 : 50)].

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.21 (t, 3 H, *J* 7 Hz), 3.41 (s, 2 H), 4.16 (q, 2 H, *J* 7 Hz), 5.21 (s, 2 H), 6.28 (s, 4 H), 7.27 (m, 2 H), 7.66 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 41.6, 61.6, 67.1, 117.1, 117.2, 121.6, 121.7, 124.8, 124.9 (2 C), 125.1, 125.9, 126.0 (2 C), 132.8, 135.2, 135.5, 135.7, 136.1, 136.2, 166.4, 166.5. MS(EI): *m*/*z* 524 (M^+).

Compound 14g

Using **8g** (0.190 g, 0.597 mmol), pyridine (72 μL, 0.896 mmol) and ethyl 3-chloro-3-oxo-propanoate (115 μL, 0.896 mmol) gave **14g** (0.161 g, 62%) as an orange solid after flash column chromatography (silica gel), eluting with DCM : petroleum spirit (50 : 50).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (t, 3 H, *J* 7.2 Hz), 3.40 (s, 2 H), 4.12 (s, 5 H), 4.18 (q, 2 H, *J* 7.2 Hz), 4.27 (m, 2 H), 4.45 (m, 2 H), 5.14 (s, 2 H), 6.67 (d, 1 H, *J* 16 Hz), 6.87 (d, 1 H, *J* 16 Hz), 7.30 (d, 2 H, *J* 8 Hz), 7.40 (d, 2 H, *J* 8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.4, 42.0, 62.0, 66.9, 67.1, 69.1, 69.2, 83.5,

125.7, 126.3, 128.1, 129.3, 134.0, 138.6, 166.8, 168.9. MS(ES): *m*/*z* 432.1040 (M^+) calc. 432.2982 for $C_{24}H_{24}O_4Fe$.

Compound 14h

Using (3-perylenyl)methanol (0.226 g, 0.80 mmol), pyridine (136 μL, 1.20 mmol) and ethyl 3-chloro-3-oxo-propanoate (151 μL, 1.20 mmol) gave **14h** (0.185 g, 58%) as a fluorescent yellow solid after flash column chromatography [silica gel, DCM : petroleum spirit (50 : 50)].

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.19 (t, 3 H, *J* 7.2 Hz), 3.43 (s, 2 H), 4.24 (q, 2 H, *J* 7.2 Hz), 5.50 (s, 2 H), 7.44 (m, 3 H), 7.64 (d, 2 H, *J* 8.1 Hz), 7.74 (d, 1 H, *J* 8.4 Hz), 8.05 (d, 1 H, *J* 8.4 Hz), 8.09 (d, 2 H, *J* 7.2 Hz), 8.14 (d, 2 H, 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 41.6, 61.5, 65.6, 119.3, 120.1, 120.4, 120.5, 123.0, 126.4 (2 × C), 126.5, 126.9, 127.9, 128.0, 128.2, 128.7, 129.9, 130.6, 130.8, 131.6, 132.1, 132.7, 134.4, 166.4, 166.5. MS(EI): *m*/*z* 396 $[M]^+$, 265 $[M - CO_2CH_2CO_2Et]^+$.

Compound 21

Using **20** (0.157 g, 0.41 mmol), pyridine (70 μL, 0.62 mmol) and ethyl 3-chloro-3-oxo-propanoate (85 μL, 0.62 mmol) gave **21** (0.152 g, 75%) as a fluorescent yellow solid after flash column chromatography [silica gel, DCM : petroleum spirit (50 : 50)].

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (t, 3 H, *J* 7.2 Hz), 3.47 (s, 2 H), 4.23 (q, 2 H, *J* 7.2 Hz), 5.24 (s, 2 H), 7.42 (d, 2 H, *J* 7.9 Hz), 7.48 (m, 2 H), 7.57 (dd, 1 H, *J* 7.5, 0.8 Hz), 7.66 (d, 2 H, *J* 7.9 Hz), 7.68 (m, 2 H), 7.71 (d, 1 H, *J* 7.9 Hz), 8.10 (d, 1 H, *J* 8.0 Hz), 8.15 (dd, 1 H, *J* 7.8, 1.0 Hz), 8.17 (dd, 1 H, *J* 7.7, 1.0 Hz), 8.20 (dd, 1 H, *J* 7.8, 1.0 Hz), 8.25 (dd, 1 H, *J* 8.2, 1.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.0, 41.6, 61.6, 66.7, 88.7, 94.9, 119.6, 120.6, 120.7, 120.9, 123.6, 126.0, 126.5, 126.6, 127.2, 128.0, 128.2 (2 C), 128.4, 129.9, 130.6, 130.9, 131.1, 131.5, 131.7, 131.8 (2 C), 131.9, 134.6, 135.4, 166.3, 166.4. MS(EI): *m*/*z* 496 $[M]^+$.

General procedure for the preparation of methanetricarboxylate esters

Sodium hydride (1.3 equiv. as a 60% suspension in oil) was added to a solution of the malonate (1.0 equiv.) in DMF (10 mL) at −20 °C. The mixture was allowed to warm to RT and stirred for 1 h. The mixture was recooled to −20 °C, ethyl chloroformate (1.3 equiv.) was added, and the reaction allowed to warm to RT after 15 min. and stirred at this temperature for a further 3 h. The reaction mixture was 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 then dried ($MgSO_4$), and concentrated *in vacuo*.

Compound 15a

Using **14a** (0.150 g, 0.56 mmol), sodium hydride (0.016 g, 0.67 mmol) and ethyl chloroformate (81 μL, 0.84 mmol) gave **15a** (0.065 g, 34%; 60% based on recovered starting material) and **14a** (0.078 g, 52%) after HPLC (toluene flow rate 2.0 mL min^{-1}) in a 1 : 1 ratio at *t* = 8.5 and 9.1 min, respectively).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (t, 6 H, *J* 7.1 Hz), 4.28 (q, 4 H, *J* 7.1 Hz), 4.47 (s, 1 H), 5.37 (s, 2 H), 7.53 (d, 2 H, *J* 8 Hz), 8.24 (d, 2 H, *J* 8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 59.2, 63.1, 66.6, 124.2 (2 C), 128.8, 142.4, 163.9, 164.0. MS(EI): *m*/*z* 339.

Compound 15b

Using **14b** (0.500 g, 1.77 mmol), sodium hydride (0.116 g, 2.66 mmol) and ethyl chloroformate (221 μL, 2.30 mmol) provided **15b** (0.280 g, 45%; 65% based on recovered starting material) and **14b** (0.154 g, 30%) after HPLC (toluene flow rate 2.0 mL) in a 1 : 2 ratio, *t* = 7.4 and 7.7 min respectively).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (t, 6 H, *J* 7.2 Hz), 3.77 (s, 6 H), 4.24 (q, 4 H, *J* 7.2 Hz), 4.44 (s, 1 H), 5.16 (s, 2 H), 6.39 (m, 1 H), 6.47 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3, 55.8, 59.3, 62.9, 68.1, 100.7, 106.2 (2 C), 137.9, 161.3, 164.2. MS(EI): *m*/*z* 354.

Compound 15c

Using **14c** (0.150 g, 0.43 mmol), sodium hydride (0.012 g, 0.52 mmol) and ethyl chloroformate (63 μL, 0.65 mmol) provided **15c** (0.088 g, 48%; 68% based on recovered starting material) and **14c** (0.052 g, 35%) after HPLC (toluene flow rate 2.0 mL min^{-1}) in a 1 : 2 ratio at *t* = 7.6 and 7.9 min respectively). UV-vis (DCM): 314 nm, 328, 344.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.15 (t, 6 H, *J* 7.1 Hz), 4.19 (q, 4 H, *J* 7.1 Hz), 4.50 (s, 1 H), 5.96 (s, 2 H), 8.05 (m, 4 H), 8.15 (m, 2 H), 8.24 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 59.0, 62.4, 66.5, 122.7, 124.5, 124.6, 124.7, 125.5, 125.6, 126.1, 127.2, 127.5, 127.9, 128.0, 128.2, 129.6, 130.1, 131.1, 131.9, 163.7, 164.0. MS(EI): *m*/*z* 418 $[M]^+$.

Compound 15d

Using **14d** (0.150 g, 0.46 mmol), sodium hydride (0.022 g, 0.55 mmol) and ethyl chloroformate (58 μL, 0.66 mmol) provided **15d** (0.096 g, 53%; 71% based on recovered starting material) and **14d** (0.032 g, 21%) after HPLC eluting with toluene (flow rate 2.0 mL min^{-1}) in a 1 : 2 ratio at *t* = 7.8 and 8.3 min, respectively).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.29 (t, 6 H, *J* 7.4 Hz), 1.57 (s, 3 H), 4.27 (q, 4 H, *J* 7.4 Hz), 4.32 (s, 2 H), 4.46 (s, 1 H), 7.32 (td, 2 H, *J* 7.1, 1.2 Hz), 7.40 (td, 2 H, *J* 7.1, 1.2 Hz), 7.50 (dt, 2 H, *J* 6.9, 0.8 Hz), 7.75 (dt, 2 H, *J* 6.9, 0.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 21.4, 49.9, 59.0, 62.5, 72.0, 120.0, 123.9, 127.3, 127.9, 140.0, 148.5, 163.7, 163.8. MS(EI): *m*/*z* 396 $[M]^+$.

Compound 15e

Using **14e** (0.090 g, 0.260 mmol), sodium hydride (0.014 g, 0.338 mmol) and ethyl chloroformate (32 μL, 0.338 mmol) gave **15e** (0.020 g, 18%; 26% based on recovered starting material) and **14e** (0.032 g, 36%) after flash column chromatography [silica gel, DCM : petroleum spirit (1 : 1)].

^{1}H NMR ($CDCl_3$, 300 MHz) of **15e**: δ 1.26 (t, 6 H, *J* 7.2 Hz), 4.16 (q, 4 H, *J* 7.2 Hz), 4.32 (s, 1 H), 4.81 (s, 2 H), 6.25 (s, 2 H), 6.32 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3, 59.1, 63.0, 63.1, 119.4 (2C), 119.5, 120.7, 131.0, 163.7, 163.8. MS(ES): *m*/*z* 420.988 $[M + H]^+$, 442.970 $[M + Na]^+$.

Compound 15f

Using **14f** (0.187 g, 0.357 mmol), sodium hydride (0.021 g, 0.535 mmol) and ethyl chloroformate (51 μL, 0.535 mmol) gave **15f** (0.070 g, 33%; 42% based on recovered starting material) and **14f** (0.040 g, 21%) after flash column chromatography [silica gel, DCM : petroleum spirit (1 : 1). UV-vis (DCM): 347 nm (sh), 433. ν (KBr)/cm^{-1} 3070, 2980, 1762, 1736, 1547, 1514, 1453, 1423, 1368, 1309, 1257, 1150, 1038, 802, 757, 649.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, 6 H, *J* 7.2 Hz), 4.21 (q, 4 H, *J* 7.2 Hz), 4.47 (s, 1 H), 5.28 (s, 2 H), 6.28 (s, 4 H), 7.28 (m, 2 H), 7.66 (m, 5 H). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 13.87, 58.99, 62.52, 67.821, 117.10, 117.14, 117.18, 117.22, 121.48, 121.64, 124.84, 124.91, 124.95, 125.12, 125.86, 125.94, 126.00, 126.02, 132.36, 135.20, 135.21, 135.63, 135.71, 136.20, 136.36, 163.75, 163.81. MS(EI): *m*/*z* 596 $[M^+]$, 394.

Compound 15g

Using **14g** (0.161 g, 0.372 mmol), sodium hydride (0.022 g, 0.559 mmol) and ethyl chloroformate (53 μL, 0.559 mmol) gave **15g** (0.058 g, 31%; 43% based on recovered starting material)

and **14g** (0.046 g, 29%) after HPLC (toluene flow rate 2.0 mL min^{-1}; 1 : 1 mixture of reactant : product at t = 7.6 min. and t = 7.9 min respectively). UV-vis (DCM): 373 (sh) nm, 468.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22 (t, 6 H, J 7 Hz), 4.14 (s, 5 H), 4.24 (q, 4 H, J 7 Hz), 4.27 (m, 2 H), 4.44 (m, 2 H), 4.45 (s, 1 H), 5.20 (s, 2 H), 6.66 (d, 1H, J 16 Hz), 6.87 (d, 1 H, J 16 Hz), 7.29 (d, 2 H, J 8 Hz), 7.40 (d, 2 H, J 8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 59.0, 62.5, 66.9, 67.9, 69.2, 69.3, 125.2, 126.2, 128.2, 129.3, 133.5, 138.7, 164.2, 164.3. MS(ES): m/z 504.1218 (M^+) calc. 504.3616 for $C_{27}H_{28}O_6Fe$.

Compound 15h

Using **14h** (0.180 g, 0.455 mmol), sodium hydride (0.011 g, 0.452 mmol) and ethyl chloroformate (43 μL, 0.452 mmol) gave **15h** (0.051 g, 24%; 34% based on recovered starting material) and **14h** (0.093 g, 52%) after flash column chromatography [silica gel, DCM : petroleum spirit (1 : 1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.20 (t, 6 H, J 7.2 Hz), 4.21 (q, 4 H, J 7.2 Hz), 4.48 (s, 1 H), 5.64 (s, 2 H), 7.51 (m, 2 H), 7.57 (m, 2 H), 7.74 (m, 2 H), 7.83 (dd, 1 H, J 8.4, 0.9 Hz), 8.17 (d, 1 H, J 7.7 Hz), 8.26 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 13.8, 59.0, 62.5, 66.5, 119.5, 120.4, 120.6, 120.7, 123.8, 126.6, 126.7, 127.2, 128.1, 128.3, 128.4, 128.8, 129.1, 129.7, 130.7, 131.0, 131.8, 132.6, 133.0, 134.6, 163.8, 164.0. MS(EI): m/z 468 $[M]^+$.

Compound 22

Using **21** (0.152 g, 0.31 mmol), sodium hydride (0.010 g, 0.40 mmol) and ethyl chloroformate (44 μL, 0.46 mmol) provided **22** (0.052 g, 30%; 83% based on recovered starting material) and **21** (0.097 g, 64%) after HPLC eluting toluene (flow rate 2.0 mL min^{-1}; 1 : 2 mixture of **22 : 21** at t = 7.3 min. and t = 7.9 min respectively). UV/vis (DCM, ε): 304 (7430) nm, 317 (6123), 332 (6252), 415 (sh, 9203), 440 (19507), 469 (23727).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.29 (t, 6 H, J 7.2 Hz), 4.48 (q, 4 H, J 7.2 Hz), 4.50 (s, 1 H), 5.29 (s, 2 H), 7.41 (d, 2 H, J 7.9 Hz), 7.51 (m, 2 H), 7.62 (dd, 1 H, J 7.5, 0.7), 7.66 (d, 2 H, J 7.9 Hz), 7.72 (d, 1 H, J 8.0 Hz), 7.73 (d, 1 H, J 8.1 Hz), 7.76 (d, 1 H, J 7.9 Hz), 8.18 (d, 1 H, J 7.9 Hz), 8.22 (dd, 1 H, J 7.7, 1.0 Hz), 8.23 (dd, 1 H, J 7.8, 1.0 Hz), 8.27 (dd, 1 H, J 7.7, 1.0 Hz), 8.29 (dd, 1 H, J 8.2, 1.0 Hz). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 13.9, 59.0, 62.6, 67.5, 88.7, 94.9, 119.7, 120.7, 120.8, 121.0, 126.1, 126.6, 126.7, 127.3, 128.1, 128.3 (2 C), 128.5, 128.6, 129.9, 130.7, 131.0, 131.1, 131.6, 131.7, 131.8 (2 C), 132.0, 134.6, 135.0, 163.7, 163.8. MALDI-TOF: m/z 569 $[M]^+$.

Preparation of trannulenes

In all of these preparations, DBU was added to $C_{60}F_{18}$ and malonate in toluene at room temperature and stirred for a further 10 min, the product being then filtered and processed. Emerald green solutions were obtained except where indicated.

Compound 2

Reagent quantities were DBU (0.52 mg, 3.39 μmol), $C_{60}F_{18}$ (3 mg, 2.82 μmol) and **1** (1.77 mg, 4.23 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 8.0 min. Concentration of the toluene solution gave the product as a green solid (4.1 mg, 78%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.45 (d, 6 H, J 12 Hz), 5.49 (d, 6 H, J 12 Hz)], 7.43 (m, 30 H). ^{19}F NMR: δ −143.24 (s, 6 F), −144.00 (s, 6 F), −136.9 (s, 3 F). MALDI-TOF (−ve ion mode): 1005 $[C_{60}F_{15}]^-$.

Compounds 4a/4b

Reagent quantities were DBU (0.4 mg, 2.82 μmol), $C_{60}F_{18}$ (3.0 mg, 2.82 μmol) and **3** (1.37 mg, 2.82 μmol). The solution changed colour from lemon yellow to olive green. HPLC (4.7 ml min^{-1}) gave fractions eluting at 8.9 min, 4.0 min and 3.8 min. Concentration of these fractions *in vacuo* provided **4a** (2.0 mg, 34%), **4b** (<1.0 mg) and **4c** (trace).

4a: ^{1}H NMR: δ 3.78 (s, 6 H), 3.79 (s, 6 H), 5.29 (d, 2 H, J 4 Hz), 5.31 (d, 2 H, J 4 Hz), 6.46 (m, 4 H), 6.49 (m, 2 H). ^{19}F NMR ($CDCl_3$): δ −158.4 (td, 1 F, J 21, 11 Hz), −156.8 (td, 1 F, J 23, 11 Hz), −154.1 (dt, 1F, J 28, 7 Hz), −147.7 (d, 1 F, J 28 Hz), −145.5 (d, 1 F), −145.0 (s, 1 F), −143.1 (s, 2 F), −142.2 (s, 1 F), −139.9 (d, 1 F, J 26 Hz), −139.5 (dt, 1 F, J 27, 4 Hz), −137.4 (s, 1 F), −136.1 (s, 1 F), −135.6 (s, 1 F), −135.1 (s, 1 F), −131.2 (d, 1 F, J 17 Hz), −107.2 (s, 1 F). MS(EI): m/z 1043 $[C_{60}F_{17}]^+$.

4b: ^{1}H NMR: δ 3.77 (s, 6 H), 3.78 (s, 6 H), 3.79 (s, 6 H), 3.81 (s, 6 H), 5.24 (m, 3 H), 5.26 (m, 3 H), 5.28 (m, 1 H), 5.30 (m, 1 H), 6.44 (m, 2 H), 6.48 (m, 4 H), 6.50 (m, 4 H), 6.52 (m, 2 H). ^{19}F NMR ($CDCl_3$): δ −156.9 (bt, 1 F), −153.3 (d, 1 F, J 26 Hz), −150.5 (d, 1 F, J 26 Hz), −146.2 (m, 1 F), −145.9 (d, 1 F, J 30 Hz), −144.2 (s, 1 F), −143.2 (s, 2 F), −142.9 (s, 1 F), −141.7 (s, 1 F), −141.5 (s, 1 F), −139.6 (d, 1 F, J 30 Hz), −139.3 (d, 1 F, J 30 Hz), −137.0 (s, 1 F), −135.0 (s, 1 F), −123.4 (s, 1 F). MS(EI): m/z 1024 $[C_{60}F_{16}]^+$.

Compound 4c

Reagent quantities were DBU (0.6 mg, 3.67 μmol), $C_{60}F_{18}$ (3.0 mg, 2.82 μmol) and **3** (2.2 mg, 4.52 μmol). HPLC (4.7 ml min^{-1}) gave a single fraction eluting at 3.8 min. Concentration of this fraction *in vacuo* provided **4c** (2.0 mg, 32%).

^{1}H NMR: δ 3.78 (bs, 36 H), 5.42 (bd, 6 H, J 11.0 Hz), 5.46 (bd, 6 H, J 11.0 Hz), 6.58 (bs, 6 H), 6.49 (bs, 12 H). ^{19}F NMR ($CDCl_3$): δ −144.0 (6 F), −143.8 (6 F), −135.9 (3 F). MS(EI): m/z 1005 $[C_{60}F_{15}]^+$.

Compound 7

This was prepared according to an earlier method.[6b]

^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.0 (s, $–CO_2CH_2\mathit{CH_3}$), 53.4 [s, $–\mathit{C}(CO_2Et)_3$], 63.8 (s, $–CO_2\mathit{CH_2}CH_3$), 71.0 (bs, C), 85.5 (m, C–F), 87.4 (m, C–F), 89.6 (t, J 238, 26 Hz; C–F), 90.3 (t, J 240, 26 Hz; C–F), 91.6 (t, J 238, 26 Hz; C–F), 92.3 (m, C–F) (all sp^3 fullerenyl); 130.9 3 [m, C], 131.7 [s, C], 135.0 [s, C], 135.1 [s, C], 146.8 [s, C], 147.2 [s, C], 148.2 [bs, C], 150.9 [s, C], 163.1 [bs, C], (all sp^2 fullerenyl) 163.8 [s, –C=O].

Compound 16a

Reagent quantities were DBU (1.28 mg, 8.46 μmol), $C_{60}F_{18}$ (9.0 mg, 8.46 μmol) and **15a** (2.87 mg, 8.46 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 7.8 min. Concentration of the toluene solution gave the product **16a** as a green solid (6.9 mg, 41%). UV/vis (DCM): 338 nm, 397, 438, 612, 667.

^{1}H NMR ($CDCl_3$, 500 MHz, 338 K): δ 1.28 (t, 18 H, J 7.2 Hz), 4.53 (q, 12 H, J 7.2 Hz), 5.27 (s, 6 H), 7.54 (d, 6 H, J 8.7 Hz), 8.21 (d, 6 H, J 8.7 Hz). ^{19}F NMR: δ −142.4 (6 F), −142.3 (6 F), −135.1 (3 F). MALDI-TOF (−ve ion mode): m/z 1005 $[C_{60}F_{15}]^-$.

Compound 16b

Reagent quantities were DBU (0.58 mg, 3.67 μmol), $C_{60}F_{18}$ (3.0 mg, 2.82 μmol) and **15b** (1.60 mg, 4.51 μmol). HPLC (4.7 mL min^{-1}) gave a single fraction at 3.3 min. Concentration of the toluene solution gave the product **16b** as a green solid (2.4 mg, 34%). UV/vis (DCM): 280 nm, 397, 612, 667.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 1.48 (t, 18 H, J 7.2 Hz), 3.86 (bs, 18 H), 4.46 (bq, 12 H, J 7.2 Hz), 5.45 (bs, 6 H), 6.58 (bs, 3 H), 6.64 (bs, 6 H). ^{19}F NMR: δ −142.6, −142.3, −134.5. MALDI-TOF (−ve ion mode): 1005 $[C_{60}F_{15}]^-$.

Compound 16c

Reagent quantities were DBU (1.67 mg, 11.0 μmol), $C_{60}F_{18}$ (9.0 mg, 8.46 μmol) and **15c** (5.5 mg, 13.53 μmol). HPLC

(2.0 mL min^{-1}) gave a single fraction at 8.5 min. Concentration of the toluene solution gave **16c** as a green solid (1.8 mg, 28%). UV/vis (DCM): 314 nm, 328, 344, 396, 440, 612, 666.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 1.18 (t, 18 H, *J* 7.2 Hz), 4.29 (q, 12 H, *J* 7.2 Hz), 6.07 (s, 6 H), 8.04 (m, 3 H), 8.08 (m, 12 H), 8.18 (9 H), 8.23 (dd, 3 H, *J* 7.2, 1.2 Hz). ^{19}F NMR: δ −142.7 (6 F), −142.5 (6 F), −135.2 (3 F). MALDI-TOF (+ve ion mode): *m*/*z* $^+$. MALDI-TOF (−ve ion mode): *m*/*z* 1163 $[C_{60}F_{15}[C(CO_2Et)_2]]^-$, 1005 $[C_{60}F_{15}]^-$.

Compound 16d

Reagent quantities were DBU (1.67 mg, 11.0 μmol), $C_{60}F_{18}$ (9.0 mg, 8.46 μmol) and **15d** (5.35 mg, 13.53 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 8.1 min. Concentration of the toluene solution gave the **16d** as a green solid (6.1 mg, 33%). UV/vis (DCM): 258 nm, 290, 301, 397, 615, 667.

^{1}H NMR ($CDCl_3$, 500 MHz, 303 K): δ 1.29 (t, 18 H, *J* 7.2 Hz), 1.57 (s, 9 H), 4.29 (q, 12 H, *J* 7.2 Hz), 4.41 (s, 6 H), 7.24 (dt, 6 H, *J* 6.9, 0.8 Hz), 7.35 (m, 6 H), 7.39 (d, 6 H, *J* 7.4 Hz), 7.71 (d, 6 H, *J* 7.4 Hz). ^{19}F NMR: δ −142.7 (6 F), −142.6 (6 F), −135.0 (3 F). MALDI-TOF (+ve ion mode): *m*/*z* 1796 $[M - ligand]^+$, 1005 $[C_{60}F_{15}]^+$.

Compound 16e

Reagent quantities were DBU (0.43 mg, 2.82 μmol), $C_{60}F_{18}$ (3.0 mg, 2.82 μmol) and **15e** (1.77 mg, 4.23 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 8.5 min. Concentration of the toluene solution gave **16e** as a green solid (1.8 mg, 28%). UV/vis (DCM): 309 nm, 318, 613, 667.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 1.49 (t, 18 H, *J* 7.2 Hz), 4.46 (q, 12 H, *J* 7.2 Hz), 4.95 (bs, 6 H), 6.38 (bs, 3 H), 6.70 (bs, 6 H). ^{19}F NMR: δ −142.6, −142.5, −134.8. MALDI-TOF (+ve ion mode): *m*/*z* 2262 $[M + H]^+$, 1843 $[C_{60}F_{15}[C(CO_2Et)_2\text{-}CO_2CH_2TTF]_2]^+$. MALDI-TOF (−ve ion mode): *m*/*z* 1163 $[C_{60}F_{15}[C(CO_2Et)_2]]^-$, 1005 $[C_{60}F_{15}]^-$.

Compound 16f

Reagent quantities were DBU (0.004 g, 24.00 μmol), $C_{60}F_{18}$ (0.015 g, 14.10 μmol) and **15f** (0.015 g, 25.40 μmol). HPLC (2.0 mL min^{-1}) afforded a single peak at *t* = 9.0 min. Concentration of the toluene solution provided **16f** as a green solid (0.010 g, 26%). UV/vis (DCM): 262 nm, 368, 436, 616, 666.

^{1}H NMR ($CDCl_3$, 500 MHz, 353 K): δ 1.31 (bs, 18 H), 4.36 (bs, 12 H), 5.52 (bs, 6 H), 6.11 (bd, 3 H, *J* 6.6 Hz), 6.19 (bs, 3 H, *J* 6.6 Hz), 6.30 (bd, 3 H, *J* 6.7 Hz), 6.39 (bd, 3 H, *J* 6.7 Hz), 7.31 (m, 6 H), 7.44 (bd, 3 H, *J* 7.5 Hz), 7.71 (m, 3 H), 7.76 (m, 6 H), 7.86 (d, 3 H, *J* 7.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −142.5 (m, 48 F), −135.3 (bs, 3 F), −135.1 (m, 6 F), −134.7 (bs, 3 F). MALDI-TOF (+ve ion mode): *m*/*z* 2790 $[M]^+$, 2195 $[M - C(CO_2Et)_2CO_2anthTTF]^+$, 1005 $[C_{60}F_{15}]^-$ (−ve mode only).

Compound 16g

Reagent quantities were DBU (1.37 mg, 9.04 μmol), $C_{60}F_{18}$ (6.0 mg, 5.65 μmol) and **15g** (5.12 mg, 10.17 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 7.9 min. Concentration of the toluene solution gave **16g** as a green solid (4.0 mg, 28%). UV/vis (DCM): 320 nm, 397, 450, 612, 667.

^{1}H NMR ($CDCl_3$, 500 MHz, 323 K): δ 1.40 (t, 18 H, *J* 7.2 Hz), 4.15 (s, 15 H), 4.36 (bt, 6 H), 4.44 (q, 12 H, *J* 7.2 Hz), 4.51 (bt, 6 H), 5.47 (s, 6 H), 6.79 (d, 3 H, *J* 16 Hz), 6.98 (d, 3 H, *J* 16 Hz), 7.43 (d, 6 H, *J* 8.0 Hz), 7.51 (d, 6 H, *J* 8.0 Hz). ^{19}F NMR: δ −142.7 (6 F), −142.6 (6 F), −135.0 (3 F). MALDI-TOF (+ve ion mode): *m*/*z* 2514 $[M]^+$.

Compound 16h

Reagent quantities were DBU (0.7 mg, 4.80 μmol), $C_{60}F_{18}$ (3 mg, 2.82 μmol) and **15h** (2.4 mg, 5.08 μmol). The solution changed colour to olive green. HPLC (2.0 mL min^{-1}) afforded two fractions at 10.8 and 14.7 min. Concentration of the toluene solutions gave **16h** as a green solid (trace) and **17** (1 mg, 18%) as an olive green solid.

16h: UV/vis (DCM): 304 nm, 332, 441, 469, 610, 663. MALDI-TOF (+ve ion mode): *m*/*z* 2406 $[M]^+$, 1005 $[C_{60}F_{15}]^-$ (−ve mode only).

17: MALDI-TOF (+ve ion mode): *m*/*z* 1024 $[C_{60}F_{16}]^+$.

Compound 23

Reagent quantities were DBU (1.7 mg, 11.0 μmol), $C_{60}F_{18}$ (9.0 mg, 8.46 μmol) and **22** (6.3 mg, 13.53 μmol). HPLC (2.0 mL min^{-1}) gave a single fraction at 10.1 min. Concentration of the toluene solution gave the product as a green solid (4.0 mg, 31%). UV/vis (DCM): 305 nm, 333, 442, 472, 611, 668.

^{1}H NMR ($CDCl_3$, 500 MHz, 323 K): δ 1.41 (t, 18 H, *J* 7.1 Hz), 4.49 (q, 12 H, *J* 7.1 Hz), 5.46 (s, 6 H), 7.39 (d, 6 H, *J* 8.1 Hz), 7.44 (m, 6 H), 7.54 (t, 3 H, *J* 7.9 Hz), 7.64 (m, 15 H), 8.09 (d, 3 H, *J* 8.0 Hz), 8.15 (dd, 3 H, *J* 8.0, 1.0 Hz), 8.18 (dd, 3 H, *J* 8.0, 1.0 Hz), 8.21 (d, 6 H, *J* 7.9 Hz). ^{19}F NMR: δ −144.0 (6 F), −143.9 (6 F), −136.5 (3 F). MALDI-TOF (+ve ion mode): *m*/*z* 2706 $[M]^+$, 1005 $[C_{60}F_{15}]^+$ (−ve ion mode only).

Crystal data: $C_{90}H_{45}F_{15}O_{18}\cdot 2(CDCl_3)$ *M* = 1938.0, triclinic, $P\bar{1}$ (No. 2), *a* = 14.2716(2), *b* = 17.0905(3), *c* = 17.5293(2) Å, *α* = 76.145(1), *β* = 74.066(1), *γ* = 80.183(1)°, *V* = 3966.45(10) Å^3, *Z* = 2, D_c = 1.62 Mg m^{-3}, *μ* (Mo-K*α*) = 0.33 mm^{-1}, *T* = 173 K. Data from a Nonius KappaCCD diffractometer, 13753 unique reflections (R_{int} = 0.065). There are two, poorly defined, disordered $CDCl_3$ solvate molecules, which were included with C–Cl and Cl ··· Cl distance constraints.

Refinement on F^2 using SHELXL-97, final residuals: R_1 = 0.090 for 10092 reflections with $I > \sigma 2(I)$, wR_2 = 0.252 for all reflections. †

† CCDC reference number 219664. See http://www.rsc.org/suppdata/ob/b3/b309959h/ for crystallographic data in .cif or other electronic format.

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