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An efficient route to the synthesis of symmetric and asymmetric diastereomerically pure fullerene triads

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ABSTRACT

A new synthetic route based on the stepwise functionalisation of fullerene cages allows the facile formation of linear, diastereomerically pure triads incorporating two different fullerene cages linked by an organic spacer group. The critical coupling step of two fullerene cages via activation by *N*,*N*′-dicyclohexylcarbodiimide was systematically investigated to reveal that the yield of the coupling is maximised in *o*-dichlorobenzene at high concentrations of the reactant fullerene nucleophile, while in more polar solvents or at lower concentrations of reactants the formation of unwanted side-products (such as guanidine-, *N*-acylurea- and anhydride-functionalised fullerenes) is favoured. The resultant triads possess an atypically good solubility for this class of compound, which enabled full detailed characterisation by ^{1}H and ^{13}C NMR, IR and UV–vis spectroscopies and by MALDI-TOF mass spectrometry.

1. Introduction

Due to their unique chemical and electron-accepting properties fullerenes are promising candidates for a variety of technological applications.[1] Furthermore, the formation of molecules where two fullerene cages are connected directly or through a molecular bridge can lead to new properties compared to individual functionalized C_{60}. Such fullerene triad compounds, often referred to as 'dimers', are of great interest for application as molecular electronic devices,[2] artificial photosynthetic systems[3] and in supramolecular chemistry.[4] The synthesis of a variety of fullerene aggregates has been reported including symmetric C_{60}/C_{60} dimers,[5] hydrogen bonding self-assembled systems,[6] and of symmetric C_{60}-donor-C_{60}[7] and C_{60}-acceptor-C_{60}[8] triads. The general synthetic strategy for such systems is based on two-fold cycloaddition with suitable bifunctional bridge molecules to link two fullerene cages in one step allowing access to symmetric triad systems (Scheme 1a). However this strategy is not readily transferrable to the synthesis of asymmetric triads, in which the fullerene cages are non-equivalent, as it often results in a statistical mixture of products (Scheme 1b) with a theoretical maximum yield of 50% possible for the desired asymmetric species. An additional problem is that the desirable asymmetric product will be extremely difficult to isolate from the symmetric co-products. As a consequence access to asymmetric fullerene triads comprising two different fullerene cages is very limited,[3,9,10] with all reported methods using stepwise procedures in which the fullerene cages are added sequentially. However, this often results in low overall yields thus limiting the amount of material, which can be synthesised and isolated. Another common difficulty is the poor solubility of such functionalised triads in common organic solvents and this significantly limits their applications.[11,12] This is usually countered by the introduction of bulky solubilising groups into the molecule, which can be cumbersome and long-winded.[13] In addition the majority of triad structures reported thus far are non-linear due to the shape of the molecular bridge used to link fullerene cages, leading to the formation of several conformers and stereomers,[14,15] making accurate control of the fullerene–fullerene distance virtually impossible. This, coupled with the presence of bulky solubilising groups, complicates the potential arrangements that the fullerene can adopt within 1D, 2D and 3D molecular arrays.

We report herein a new synthetic route for the preparation of a series of linear, diastereomerically pure fullerene triads, which are soluble in common organic solvents. Our method allows the flexible introduction of fullerene cages into the molecule in a stepwise fashion, which makes it possible to obtain a wide range of symmetric and non-symmetric fullerene structures connected through various spacers.

2. Results and discussion

Fullerene cages were functionalised in high yield via a Prato reaction to form a pyrrolidine ring across the [6,6] bond of the cage.[16] The resultant pyrrolidine function contains a nitrogen atom that can be readily functionalised with a monoprotected

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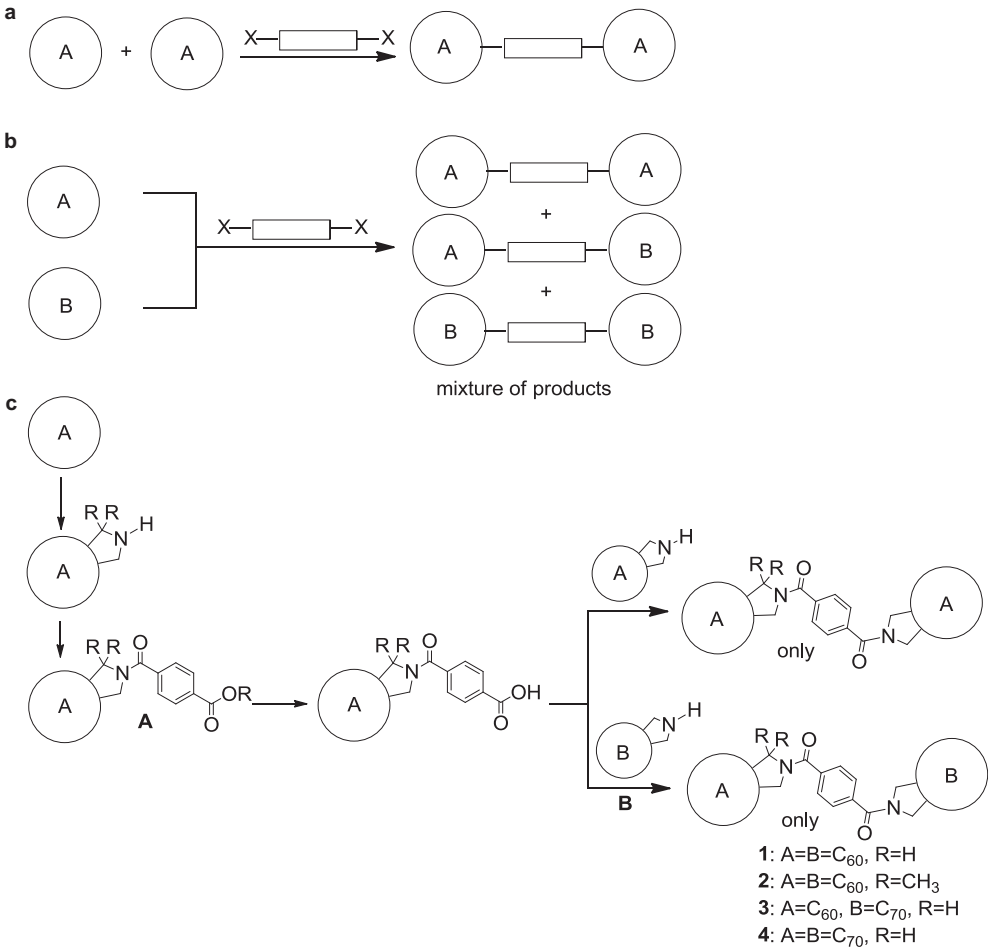


Scheme 1. View of synthetic routes to linked fullerenes via (a) a one step approach leading to the formation of symmetric systems, (b) the formation of asymmetric systems in one step and (c) the multi-step formation of symmetric and asymmetric products in which different fullerene cages are added sequentially.

dicarboxylic acid to yield precursor **A** (Scheme 1c). This synthetic strategy allows isolation of materials where the functional group points directly away from the fullerene cage, and has only a single stereomer. In contrast, introducing functionality through the CH_2 group of the pyrrolidine ring, which is more commonly reported, results in a bent conformation and the formation of a stereogenic C-centre, and thus leads to a diastereomeric mixture of products.[14] Furthermore, addition of groups at the N-atom of fulleropyrrolidines significantly increases the solubility of the resultant functionalised fullerene[17] and this removes the necessity of adding bulky solubilising groups elsewhere within the molecule. Deprotection of the carboxylic group in **A** allows subsequent attachment of a second fullerene cage using an *N*,*N*′-dicyclohexylcarbodiimide (DCC) activated amidation reaction with the corresponding fulleropyrrolidine, **B** to give the target fullerene triads **1**–**4** (Scheme 1c).

This route provides flexibility such that a range of fullerenes can be introduced using the same methodology with the second fullerene cage being added in a stepwise fashion. By varying the dicarboxylic bridging group, it is also possible to form triads of different lengths and hence directly control the interfullerene spacing and even introduce redox active groups as a pathway to generate donor–acceptor systems or metal coordinating dimer species. Importantly, all these dimer molecules have no stereogenic carbon atoms in their structures, and this eliminates the problem of formation of diastereomeric products. To demonstrate the effectiveness of this approach, four different systems have been prepared, including symmetric C_{60}/C_{60} and C_{70}/C_{70} molecules, **1** and **4**, respectively, an asymmetric C_{60}/C_{60} system, **2**, in which the two different pyrrolidine linkers have been incorporated, and finally an asymmetric C_{60}/C_{70} dimer, **3**, containing two different fullerene cages.

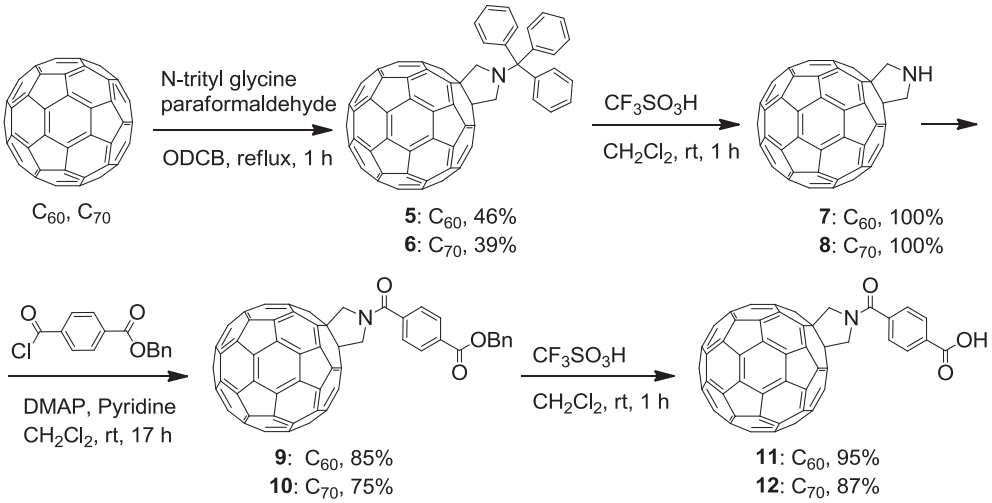
2.1. Synthesis of the precursors

The carboxylic acid derivatives, **11** and **12**, were prepared via the fulleropyrrolidines, **7** and **8**, respectively (Scheme 2).

Fullerenes C_{60} and C_{70} were functionalised utilising a modified Prato reaction procedure[16,18] to give the *N*-trityl protected derivatives of C_{60}, **5**,[16,18] and C_{70}, **6**, in 46 and 39% yields, respectively. Because C_{70} has four non-equivalent [6,6]-bonds, its fulleropyrrolidine derivative, **6**, can theoretically exist in four different regio-isomers. However, we obtained only two regio-isomers **6a**/**6b** in a molar ratio of 58:42. The structures and the ratio of the isomers were determined by ^{1}H NMR spectroscopy analysing the coupling and multiplicity of the pyrrolidine ring signals[19] (Fig. 1).

The isomers were assigned to be the (8,25)- and (7,22)-functionalised [70]fulleropyrrolidines (**6a** and **6b**, respectively) showing two singlets for the non-equivalent CH_2 groups with equivalent protons for **6a**, and two doublets for **6b**.[19] There was no evidence of formation of isomers **6c** and **6d** that would exhibit qualitatively different splitting patterns in their ^{1}H NMR spectra. Deprotection of **5** and **6** was carried out using CF_3SO_3H[18] and gave the corresponding fulleropyrrolidines **7**[18] and **8** in quantitative yields.

Acylation of fulleropyrrolidines **7** and **8** was carried out using the protected bridge molecule, terephthalic acid mono benzyl ester mono acyl chloride, in the presence of DMAP and pyridine[18] to give the desired compounds **9** and **10** in 85 and 75% yields, respectively



Scheme 2. Synthesis of precursors **7**, **8** and **11**, **12**.

(Scheme 2). Benzyl esters **9** and **10** were hydrolysed to carboxylic acids **11** and **12** using CF_3SO_3H in 95 and 87% yields, respectively, and these were used as the precursors for triad formation.

The precursor, **14**, to the asymmetric C_{60}/C_{60} species **2** was prepared using a slightly modified synthetic route. The 2,2-dimethyl fulleropyrrolidine building block, **13**, was prepared in one step from C_{60}, 2-aminoisobutyric acid and paraformaldehyde in 29% yield.[20] Acylation of **13** with the terephthalic acid mono benzyl ester mono chloride was found to proceed in significantly lower yield than the analogous reaction with the unsubstituted [60]fulleropyrrolidine, **5**, due to the steric hindrance caused by the two methyl groups on the pyrrolidine ring. Mass spectrometry analysis of the reaction mixture for the acylation of **13** with terephthalic acid mono benzyl ester mono acyl chloride in the presence of DMAP and pyridine showed incomplete conversion (less than 30%), and the product was found to be difficult to separate from the starting material. Thus, another route for preparation of **14** was explored (Scheme 3). Thus, 2,2-dimethyl fulleropyrrolidine, **13**, was successfully acylated with 1 equiv of terephthaloyl chloride followed by hydrolysis to give carboxylic acid **14** in a 31% yield.

2.2. DCC-activated acid–amine coupling

The individual fullerene precursors were then combined to form the triads, **1**–**4**, via a DCC-activated acid–amine coupling.[21] Although this reaction is well-established, several side reactions make the procedure more complicated[21] (Scheme 4). In the ideal case, the deprotonated carboxylic acid, **11**, reacts with a molecule of DCC to form an *O*-acylisourea as an intermediate, which is subsequently attacked by the nucleophilic N-centre of the fulleropyrrolidine, **7**, resulting in the formation of the desired amide **1**. However the *O*-acylisourea intermediate can also rearrange into the more stable *N*-acylurea, **1c**, or react with another equivalent of carboxylic acid to form the bridging anhydride group, **1b**. In addition, fulleropyrrolidine itself can also react with DCC to form the guanidine **1a** (Scheme 4).

In order to optimise the procedure for triad formation the reaction conditions were systematically varied and formation of the symmetric C_{60}/C_{60} product **1** monitored. All reactions were carried out under an Ar atmosphere on a 1 mg scale of fulleropyrrolidine and were monitored by MALDI-TOF mass spectrometry. While mass spectrometry does not provide information about the overall yield of the products formed, it can serve as a quick and efficient test to probe changes in the ratio of products in response to different reaction conditions, and thus helps to optimise reactions. The effects of varying both the solvent and the concentration of reactants were found to be significant for the outcome of this reaction. A summary of the reaction conditions and ratios of resultant products are presented in Table 1.

It was found that although triad formation is observed under all conditions, the concentration and number of byproducts vary

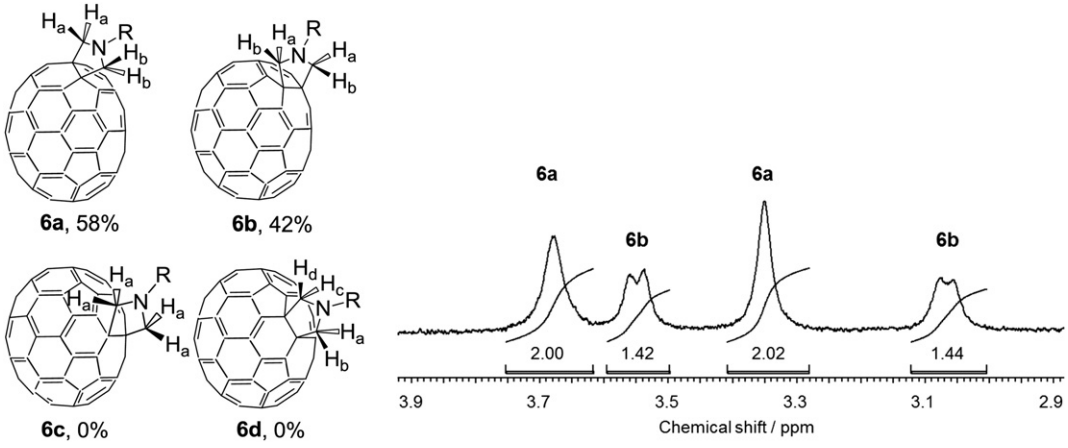
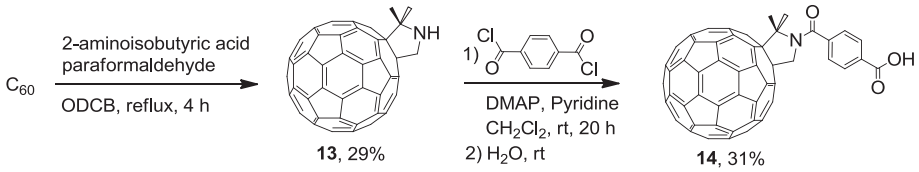


Fig. 1. The four possible regio-isomers of C_{70} *N*-trityl fulleropyrrolidine, **6**, labelled **6a**–**6d** (left) and the ^{1}H NMR spectra of the two regio-isomers of C_{70} *N*-trityl fulleropyrrolidine obtained, **6a** and **6b** (right).



Scheme 3. Synthesis of 2,2-dimethyl substituted precursors **13** and **14**.

considerably. In dichloromethane (DCM) the formation of **1c**, the rearrangement product of the DCC adduct of **11**, dominates due to the low solubility of the fulleropyrrolidine, **7**. As the concentration of **7** in solution is low, rearrangement of the DCC adduct of **11** occurs faster than attack of the nucleophile **7**. To counteract this process dimethylformamide (DMF), a solvent in which **7** is more soluble, was used. However the yield of **1** in DMF was even lower than for the analogous reaction in DCM (5% compared to 20%). The main product formed in DMF was the bridging anhydride, **1b**, formed from 2 equivalents of the carboxylic acid **11**. This can be explained by considering the polarity of the solvent. As DMF is a very polar solvent and a base, it can facilitate de-protonation of the carboxylic group and promote the attack of the carboxylate on the DCC adduct of **11**. In *o*-dichlorobenzene (ODCB) the desired triad is the major product (40–55% yield), while the percentage of all byproducts is much lower (22–35%). This is attributed to the fact that ODCB is both a good solvent for the fullerene, thus maintaining a high concentration of the nucleophile **7**, yet not sufficiently polar to cause extensive de-protonation of the carboxylic acid. However, even in ODCB there is still evidence of significant formation of the rearrangement product, **1a**, and the fulleropyrrolidine–DCC adduct, **1c** (Fig. 2).

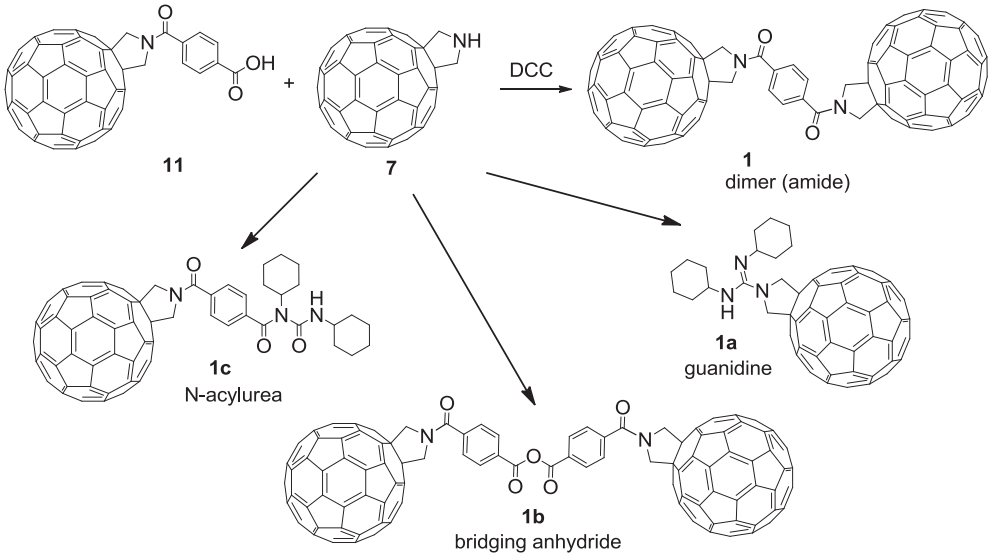
In order to optimise the yield of the required triad, we studied the effects of concentration of the reactants. We carried out a series of test reactions in which the concentration of **7** was varied from 0.0013 M to 0.0052 M in ODCB. It was found that at higher concentration triad formation was more favoured over byproduct formation, as there was more fulleropyrrolidine nucleophile available to attack the DCC adduct of **11** before rearrangement or anhydride formation could occur. Further increase in concentration of the reactant **7** was limited by the finite solubility of the fullerene, and thus the yield of **1** could not be increased beyond 55%.

The conditions optimised for the symmetric C_{60}/C_{60} product **1** were then utilized to give products **2**–**4** in 27, 30 and 36% yields, respectively. Reaction of 2,2-dimethyl fulleropyrrolidine **13** with **11** did not lead to formation of the desired product **2**, and formation of byproducts containing the carboxylic acid was observed. It was found that the reactivity of 2,2-dimethyl fulleropyrrolidine **13** was significantly lower compared to the unsubstituted fulleropyrrolidine **7**, so the former does not participate in the coupling reaction due to the steric hindrance caused by the two methyl groups. To prepare **2** a coupling reaction between the unsubstituted fulleropyrrolidine **7** and 2,2-dimethyl carboxylic acid **14** was used (Scheme 5).

The products **1**–**4** were purified by column chromatography on silica gel using ODCB/^{i}PrOH (99.5:0.5) mixture as eluent. The purity of compounds was confirmed by HPLC (Experimental section and Supplementary data file).

2.3. Characterisation of products

In contrast to the fullerene systems reported previously,[9,22] **1**–**4** are soluble in common organic solvents such as CS_2 and ODCB, and enabled detailed characterisation by MALDI-TOF mass spectrometry, ^{1}H and ^{13}C NMR, IR and UV–vis spectroscopy. MALDI mass spectrometry shows a molecular ion peak [M^-] with the correct isotopic pattern for each product. The ^{1}H NMR spectra of **1**–**4** (Fig. 3) show the signals of the CH_2 groups of the pyrrolidine rings as singlets at 5.4–5.6 ppm for the [60]fulleropyrrolidines, or as a set of four signals corresponding to the two isomeric [70]fulleropyrrolidines between 4.5 and 5.2 ppm. The aromatic protons of the phenyl ring correspond to AX, AB or A_2 spin systems showing the singlet for the symmetric C_{60}/C_{60} triad at 8.09 ppm (A_2 system), two very close doublets at 8.07–8.08 ppm for the asymmetric C_{60}/C_{60} dimer (AB system) or two sets of doublets for the asymmetric C_{60}/C_{70} dimer (AX system). The C_{70}/C_{70} product was obtained as a mixture of two symmetric isomers and one asymmetric isomer, **aa**, **bb** and **ab**, in the ratio 7:3:10, respectively, with **a** corresponding



Scheme 4. Acid–amine coupling of **7** and **11** in the presence of DCC and byproducts of this reaction.

Table 1
Coupling reaction conditions and ratios of products estimated by MALDI-TOF mass spectrometry (DCM=dichloromethane, DMF=dimethylformamide, ODCB=*o*-dichlorobenzene)

Solvent	Concentration of reactants, M	Triad (**1**), %	*N*-Acylurea (**1c**), %	Guanidine (**1a**), %	Anhydride (**1b**), %
DCM	0.0013	20	50	30	—
DMF	0.0013	5	10	15	70
ODCB	0.0013	40	35	25	—
ODCB	0.0026	50	30	20	—
ODCB	0.0052	55	22	22	—

to the (8,25) functionalised C_{70} and **b** corresponding to the (7,22) functionalised C_{70}. The singlets at 7.93 and 7.73 ppm correspond to **aa** and **bb**, respectively, and two doublets at 7.85 and 7.81 ppm correspond to the asymmetric **ab**.

^{13}C NMR spectroscopy shows the signals of the carbonyl groups between 168 and 171 ppm: one is observed for the symmetric C_{60}/C_{60} triad, **1**, two for the asymmetric C_{60}/C_{60}, **2**, three for the C_{60}/C_{70}, **3**, and three for the C_{70}/C_{70} **4**. Resonances for the carbon centres of the fullerene cage are observed between 130 and 160 ppm; **1** shows 17 signals consistent with a C_{2v} symmetry for the functionalised cage, and a complex pattern of signals is observed for the asymmetric products **2**–**4**.

IR spectroscopy shows a strong carbonyl stretch between 1650 and 1660 cm^{-1} for all triads. Interestingly, for all the asymmetric products only one carbonyl signal is observed, indicating no measurable impact of the type of the fullerene cage on the resultant C=O vibrations.

UV–vis spectra of compounds **1**–**4** (Fig. 4) are dominated by transitions due to the fullerene cages and can be viewed as a superposition of UV–vis spectra of the individual C_{60} and C_{70} constituents. The intensity of the absorptions of **1**–**4** are all equal to the sum of the corresponding monomeric precursors, consistent with the presence of two fullerene cages per molecule. Thus for **1** and **2** containing only C_{60} cages, absorption bands at 716 and 436 nm are observed, characteristic for [6,6]-adducts of C_{60}.[23] For the C_{70}-containing products **3** and **4**, four characteristic bands are observed at 542 nm and 465 nm for the (8,25)-adduct **a**, and at 446 nm for the (7,22)-adduct **b** confirming that both isomers are present in the mixture.[24] For the asymmetric C_{60}/C_{70} species **3**, characteristic bands for both fullerene cages are present.

3. Conclusions

We have developed a new synthetic route for the preparation of linear fullerene triads that allows the introduction of the fullerene cages into the molecule in a stepwise fashion and allows the facile formation of asymmetric fullerene triads containing two different fullerene cages without the formation of diastereomeric mixtures. The nature of the solvent and the concentration of the reactant nucleophile were found to control the yields of products formed. The triads possess good solubility in solvents such as CS_2 and ODCB, without the need for further solubilising groups to be incorporated onto the fullerene thus enabling full spectroscopic characterisation and determination of the structures of the new family of fullerene triads.

4. Experimental

4.1. General

C_{60} (99.5%) and C_{70} (95%) were purchased from SES Research and MER Corporation, respectively. Anhydrous CH_2Cl_2 was distilled over CaH_2 before use. All other reagents and solvents were purchased from Aldrich and were used without further purification. Infrared spectra were measured as KBr discs using a Nicolet Avatar 380 FT-IR spectrometer over the range 400–4000 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained using Bruker DPX 300, Bruker DPX 400, Bruker AV(III) 400 or Bruker AV(III) 500 spectrometers. Mass spectrometry was carried out using an ESI MS spectrometer and a MALDI-TOF spectrometer. UV–vis spectra were measured using a Lambda 25 Perkin Elmer Spectrometer. The purity of compounds **1**–**4** was checked by analytical HPLC (column: SiO_2, 4.6×250 mm, Fortis HILIC 10 μm; flow rate: 2 mL/min; eluent: ODCB/^{i}PrOH=99.5:0.5; detected at 312 nm with an UV spectrophotometric detector, Shimadzu SPD-M20A), see Supplementary data file.

4.2. *N*-Triphenylmethyl [60]fulleropyrrolidine, 5

C_{60} Fullerene (500 mg, 0.69 mmol), *N*-trityl glycine (220 mg, 0.69 mmol) and paraformaldehyde (105 mg, 3.47 mmol) were dissolved in anhydrous ODCB (100 mL), degassed with Ar for 30 min and refluxed under Ar atmosphere for 1 h. The reaction mixture was cooled down to room temperature, filtered through a silica gel

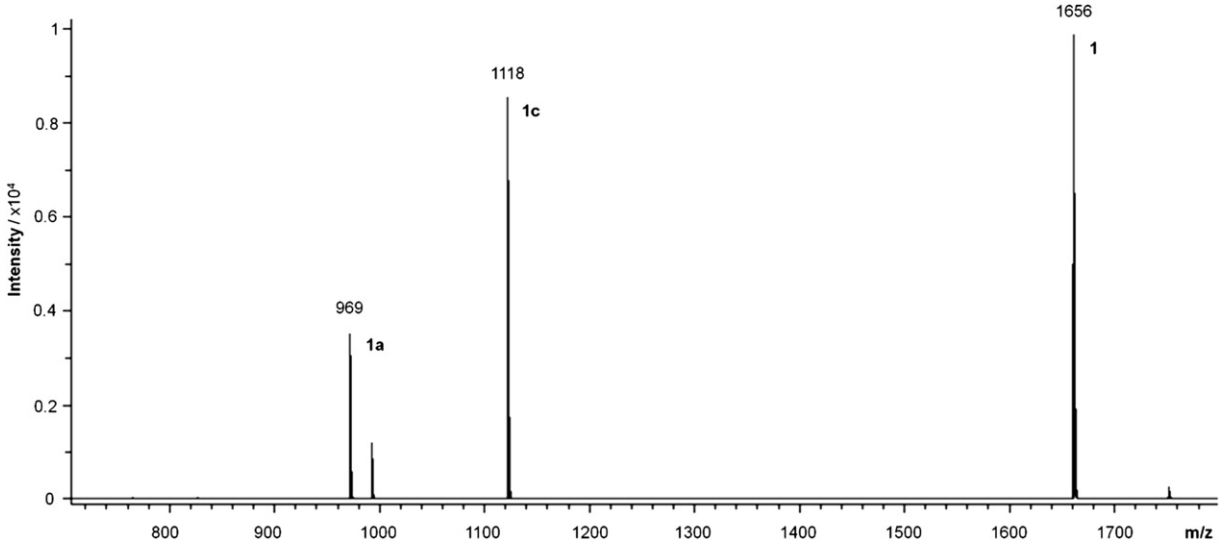
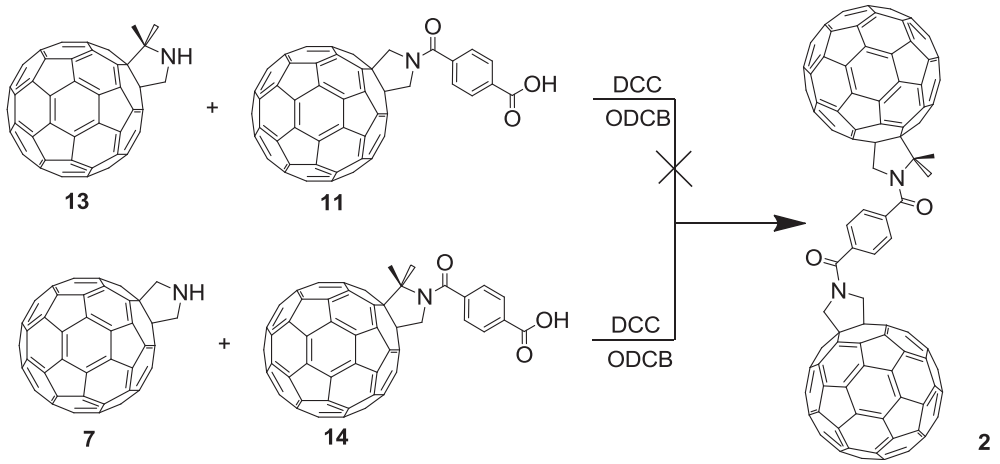


Fig. 2. MALDI-TOF mass-spectrum of the crude reaction mixture to form **1** in ODCB, using a 0.0013 M solution of fulleropyrrolidine, **5**.



Scheme 5. Synthesis of the asymmetric triad **2**.

pad and the solvent was removed in vacuum. The resultant brown solid was purified by column chromatography (silica gel, CS_2). Further purification was carried out by washing of the product with MeOH (40 mL), petroleum ether (40 mL) and diethyl ether (40 mL) and drying in vacuum to give *N*-trityl fulleropyrrolidine as black powder (320 mg, 46%). ^{1}H NMR (300 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 7.90 (d, 6H, J=7.7 Hz, ArH), 7.43 (t, 6H, J=7.7 Hz, ArH), 7.30 (t, 3H, J=7.4 Hz, ArH), 4.19 (s, 4H, CH_2).

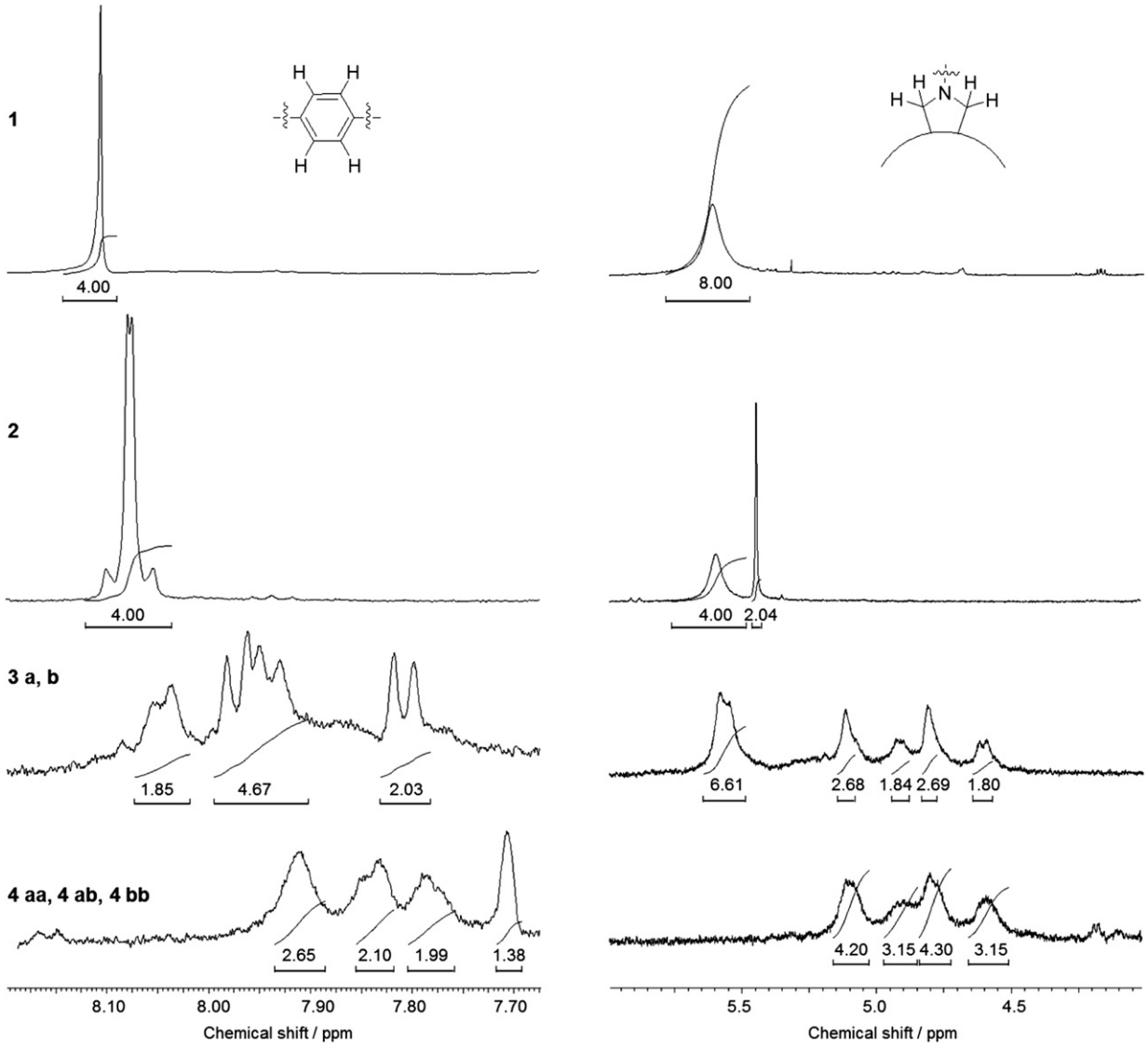


Fig. 3. ^{1}H NMR spectra of fullerene triads **1**–**4**: aromatic (left) and aliphatic region (right).

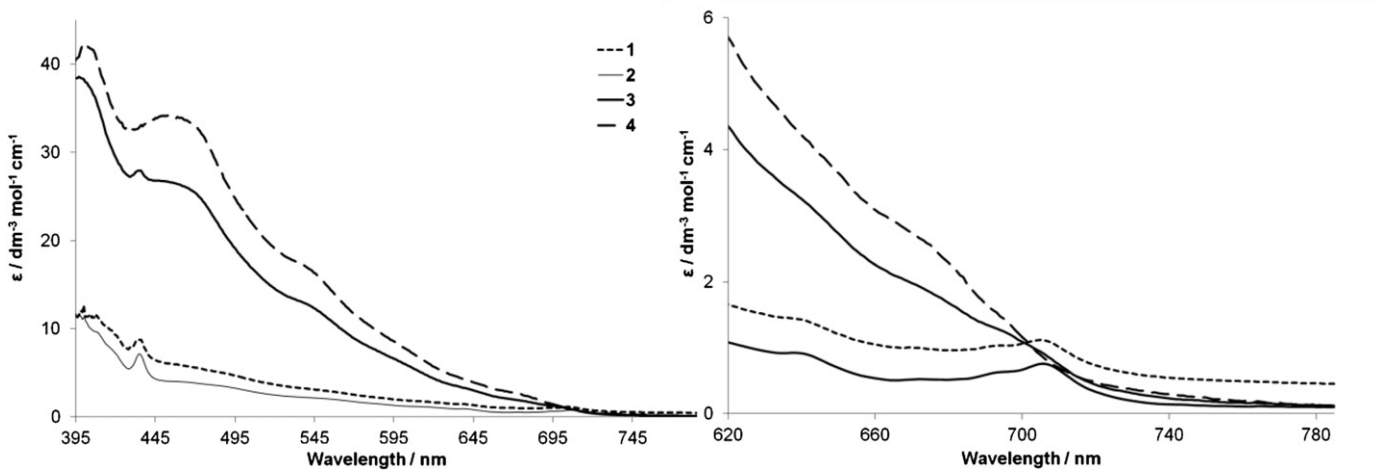


Fig. 4. UV–vis spectra of triads **1**–**4** in CS_2: full spectrum (left) and 620–780 nm region (right).

^{13}C NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 154.56, 147.19, 146.19, 146.05, 146.02, 145.55, 145.43, 145.22, 144.50, 143.01, 142.61, 142.29, 142.00, 141.85, 140.21, 136.47, 130.45, 129.19 (fullerene cage sp^2 carbons, 18 environments), 128.28, 128.21, 127.49, 126.95 (Ar C), 73.97, 69.36 (pyrrolidine ring C), 60.71 ($C(Ph)_3$).

MALDI-TOF MS (DCTB/MeCN, m/z): 1005.2 (M^-).

IR (KBr, ν, cm^{-1}): 2804 (w), 1447 (w), 1184 (w), 1075 (w), 698 (m), 527 (m).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 716 (0.13), 436 (4.24).

4.3. [60]Fulleropyrrolidine, 7

N-Triphenylmethyl [60]fulleropyrrolidine **5** (200 mg, 0.2 mmol) was suspended in dichloromethane (100 mL), trifluoromethanesulfonic acid (0.8 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuum and the resultant brown solid was suspended in diethyl ether (30 mL). The precipitate was separated by centrifugation, the ether was removed, and the procedure was repeated three times. The resultant brown solid was dried in vacuum to give the product, **7** (152 mg, 100%).

MALDI-TOF MS (DCTB/MeCN, m/z): 763.0 (M^-).

IR (KBr, ν, cm^{-1}): 3446 (s, NH), 2360 (w), 1385, 1274, 1171, 1026, 636.

4.4. Terephthalic acid mono benzyl ester

Terephthalic acid (500 mg, 3.0 mmol) was dissolved in anhydrous DMF (50 mL), the solution was then degassed with Ar for 15 min, cooled down to 0 °C, and NaH (72 mg, 3.0 mmol) was added in one portion. The reaction mixture was stirred for 10 min, and a solution of benzyl bromide (515 mg, 3.0 mmol) in DMF (3 mL) was added. The reaction mixture was warmed up to room temperature and stirred for 18 h. The solvent was then removed in vacuum and the resultant white solid was washed sequentially with 1 M HCl (20 mL) and water (50 mL) and then dried under vacuum. The solid was then extracted into CH_2Cl_2 (150 mL) in a Soxhlet apparatus for 48 h and then the extract was purified by column chromatography (silica gel, $CHCl_3$/MeOH 99:1) to give the product (110 mg, 15%).

^{1}H NMR (300 MHz, 297 K, DMSO-d_6, δ, ppm): 13.36 (s, 1H, COOH), 8.08 (dd, 4H, ArH, J=16.8, 2.5 Hz), 7.36–7.50 (m, 5H, $CH_2C_6H_5$), 5.38 (s, 2H, $CH_2C_6H_5$).

^{13}C NMR (300 MHz, 297 K, DMSO-d_6, δ, ppm): 167.01 (C=O), 165.43 (C=O), 136.32, 135.38, 133.59, 130.12, 129.90, 129.02, 128.69, 128.59 (Ar C), 67.07 ($PhCH_2O$).

ESI MS (MeOH, m/z): 279.06 $(M+Na)^+$.

4.5. Terephthalic acid mono benzyl ester mono chloride

Terephthalic acid mono benzyl ester (50 mg, 0.2 mmol) was dissolved in thionyl chloride (15 mL) and refluxed for 5 h. The solvent was then removed using reduced pressure and the resulting oil was dissolved in CH_2Cl_2 (2 mL) and passed through a silica gel pad, concentrated and dried under vacuum to give the product as a yellow oil (52 mg, 90%).

^{1}H NMR (300 MHz, 297 K, $CDCl_3$, δ, ppm): 8.19 (m, 4H, ArH), 7.37–7.49 (m, 5H, $CH_2C_6H_5$), 5.41 (s, 2H, $CH_2C_6H_5$).

^{13}C NMR (300 MHz, 297 K, $CDCl_3$, δ, ppm): 167.90 (C=O), 164.96 (C=O), 136.67, 135.90, 135.39, 131.43, 131.19, 130.12, 128.73, 128.39 (Ar C), 67.49 ($COOCH_2Ph$).

ESI MS (MeOH, m/z): 297.03 $(M+Na)^+$.

4.6. Benzoic acid, 4-([60]fulleropyrrolidinyl carbonyl), phenyl methyl ester, 9

Fulleropyrrolidine, **7** (150 mg, 0.20 mmol) was suspended in freshly distilled CH_2Cl_2 (150 mL), DMAP (100 mg) and pyridine (2.5 mL) were added, and the mixture was stirred for 15 min at room temperature. A solution of terephthalic acid mono benzyl ester mono chloride (300 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) was then added, and the reaction mixture was stirred for 18 h at room temperature. After completion the solvent was removed by using reduced pressure, and the resultant dark-brown solid was purified by column chromatography (silica gel, toluene/MeOH 8:1). Further purification was carried out by suspending the solid in MeOH (20 mL), filtering, washing with MeOH (30 mL) and petroleum ether (50 mL) and drying under vacuum to give the desired product as a dark-brown solid (170 mg, 85%).

^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.24 (d, 2H, ArH, J=8.0 Hz), 7.95 (d, 2H, ArH, J=8.0 Hz), 7.32–7.46 (m, 5H, ArH), 5.53 (s, 4H, CH_2), 5.39 (s, 2H, $COOCH_2Ph$).

^{13}C NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 168.54 (C=O), 164.57 (C=O), 159.58, 153.15, 149.23, 147.42, 146.44, 146.24, 145.75, 145.56, 145.44, 145.06, 144.55, 143.22, 142.81, 142.30, 142.19, 142.04, 141.09, 140.40, 138.96, 137.51, 136.01, 135.89, 132.60, 130.23 (fullerene cage sp^2 carbons, 24 environments), 128.81, 128.55, 128.46, 128.43 (Ar C), 72.99, 67.04 (pyrrolidine C), 61.30 ($PhCH_2O$).

MALDI-TOF MS (DCTB/MeCN, m/z): 1001.2 (M^-).

IR (KBr, ν, cm^{-1}): 3448 (s), 2925 (m), 2361 (s), 2342 (s), 1719 (s), 1654 (m), 1384 (s), 1265 (m), 1099 (m), 527 (w).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 716 (0.17), 436 (3.84).

4.7. Benzoic acid, 4-([60]fulleropyrrolidinyl carbonyl), 11

Benzoic acid, 4-([60]fulleropyrrolidinyl carbonyl), phenyl methyl ester, **9** (100 mg, 0.1 mmol) was suspended in CH_2Cl_2 (100 mL), CF_3SO_3H (0.3 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The solvent was then removed under reduced pressure, and the resultant brown residue was purified by washing with diethyl ether (3×30 mL) separating the resultant precipitate by centrifugation. The solid was then dried under vacuum to give the product as a brown solid (85 mg, 95%).

^{1}H NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 8.31 (d, 2H, ArH, J=8.0 Hz), 8.00 (d, 2H, ArH, J=8.0 Hz), 5.55 (s, 4H, CH_2).

^{13}C NMR (500 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 169.76 (C═O), 168.79 (C═O), 152.83, 148.06, 147.44, 146.45, 146.24, 145.75, 145.55, 145.45, 145.26, 144.55, 143.23, 142.82, 142.27, 142.18, 142.04, 141.45, 140.39, 139.84, 135.96 (fullerene cage sp^2 carbons, 19 environments), 131.44, 130.85, 128.44, 127.70 (Ar C), 77.92, 70.14 (pyrrolidine ring C).

MALDI-TOF MS (DCTB/MeCN, m/z): 910.9 (M^-).

IR (KBr, ν, cm^{-1}): 3447 (s), 2922 (w), 2361 (w), 1717 (s, C═O), 1636 (s, C═O), 1429 (s), 1259 (m), 1119 (w)m 737 (w), 527 (m).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 716 (0.19), 436 (3.67).

4.8. 2,2-Dimethyl fulleropyrrolidine, 13

C_{60} (500 mg, 0.69 mmol), paraformaldehyde (104 mg, 3.47 mmol) and 2-aminoisobutyric acid (72 mg, 3.47 mmol) were dissolved in anhydrous ODCB (100 mL), degassed with Ar for 30 min and heated to reflux temperature for 3.5 h. The solvent was then removed using reduced pressure, and the residue was then purified by column chromatography (silica gel, toluene, then toluene/EtOAc 97:3). Further purification was carried out by washing with MeOH (50 mL) and petroleum ether (50 mL) to give the product (158 mg, 29%) as a brown solid.

^{1}H NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 4.88 (s, 2H, CH_2), 2.14 (s, 6H, CH_3).

^{13}C NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 155.85, 154.50, 147.09, 146.29, 146.24, 146.11, 146.04, 145.79, 145.56, 145.40, 145.34, 145.29, 145.27, 144.48, 144.46, 143.29, 142.78, 142.76, 142.31, 142.25, 141.98, 141.86, 140.34, 140.08, 135.81, 135.63, 128.45, 126.41, 124.52 (fullerene cage sp^2 carbons, 29 environments), 76.08, 71.63, 61.46 (pyrrolidine ring C), 28.62 (CH_3).

MALDI-TOF MS (DCTB/MeCN, m/z): 791.1 (M^-).

IR (KBr, ν, cm^{-1}): 3447 (s, NH), 2960 (w), 1514 (w), 1458 (w), 1425 (w), 1143 (w), 777 (w), 527 (m).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 713 (0.41), 436 (4.75).

4.9. Benzoic acid, 4-(2,2-dimethyl-[60]fulleropyrrolidinyl carbonyl), 14

2,2-Dimethyl fulleropyrrolidine, **13** (100 mg, 0.13 mmol) was suspended in freshly distilled CH_2Cl_2 (100 mL), DMAP (50 mg) and pyridine (1.5 mL) were added, and the reaction mixture was stirred for 10 min at room temperature. Terephthaloyl chloride (300 mg, 1.50 mmol) was added, and the reaction mixture was stirred for 18 h at room temperature. The solvent was then removed using reduced pressure, and the resulting mixture was redissolved in CS_2 (20 mL) and passed through a silica gel pad (toluene/MeOH 4:1). The solution was then washed with water (40 mL), the water layer extracted with CS_2 (3×20 mL), the organic fractions were combined, concentrated and purified by column chromatography (silica gel, ODCB/^{i}PrOH 99.5:0.5 followed by ODCB/^{i}PrOH 97:3). Further purification was carried out by washing with MeOH (30 mL) and petroleum ether (50 mL) to give the product (36 mg, 31%) as a brown solid.

^{1}H NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 8.30 (d, 2H, ArH, J=7.2 Hz), 7.97 (d, 2H, ArH, J=7.2 Hz), 5.35 (s, 2H, CH_2), 2.54 (s, 6H, CH_3).

^{13}C NMR (500 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 170.39 (C═O), 169.27 (C═O), 154.10, 152.74, 147.53, 146.53, 146.65, 146.26, 146.23, 146.14, 145.74, 145.64, 145.59, 145.48, 145.37, 145.29, 144.62, 144.59, 143.32, 142.90, 142.85, 142.37, 142.35, 142.18, 142.03, 142.00, 141.98, 141.90, 140.43, 139.97, 136.30, 136.16 (fullerene cage sp^2 carbons, 30 environments), 131.12, 130.99, 128.44, 127.97 (Ar C), 79.70, 70.54, 67.94, 60.60 (pyrrolidine ring C), 26.70 (CH_3).

MALDI-TOF MS (DCTB/MeCN, m/z): 938.9 (M^-).

IR (KBr, ν, cm^{-1}): 3446 (s, OH), 1720 (s, COOH), 1659 (s, CON), 1384 (s), 1250 (m), 527 (s).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 713 (0.31), 436 (4.15).

4.10. *N*-Triphenylmethyl [70]fulleropyrrolidine, 6

Fullerene C_{70} (100 mg, 0.12 mmol), paraformaldehyde (18 mg, 0.60 mmol) and *N*-trityl glycine (57 mg, 0.18 mmol) were dissolved in dry ODCB (50 mL) by sonicating for 15 min. The resultant solution was degassed with Ar for 30 min and heated to reflux for 2 h. The reaction mixture was then cooled to room temperature and passed through a silica gel pad. The solvent was removed using reduced pressure, and the mixture was then purified by column chromatography (silica gel, CS_2). The product was concentrated and further purification was carried out by washing with MeOH (30 mL) and petroleum ether (50 mL) to give the product as a mixture of two isomers (52 mg, 39%) as a black solid.

Compound ***6a***: ^{1}H NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 7.75 (d, 6H, J=7.5 Hz), 7.42 (t, 6H, J=7.5 Hz), 7.25 (t, 3H, 7.5 Hz), 3.70 (s, 2H, CH_2), 3.37 (s, 2H, CH_2).

Compound ***6b***: ^{1}H NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 7.62 (d, 6H, J=7.5 Hz), 7.38–7.30 (m, 9H), 3.56 (d, 2H, 8.5 Hz, C*H*H), 3.07 (d, 2H, 8.5 Hz, CH*H*).

^{13}C NMR (400 MHz, 297 K, CS_2/$CDCl_3$ 7:1 v/v, δ, ppm): 157.94, 155.81, 151.62, 151.49, 151.40, 151.01, 150.81, 150.73, 150.26, 150.09, 149.89, 149.76, 149.66, 149.43, 149.21, 149.09, 148.87, 147.52, 147.15, 147.11, 147.08, 146.56, 146.34, 145.89, 145.60, 145.43, 144.57, 143.96, 143.44, 143.31, 142.88, 141.07, 140.75, 137.94, 133.94, 133.76, 131.67 (fullerene cage sp^2 carbons, 37 environments), 131.32, 131.29, 129.18, 129.05, 128.27, 128.16, 127.034, 126.96 (Ar C), 73.82, 66.11, 62.66, 60.84, 60.74, 59.66, 59.00, 56.83 (pyrrolidine ring C and *C*(Ph)$_3$).

IR (KBr, ν, cm^{-1}): 3054 (w), 2805 (w), 1428 (s), 1154 (w), 1032 (w), 806 (m), 742 (m), 706 (s), 534 (w).

MALDI-TOF MS (DCTB/MeCN, m/z): 1125.0 (M^-).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 672 (1.61), 542 (10.47), 465 (19.96), 445 (20.06), 402 (25.05).

4.11. [70]Fulleropyrrolidine, 8

N-Triphenylmethyl [70]fulleropyrrolidine, **6** (20 mg, 0.02 mmol) was suspended in CH_2Cl_2 (15 mL). CF_3SO_3H (0.1 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The solvent was then removed using reduced pressure and the resultant brown solid was suspended in diethyl ether (15 mL). The precipitate was separated by centrifugation, and the solid was repeatedly washed with diethyl ether (3×15 mL). The brown solid was then dried under vacuum to give the product (15 mg, 100%).

MALDI-TOF MS (DCTB/MeCN, m/z): 883.0 (M^-).

IR (KBr, ν, cm^{-1}): 3446 (s, NH), 2360 (w), 1428 (s), 1274 (s), 1170 (s), 1025 (m), 638 (m).

4.12. Benzoic acid, 4-([70]fulleropyrrolidinyl carbonyl), phenyl methyl ester, 10

[70]Fulleropyrrolidine, **8** (42 mg, 0.048 mmol) was suspended in freshly distilled CH_2Cl_2 (20 mL), DMAP (25 mg) and pyridine (0.8 mL) were added, and the mixture was stirred for 15 min at room temperature. A solution of terephthalic acid mono benzyl ester mono chloride (200 mg, 0.73 mmol) in CH_2Cl_2 (15 mL) was then added, and the reaction mixture was stirred for 18 h at room temperature. After completion the solvent was removed by using reduced pressure, and the resultant dark-brown solid was purified by column chromatography (silica gel, toluene/MeOH 99:1). Further purification was carried out by suspending the solid in MeOH (20 mL), filtering, washing with MeOH (30 mL) and petroleum ether (50 mL) and drying under vacuum to give the desired product as a dark-brown solid (40 mg, 75%).

Compound ***10a***: ^{1}H NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.24 (br s, 2H, ArH), 7.82 (br s, 2H, ArH), 7.33–7.45 (m, 5H, $CH_2C_6H_5$), 5.40 (s, 2H, $CH_2C_6H_5$), 5.05 (br s, 2H, CH_2), 4.79 (br s, 2H, CH_2).

Compound ***10b***: ^{1}H NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.17 (d, 2H, J=8.51 Hz, ArH), 7.69 (d, 2H, J=8.51 Hz, ArH), 7.33–7.45 (m, 5H, $CH_2C_6H_5$), 5.37 (s, 2H, $CH_2C_6H_5$), 4.79 (br s, 2H, CH_2), 4.56 4.79 (br s, 2H, CH_2).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 168.46 (C=O), 168.31 (C=O), 164.68 (C=O), 164.63 (C=O), 157.05, 155.06, 154.56, 151.73, 151.42, 151.39, 151.06, 150.97, 150.75, 150.70, 150.62, 150.32, 149.92, 149.89, 149.80, 149.42, 149.37, 149.31, 149.25, 149.08, 149.02, 149.01, 148.80, 148.38, 148.07, 147.48, 147.34, 147.20, 147.07, 147.03, 147.00, 146.90, 146.82, 146.60, 146.56, 146.24, 146.17, 146.03, 145.89, 145.66, 145.53, 144.98, 144.81, 144.50, 144.25, 144.12, 140.83, 140.40, 138.74, 138.59, 137.55, 137.39, 135.82, 135.80, 133.74, 133.71, 132.58, 132.51, 132.40, 132.10, 131.69, 131.35, 131.24, 130.21, 130.12, 129.16, 128.83, 128.81, 128.58, 128.57, 128.48, 128.47, 128.42, 128.30, 128.19, 128.10, 125.87, 125.53 (fullerene cage sp^2 carbons and aromatic carbons), 72.53, 72.37, 71.68, 68.82, 67.88, 67.32 (pyrrolidine ring C), 67.10, 67.07 ($CH_2C_6H_5$).

MALDI-TOF MS (DCTB/MeCN, m/z): 1120.4 (M^-).

IR (KBr, ν, cm^{-1}): 3054 (w), 2805 (w), 2360 (w), 1719 (CO, s), 1649 (CO, s), 1427 (s), 12.63 (s), 1018 (m), 728 (m), 693 (m), 670 (m), 579 (m).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 672 (1.32), 542 (9.19), 464 (18.47), 443 (18.14), 401 (23.06).

4.13. Benzoic acid, 4-([70]fulleropyrrolidinyl carbonyl), 12

Benzoic acid, 4-([70]fulleropyrrolidinyl carbonyl), phenyl methyl ester, **10** (10 mg, 0.009 mmol) was suspended in CH_2Cl_2 (10 mL), CF_3SO_3H (0.05 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The solvent was then removed under reduced pressure, and the resultant brown residue was purified by washing with diethyl ether (3×30 mL) separating the resultant precipitate by centrifugation. The solid was then dried under vacuum to give the product as a brown solid (8 mg, 87%).

Compound ***12a***: ^{1}H NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.30 (br s, 2H, ArH), 7.86 (br s, 2H, ArH), 5.08 (br s, 2H, CH_2), 4.79 (br s, 2H, CH_2).

Compound ***12b***: ^{1}H NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.21 (d, 2H, J=8.3 Hz, ArH), 7.74 (d, 2H, J=8.3 Hz, ArH), 4.79 (br s, 2H, CH_2), 4.58 (br s, 2H, CH_2).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 169.33, 168.21, 168.06 (CO), 155.05, 154.56, 151.74, 151.43, 150.98, 150.76, 150.70, 150.33, 149.93, 149.90, 149.82, 149.43, 149.37, 149.31, 149.26, 149.08, 149.02, 148.80, 148.40, 148.09, 147.48, 147.34, 147.20, 147.07, 147.04, 147.00, 146.90, 146.84, 146.60, 146.57, 146.24, 146.18, 146.04, 145.89, 145.65, 145.54, 144.98, 144.82, 144.51, 144.26, 144.13, 143.47, 143.31, 143.08, 142.99, 140.83, 140.40, 133.75, 133.72, 132.40, 132.11, 131.70, 131.35, 131.24, 130.77, 130.67, 128.45, 128.41, 128.30 (fullerene cage sp^2 carbons and aromatic carbons), 74.65, 74.01, 73.67, 70.49, 70.10, 68.94 (pyrrolidine ring C).

MALDI-TOF MS (DCTB/MeCN, m/z): 1030.5 (M^-).

IR (KBr, ν, cm^{-1}): 3446 (s, OH), 3054 (w), 2805 (w), 2360 (w), 1684 (w, CO), 1635 (m, CO), 1429 (s), 1260 (m), 796 (w), 580 (w).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 672 (1.78), 542 (9.37), 464 (17.63), 442 (17.53), 400 (21.62).

4.14. General procedure for fullerene triad synthesis via DCC-activated acid–amine coupling

Fulleropyrrolidine (1 equiv), carboxylic acid (1 equiv) and DCC (1 equiv) were dissolved in anhydrous ODCB (concentration of fulleropyrrolidine 0.0052 M) and stirred at room temperature under Ar atmosphere for 20 h. The resulting mixture was purified by column chromatography (silica gel, ODCB/^{i}PrOH 99.5:0.5). Further purification was carried out using the standard procedure by washing product with MeOH and petroleum ether and drying under vacuum.

4.14.1. Benzoic acid, 4-([60]fulleropyrrolidinyl carbonyl), [60]fulleropyrrolidinyl amide, ***1***. Starting from [60]fulleropyrrolidine, **7** (10 mg, 0.013 mmol), C_{60}-fulleropyrrolidine carboxylic acid, **11** (12 mg, 0.013 mmol) and DCC (3 mg, 0.013 mmol) yielded compound **1** (11 mg, 52%) as a brown solid.

^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.09 (s, 4H, ArH), 5.60 (br s, 8H, CH_2).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 168.52 (C=O), 153.09, 147.43, 146.46, 146.25, 145.78, 145.56, 145.45, 144.56, 143.24, 142.83, 142.30, 142.20, 142.07, 140.43, 137.49, 136.03, 130.63 (fullerene cage sp^2 carbons, 17 environments), 128.96, 128.45 (Ar C), 71.06, 67.70 (pyrrolidine ring C).

MALDI-TOF MS (DCTB/MeCN, m/z): 1656.2 (M^-).

IR (KBr, ν, cm^{-1}): 2920 (w), 2360 (w), 2342 (w), 1653 (s, C=O), 1384 (m), 574.36 (s).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 716 (0.86), 436 (9.15), 400 (13.26).

4.14.2. Benzoic acid, 4-(2,2-dimethyl-[60]fulleropyrrolidinyl carbonyl), [60]fulleropyrrolidinyl amide, ***2***. Starting from [60]fulleropyrrolidine, **7** (10 mg, 0.013 mmol), dimethyl C_{60}-fulleropyrrolidine carboxylic acid, **14** (12.3 mg, 0.013 mmol) and DCC (3 mg, 0.013 mmol) yielded compound **2** (6 mg, 27%) as a brown solid.

^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.06 (m, 4H, ArH), 5.58 (s, 4H, CH_2), 5.44 (s, 2H, CH_2), 2.56 (s, 6H, CH_3).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 170.60 (C=O), 169.95 (C=O), 154.13, 152.80, 147.52, 147.43, 146.53, 146.45, 146.24, 146.14, 145.76, 145.64, 145.59, 145.55, 145.48, 145.44, 145.36, 145.35, 144.61, 144.60, 144.55, 143.32, 143.23, 142.89, 142.85, 142.82, 142.36, 142.35, 142.29, 142.19, 142.05, 142.02, 141.98, 141.90, 140.45, 140.41, 139.97, 139.77, 137.22, 136.30, 136.17 (fullerene cage sp^2 carbons, 39 environments), 130.61, 129.01, 128.44, 127.69 (Ar C), 79.73, 74.28, 70.55, 67.99, 66.14, 60.73 (pyrrolidine ring C), 26.69 (CH_3).

MALDI-TOF MS (DCTB/MeCN, m/z): 1684.5 (M^-).

IR (KBr, ν, cm^{-1}): 2920 (w), 2360 (m), 2342 (m), 1653 (s, C=O), 1384 (m), 574 (s).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}$/dm^{-3} mol^{-1} cm^{-1}): 713 (0.53), 436 (6.77), 397 (11.26).

4.14.3. Benzoic acid, 4-([60]fulleropyrrolidinyl carbonyl), [70]fulleropyrrolidinyl amide, ***3***. Starting from [70]fulleropyrrolidine, **8** (5 mg, 0.0057 mmol), C_{60} carboxylic acid, **11** (5.2 mg, 0.0057 mmol)

and DCC (1.25 mg, 0.0057 mmol) yielded compound **3** (3 mg, 30%) as brown solid.

Compound **3a**: ^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 7.98 (d, 2H, J=8.2 Hz, ArH), 7.82 (d, 2H, J=8.2 Hz, ArH), 5.59 (s, 4H, [60]fulleropyrrolidine CH_2), 5.12 (s, 2H, [70]fulleropyrrolidine CH_2), 4.81 (s, 2H, [70]fulleropyrrolidine CH_2).

Compound **3b**: ^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 8.04 (d, 2H, J=8.0 Hz, ArH), 7.95 (d, 2H, J=8.0 Hz, ArH), 5.59 (s, 4H, [60]fulleropyrrolidine CH_2), 4.90 (d, 2H, [70]fulleropyrrolidine CH_2), 4.64 (d, 2H, [70]fulleropyrrolidine CH_2).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 168.76, 168.58, 168.42 (CO), 155.09, 154.57, 153.05, 151.74, 151.42, 151.40, 151.06, 150.99, 150.77, 150.71, 150.63, 150.33, 149.93, 149.90, 149.82, 149.42, 149.37, 149.32, 149.26, 149.08, 149.02, 148.80, 148.40, 148.09, 147.48, 147.44, 147.34, 147.20, 147.08, 147.04, 147.00, 146.90, 146.83, 146.85, 146.46, 146.25, 146.17, 146.04, 145.89, 145.77, 145.76, 145.68, 145.55, 145.54, 145.45, 144.98, 144.82, 144.55, 144.50, 144.28, 144.12, 143.46, 143.31, 143.24, 143.07, 142.99, 142.83, 142.29, 142.20, 142.07, 140.83, 140.43, 1375.52, 137.43, 137.28, 137.14, 136.01, 133.75, 133.72, 132.40, 132.11, 131.71, 131.35, 131.24, 128.86, 128.79, 128.75, 128.67, 128.57, 128.43, 125.89, 125.80 (fullerene cage sp^2 carbons and aromatic carbons), 76.81, 76.56, 76.26, 75.17, 73.18, 70.86, 69.93 (pyrrolidine ring carbons).

MALDI-TOF MS (DCTB/MeCN, m/z): 1776.1 (M^-).

IR (KBr, ν, cm^{-1}): 2922 (w), 1653 (C=O, s), 1428 (m), 1384 (m), 1260 (w), 527 (w).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}/dm^{-3}\,mol^{-1}\,cm^{-1}$): 674 (1.87), 542 (12.64), 465 (25.91), 442 (26.89), 436 (27.89), 395 (38.44).

4.14.4. Benzoic acid, 4-([70]fulleropyrrolidinyl carbonyl), [70]fulleropyrrolidinyl amide, ***4****.* Starting from [70]fulleropyrrolidine, **8** (4.3 mg, 0.0049 mmol), C_{70} carboxylic acid, **12** (5.0 mg, 0.0049 mmol) and DCC (1.0 mg, 0.0049 mmol) yielded compound **4** (3.3 mg, 36%) as brown solid.

Compound ***4aa***: ^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 7.91 (s, 4H, ArH), 5.10 (s, 4H, CH_2), 4.80 (s, 4H, CH_2).

Compound ***4bb***: ^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 7.71 (s, 4H, ArH), 4.90 (br s, 4H, CH_2), 4.59 (br s, 4H, CH_2).

Compound ***4ab***: ^{1}H NMR (400 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 7.83 (d, 2H, J=6.3 Hz, ArH), 7.79 (d, 2H, J=6.3 Hz, ArH), 5.10 (s, 2H, CH_2), 4.90 (br s, 2H, CH_2), 4.80 (s, 2H, CH_2), 4.59 (br s, 2H, CH_2).

^{13}C NMR (500 MHz, 297 K, $CS_2/CDCl_3$ 7:1 v/v, δ, ppm): 168.64, 168.61, 168.47 (CO), 157.25, 155.08, 151.75, 151.43, 151.06, 150.99, 150.78, 150.71, 150.62, 150.33, 150.32, 149.93, 149.90, 149.83, 149.42, 149.38, 149.32, 149.25, 149.08, 149.02, 148.79, 148.38, 148.09, 147.48, 147.20, 147.08, 147.04, 146.99, 146.89, 146.83, 146.58, 146.24, 146.17, 146.03, 145.89, 145.69, 145.66, 145.54, 144.98, 144.81, 144.49, 144.27, 144.25, 144.12, 143.46, 143.30, 143.07, 142.98, 140.83, 140.45, 140.39, 136.59, 133.75, 133.71, 132.41, 132.10, 131.70, 131.35, 131.24, 128.72, 128.60, 128.49, 128.42, 125.87 (fullerene cage sp^2 carbons and aromatic carbons), 70.77, 70.63, 70.45, 70.17, 69.54, 69.06 (pyrrolidine ring carbons).

MALDI-TOF MS (DCTB/MeCN, m/z): 1895.8 (M^-).

IR (KBr, ν, cm^{-1}): 2920 (s), 2361 (s), 2342 (s), 1653 (m, CO), 1428 (m), 1260 (w), 1000 (w), 669 (m).

UV–vis (CS_2): λ_{max} ($\varepsilon\times10^{-3}/dm^{-3}\,mol^{-1}\,cm^{-1}$): 672 (2.67), 542 (16.79), 465 (33.66), 446 (33.85), 399 (42.16).

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.061.

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