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Piperazine additions to C_{60}—a facile approach to fullerene substitution

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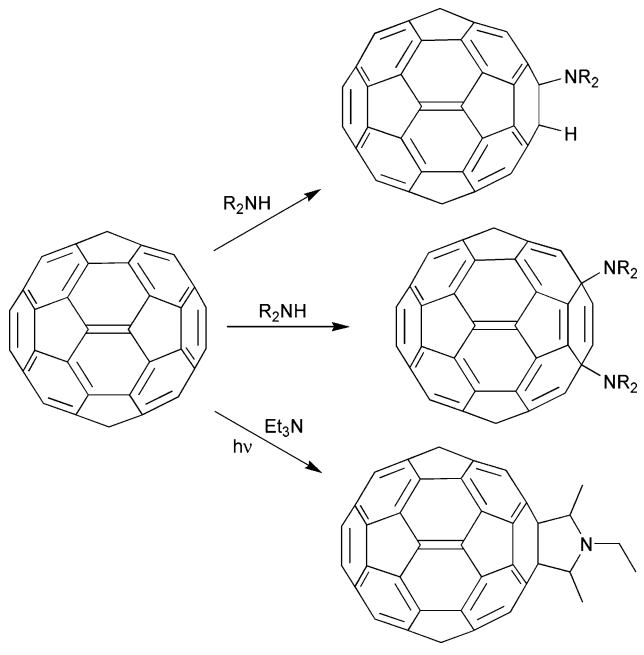
A range of fullerene monoadducts can be generated *via* the photochemical reaction of piperazine derivatives with C_{60}. Addend functionality can also be efficiently incorporated by transformation of the hydroxyl-substituted adduct prepared in this fashion. Reaction yields and process simplicity compete with current standard procedures for fullerene mono-functionalisation.

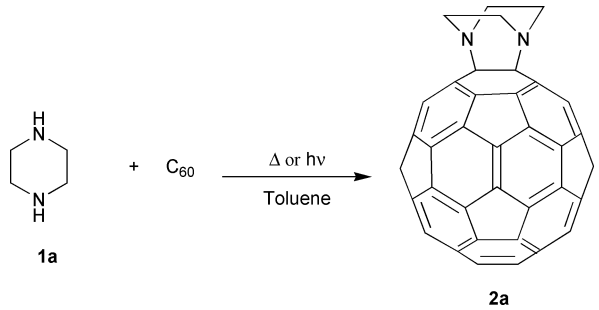
Introduction

The numerous chemical reactions of fullerenes[1] have been well documented over the last decade. The Bingel addition–elimination of halomalonates, Prato's dipolarcycloadditions of azomethine ylids and Diels–Alder reactions of quinodimethanes are probably the most general, substrate tolerant methods for addition to C_{60} and find numerous applications including materials synthesis.[2] By comparison, most other addition methods give low yields and are often highly substrate specific.

We have been interested in developing the reaction of C_{60} with amines into a useful synthetic technique for monoaddition to fullerenes. The reactions of C_{60} with amines[3] (Scheme 1) and diamines[4] (Scheme 2) have been employed in a small number of studies. However, in a synthetic sense, these have been neither particularly facile nor selective. Indeed the predominant product formed is highly dependent on the reaction conditions and reagents chosen. Reactions of secondary amines with C_{60} can give 1,2-hydroamination and 1,4-hydroamination products,[5] or 1,4-dehydroamination adducts,[6] while the photochemical reaction of a tertiary amine gives the corresponding pyrollidines (Scheme 1). To exacerbate these difficulties, exposure of these reaction mixtures to oxygen can give rise to alternative products, such as adduct-oxides[7] and fullerene dimers.[6] In the case of diamine reactions with C_{60}, these procedures have been shown to form only 1,2-dehydroaminylated adducts (Scheme 2).[4]



Scheme 1 Typical reactions of C_{60} with amines.



Scheme 2 Reaction of a diamine (piperazine) with C_{60}.

In all cases, the reactions of amines (and diamines) with C_{60} are believed to proceed *via* electron transfer from the amine donor to the readily reduced fullerene.[3] These processes are promoted by UV irradiation as the photochemical reaction proceeds *via* photon absorption to give $^3C_{60}$* (*via* $^1C_{60}$*), which readily undergoes the single electron transfer with the amine donor to give the radical anion–cation pair. Radical–radical coupling and proton transfer within this radical anion–cation pair generates the hydroaminated adducts but the latter stages of the dehydrogenative diamination mechanism are not clear.

The low yields of monoadduct and variety of regiochemical outcomes from C_{60}–amine reactions has effectively prevented the development of any synthetic utility in this method of fullerene adduct generation. Prior to our work in the field,[8,9] the only reported yield above 25% for a diamine–C_{60} monoadduct was 50%,[4] for the preparation of monoadduct **2a** from the reaction of 8 eq. of piperazine with C_{60} for 3 d at 80 °C. A more rapid photochemical procedure ($KMnO_4$ filter, 505 nm cutoff) for the preparation of **2a** was subsequently reported by Sun *et al.*[10] which required only 70 min at room temperature, but gave a relatively low yield of monoadduct **2a** (<25%) and still employed a significant excess (7 eq.) of the diamine reagent. Acyclic diamines required larger excesses of amine and gave much lower yields than piperazine under all reaction conditions. Recently we have reported an efficient preparation of the piperazine–C_{60} adduct **2a** in 73% yield[8] although application of this method to acyclic diamines has been frustratingly unsuccessful.

The limited substrate flexibility can be addressed by preparing a fullerene adduct which contains a reactive functional group. This adduct can then be transformed, *via* its reactive functional group, into a range of desired products using conventional synthetic methods—the concept of the fullerene 'synthon'. These materials should be more prone to synthetic manipulation than the parent fullerenes and, as fullerene adducts are more soluble

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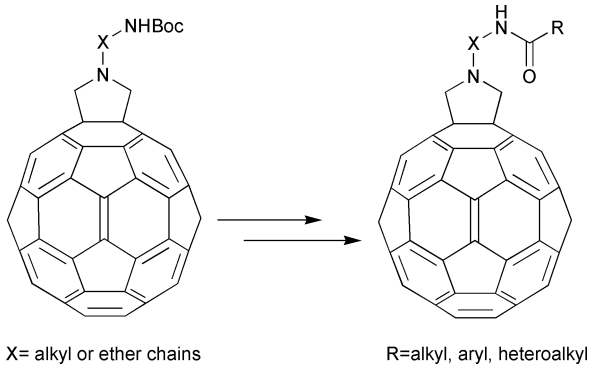
than their parent compounds, these 'synthons' possess a much broader synthetic scope. Kordatos *et al.* recently outlined such transformations of fulleropyrrolidines containing an *N*-Boc protected primary amine (Scheme 3).[11] Reaction of the amine group gave access to a variety of fullerene-derived compounds. This general approach to fullerene functionalisation has also previously been reported by a few others, notably the early use of hydroxyl-substituted quindimethano-derivatives by Zhang and Foote[12] and later Nakamura *et al.*[13]



Scheme 3 Generic transformations of the fullerene 'synthons' of Kordatos *et al.*[11]

This study describes the optimisation of piperazine–C_{60} photochemical reaction conditions, the generation, structural characterisation and some illustrative examples of reactions of substituted piperazine–C_{60} monoadducts.

Results and discussion

Reaction optimisation

Irradiation wavelength. Conditions for the photochemical reaction were optimised for the preparation of piperazine–C_{60} adduct **2a**, using an unfiltered medium pressure mercury lamp in a quartz water jacket, generally immersed in the reaction solution. While small variations in temperature should not play a significant role in the photochemical addition reaction, the reaction mixture was maintained at 23 °C by immersion of the photolysis vessel in a thermostatic water bath. Reactions were monitored by UV-vis spectroscopy performed on aliquots removed from the reaction mixture at appropriate intervals and all yields discussed are after isolation.

It appears that the wavelength of radiation incident on the sample is critical to the success of photochemical additions of piperazines to C_{60}. The irradiation of toluene solutions of C_{60} (1 mg ml^{-1}) and piperazine (2 eq.) at 265 and 366 nm respectively was monitored by UV-vis spectroscopy on regular aliquots. A steady increase in the absorbance of the aliquots at 440 nm was observed with time in both cases. This absorbance change is indicative of 1,2-adduct formation across a double bond between two six-membered rings of the fullerene[14] (a 6,6-monoadduct) in both experiments. However, the absorbance increase at 439 nm was approximately 4 times faster in the UV-vis spectrum of solutions irradiated at 265 nm. Similarly, unfiltered irradiation of a toluene solution of C_{60} (1 mg ml^{-1}) and piperazine (1 eq.) contained in a pyrex vessel (*ca.* 50% transmission at 310 nm) gave essentially no conversion under conditions where significant monoadduct formation was observed in reactions contained in quartz vessels. This suggests that the shorter of the principal emission wavelengths of a mercury lamp (254, 265, 297, 313 and 366 nm) are the most effective in promoting diamine addition to C_{60}. Hence all reactions were performed using unfiltered radiation from a medium-pressure mercury lamp through a quartz water jacket.

Oxygen. The effect of molecular oxygen on the photochemical reactions of amines and C_{60} is somewhat unclear. Hirsch[3] suggested that the presence of dioxygen in these mixtures allowed radical mechanisms to proceed, hence promoting *N*,*N*′-dehydroaddition products rather than hydroamination. Bernstein and Foote[15] also implicated singlet oxygen in the mechanism of the photochemical reaction of C_{60} with a tertiary propargylamine since addition of the competitive quencher DABCO was observed to reduce the yield of addition products. Similarly, thermal generation of singlet oxygen in the presence of C_{60} and the tertiary amine gave rise to the expected addition products. These same reactions performed under inert atmospheres were reported to give reduced yields. This contrasts with the reports by Kampe *et al.*[4] in which highly efficient formation of the C_{60}–piperazine monoadduct **2a** could be achieved under a nitrogen atmosphere.

In our hands, it was found that a highly oxygenated atmosphere was detrimental to the photochemical procedure, leading to a rapid colour change from the typical purple C_{60}–toluene solution to brown. The UV-vis absorption spectrum of the resulting mixture did not correspond to that of a typical 6,6-monoadduct (no peak at 440 nm was observed) and only a very small amount of adduct could be isolated. The majority of the fullerene-based material formed an insoluble precipitate during photolysis and workup, which could not be analysed. This is consistent with the photochemical formation of fullerene dimers in the presence of oxygen.[16] Exclusion of oxygen by N_2 purging and/or freeze-thaw cycling of all solutions prior to irradiation and conducting all manipulations and irradiation under an inert atmosphere, all gave the expected result—high reaction yields of the monoadduct **2a** (typically >50% depending on reaction stoichiometry) and no apparent precipitation.

Solvent. Changes in reaction solvent were examined, in the main to ascertain whether higher concentrations of C_{60} could be employed in these photochemical procedures. The limiting concentration of C_{60} in toluene is around 2.8 mg ml^{-1},[14] however preparing solutions at even these low concentrations requires extended sonication of solid C_{60} in toluene. Irradiation of chlorobenzene or dichlorobenzene solutions of C_{60} (limiting solubilities 7.0 mg ml^{-1} and 27.0 mg ml^{-1}, respectively)[14] and piperazine gave rise to a rapid reaction of the C_{60} as assessed by monitoring the UV-vis spectrum of the mixture. However, no marked increase in absorbance at around 440 nm was observed, suggesting a lack of monoadduct formation. Indeed a ^{1}H NMR spectrum of the product mixture showed a complex composition, including multiple aromatic products and attempts to separate or identify any C_{60}-containing materials were unsuccessful. A control experiment in chlorobenzene, conducted without the piperazine, gave a similar result indicating that the observed reaction is independent of the diamine-addition mechanism. Chlorobenzene is known[17] to dissociate under irradiation at 266 nm into chlorine and phenyl radicals which will react very rapidly with C_{60}. The high concentration of radicals likely to be formed under the irradiation of a chlorobenzene–C_{60} mixture would give rise to a complex mixture of aromatic, chlorinated and C_{60}-polyaddition products, as observed. It was also found that the addition of CS_2, another reasonable solvent for C_{60} (7.9 mg ml^{-1}),[14] to the toluene solutions severely inhibited the solubility of the piperazine reagent. Hence toluene remains the solvent of choice for these procedures.

Stoicheiometry and time. The ratio of piperazine : C_{60} required for efficient photochemical reaction was examined. In previous thermal and photochemical studies[4,10] a large excess of diamine has been used and low yields obtained. We assumed that these low yields were due to significant formation of bis-addition products at extended reaction times. Table 1 shows representative yield data for the generation of monoadduct **1** by reaction of piperazine with C_{60} (1 mg ml^{-1}). It is clear that near-stoichiometric quantities of diamine reagent are preferable to maximise the yield of monoadduct. Reaction times significantly above 18 h were found to reduce yields of monoadduct **1** slightly.

Table 1 Optimisation of diamine–C_{60} ratios and reaction times for the photochemical addition of piperazine to C_{60} (80 mg) in toluene (80 ml)

Entry	Ratio of piperazine : C_{60}	Irradiation time/h	Yield (%)
1	20 : 1	0.25	32
2	5 : 1	0.5	37
3	3 : 1	2	40
4	2 : 1	2	40
5	1 : 1	7	50
6	1 : 1	18	73

Synthetic utility

Photochemical reactions of 2-substituted piperazine derivatives with C_{60}. We have previously reported[9] that the photochemical reactions of 2-substituted piperazines with C_{60} are similarly facile under these conditions. Yields and conditions for successful monoadditions to generate 2-substituted adducts **2a**–**g** are shown in Table 2. The substituted piperazines were either purchased or prepared by modifications of the methods of Rondu *et al.*[18] and Bihan *et al.*[19] In all cases, it was found that the photochemical monoaddition of 2-substituted piperazines to C_{60} proceeded significantly more slowly than that of the parent piperazine. The consequent need for extended reaction times led to lower yields, however, increasing the diamine : C_{60} ratio to 3 : 1 and irradiating for around 64 h was found to offset this sufficiently such that yields approaching 45% could be achieved reproducibly for 2-methylpiperazine. The especially low yield achieved for the primary amide adduct **2d** appears to be due to the low solubility of the piperazine reagent in the toluene solvent, even at extended reaction times.

In some cases, (R = CO_2Et, $OSiMe_2{}^tBu$) no monoadduct could be isolated from the reaction mixture, despite the observation of the expected purple to brown colour change over a period of time. In both cases, the excess piperazine reagents could not be re-isolated from the reaction mixtures and it appears that the diamine reagents are not stable under the reaction conditions. Presumably coupling of the piperazine decomposition products with C_{60} gives rise to the observed colour change. As irradiation of the substituted piperazine in the absence of C_{60} does not lead to decomposition of the heterocycle, it seems likely that the intermediate radical cation of these piperazine derivatives is unstable and decomposes prior to radical recombination with the fullerene radical anion.

Transformations of adduct 2f. The hydroxymethyl adduct **2f**, which is readily prepared in a 43% yield (Table 2) by the photochemical addition procedure, can also be employed as a fullerene 'synthon' for further transformations. Scheme 4 outlines the results of simple transformations of adduct **2f** *via* the nucleophilic hydroxyl group. While adduct **2f** is significantly more soluble than C_{60} in standard organic solvents, all of the reactions were performed in 1 : 1 dichloromethane–chlorobenzene solvent mixtures to ensure rapid dissolution.

Esterification of adduct **2f** with acroyl chloride or *para*-bromobenzoyl chloride gave the corresponding esters **2h** and **2i** in 71 and 62% yields respectively following column chromatography. Analogous reactions employing a carboxylic acid reagent and thionyl chloride to prepare the corresponding acid chloride *in situ* gave comparable results. Incorporation of the acid moiety was confirmed by integration of the ^{1}H NMR spectra of the isolated adducts, ^{13}C NMR spectroscopy and observation of the parent ions at 889 and 1017 a.m.u. respectively.

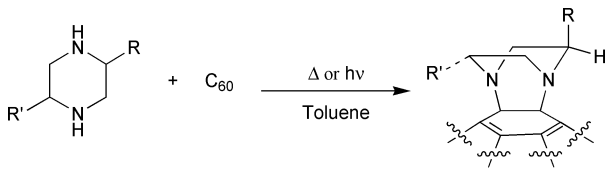
The reaction of adduct **2f** with t-butyldimethylsilyl (TBDMS) chloride at room temperature successfully generated the corresponding silyl ether **2j** in 67% yield. Incorporation of the silyl moiety was confirmed by the presence and correct integration of the methyl and t-butyl resonances in the ^{1}H NMR spectrum of adduct **2j** and the observed parent ion at 949 a.m.u. As mentioned above, adduct **2j** could not be prepared directly by addition of the silyl ether of **1f** to C_{60}, due to the instability of the substituted piperazine under the photochemical reaction conditions.

Sulfonic acid esters of adduct **2f** were prepared by mixing adduct **2f** with *p*-toluenesulfonyl chloride or methanesulfonyl chloride for 48 h at room temperature. The sulfonyl esters **2k** and **2l** were isolated in 54 and 46% yields respectively after chromatography. The incorporation of the sulfonyl group in both adducts **2k** and **2l** was confirmed by integration of the ^{1}H NMR spectra and observation of the parent ions at 913 and 989 a.m.u. respectively. The insolubility of the mesylate adduct in standard NMR solvents (including CS_2 admixtures) prevented a reasonable ^{13}C NMR spectrum from being obtained.

The sulfonyl esters **2k** and **2l** are themselves potential electrophilic fullerene synthons. Indeed, the reaction of adduct **2l** with sodium iodide in 2 : 3 acetone–chlorobenzene, furnished the corresponding iodomethyl adduct **2m** in a 43% yield following column chromatography. Again, this material proved too insoluble for characterisation by ^{13}C NMR spectroscopy, but the ^{1}H NMR spectrum of **2m** showed the lack of a methyl resonance in the product. The parent ion was also observed at 945 a.m.u.

Somewhat surprisingly, attempts to generate alkyl, allyl or aryl ethers of adduct **2f** by modified Williamson ether synthesis (in ether–chlorobenzene) or Mitsunobu-type reactions (in toluene) were unsuccessful. In the former case, no reaction

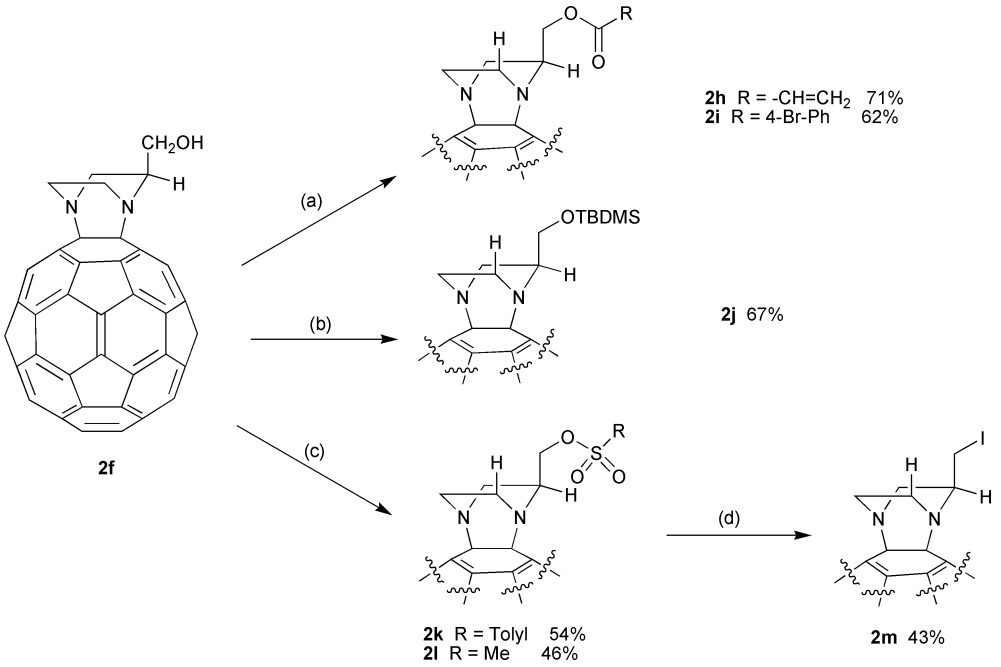
Table 2 Yields of monoadducts **2a**–**g** from the photochemical reaction of 3 eq. piperazines **1a**–**g** with C_{60} (80 mg) in toluene (80 ml)



2a-g

Entry	Addend	Adduct	R	R′	time/h	Yield (%)
1	**1a**	**2a**	H	H	18	73[a]
2	**1b**	**2b**	CH_3	H	64	41
3	**1c**	**2c**	$CH_2OC_6H_{13}$	H	64	10
4	**1d**	**2d**	$CONH_2$	H	64	6
5	**1e**	**2e**	$CONHC_3H_7$	H	64	27
6	**1f**	**2f**	CH_2OH	H	64	43
7	**1g**	**2g**	CH_3	CH_3	64	20[b]

[a] Reaction employed 1 equivalent of piperazine **1a**; [b] Reaction employed 5 equivalents of **1g**.



Scheme 4 Preparation and reactions of fullerene adduct **2f**; (a) RCOCl, NEt_3, DMAP, 1 : 1 CH_2Cl_2–chlorobenzene; (b) ^{t}butyldimethylsilyl chloride, imidazole, 1 : 1 CH_2Cl_2–chlorobenzene; (c) RSO_2Cl, triethylamine, 1 : 1 CH_2Cl_2–chlorobenzene; (d) **2l**, NaI, 2 : 3 acetone–chlorobenzene.

whatsoever could be observed and the starting material **2f** was re-isolated. In the latter case, all of the initial adduct **2f** was consumed, but no identifiable product could be isolated. It seems likely that monoadduct **2f** reacts with the intermediate 1,3-dipole generated by the reaction of triphenylphosphine with diisopropylazo(dicarboxylate) (DIAD). Similarly, attempts to oxidise the primary hydroxyl group to an aldehyde, using the Dess–Martin periodinane or Swern conditions were ineffective. Direct halogenation of **2f** by reaction with triphenylphosphine and carbon tetrahalides was also unsuccessful. In all instances control reactions with a model compound, *N*,*N*′-dibenzyl-2-(hydroxymethyl)piperazine, were successful in the appropriate solvent.

Configuration of 2-substituted adducts

The structure of the adduct **2a** was confirmed by X-ray crystallography[20] as the 1,2-dihydrofullerene with the piperazine adopting a 'boat' configuration. The introduction of a substituent on the piperazine ring both decreases the symmetry of the resultant adduct and allows two possible configurations in the resultant monoadduct, *exo* or *endo* (Fig. 1). We have previously reported that the reaction of 2-methylpiperazine with C_{60}[8] results in only a single configuration in the monoadduct **2b**, in which the methyl-substituent was found to be *exo* with respect to the fullerene substituent. This was established by the observation of a small NOE between the C2′-methyl resonance and a C6′-proton resonance, which could only arise if both groups occupy *exo* positions on the piperazine ring. The reason for this preferred arrangement is presumably thermodynamic in origin, although semi-empirical calculations (AM1) on both configurations of **2b** and the corresponding C2′-ethyl analogue suggest that there is little steric difference between the two configurations.

The configuration of adducts **2h** and **2i**, prepared by transformation of hydroxymethyl adduct **2f**, can also be confirmed by COSY and NOE NMR experiments. In both cases an NOE is observed between the C2′-methylene protons and the H6′-*exo* proton confirming their 1,3-diaxial arrangement. The analogous NOE is not observed for the precursor **2f**. However, given the configuration of **2h** and **2i** it seems clear that the hydroxymethyl group of adduct **2f** must indeed occupy an *exo* position, which is retained by its derivatives. Extension of this suggests that adducts **2j**–**m** must also all be *exo* configured.

The configuration of all other 2-substituted adducts in this report could not be unequivocally confirmed as NOE enhancements were not observed between resonances for protons on the C2′-substituent (where present) and a C6′-proton in these cases. However, comparison of the detailed assignments of the ^{1}H NMR spectra of adducts with known configurations (**2b** and **2f**–**m**) with amide adducts **2d** and **2e** shows a significant deshielding of the C3′-*exo* protons in the latter instances. This can be rationalised by the through-space effect of the C2′-carbonyl group—which would require the assignment of the C2′-substitution as *exo* once again. Finally, we have previously noted[8] that the ^{1}H NMR resonances of *exo*-protons in the fully assigned adducts **2a** and **2b**were consistently upfield of the analogous *endo*-protons. The assignment of the ^{1}H NMR spectra of the remaining adducts **2c**–**m**, assuming *exo* configurations of the C2′-substituent, is entirely consistent with this and at this stage we are confident that all C2′-substituted piperazine-C_{60} adducts can be assumed to be *exo* configured.

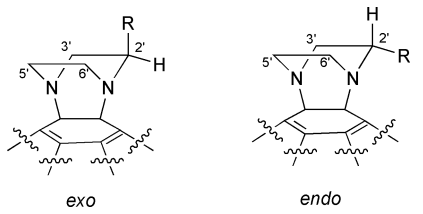


Fig. 1 Possible addend configurations in adducts **2**.

Conclusions

The photochemical reaction of piperazines with C_{60} is an effective method for generating generic fullerene monoadducts. Further transformations of the hydroxyl substituent in adduct **2f** demonstrate the facility with which a broad range of fullerene adducts can be readily prepared. In contrast to the substrate-dependent fullerene addition reactions, the success of these latter transformations is relatively independent of the nature of the piperazine substituents. The yields and facility of the generation

of adducts of type **2** compare favourably with current standard methods for fullerene functionalisation.

Experimental

General notes

Photochemical experiments were conducted using an unfiltered medium pressure mercury lamp surrounded by a quartz water jacket, which was immersed in the reaction solution. All photochemical reaction solutions and reagents were purged extensively with nitrogen immediately before photolysis. Piperazine **1a** (Lancaster Chemicals), 2-methylpiperazine **1b** (Avocado Chemicals), *trans*-2,5-dimethylpiperazine **1g** (Avocado Chemicals) were purified by sublimation prior to use. MALDI mass spectra were obtained with a Bruker Reflex III MALDI-TOF Mass Spectrometer. Nuclear Magnetic Resonance spectroscopy was performed on a Brucker DRX400 or a Bruker ACF-300. Semi-empirical calculations (AM1) were performed using Chem3D software version 5.0 (CambridgeSoft).

General procedure for photochemical addition of piperazines to C_{60}

A toluene solution (*ca.* 5 ml) of the diamine (*ca.* 0.33 mmol) was added to a toluene solution (total volume 80 ml) of C_{60} (80 mg, 0.11 mmol). Following nitrogen-purging, the solution was irradiated for the appropriate period. The resulting product mixture was separated by flash silica column chromatography. C_{60} was eluted with a concentration gradient of hexane–toluene before the monoadducts were eluted with toluene–methanol (99 : 1). Elution with methanol gave no further products. Products were isolated as brown powders after removal of solvent *in vacuo*.

2-(Hexoxymethyl)piperazine (1c). A solution of 1,4-dibenzyl-2-hexoxymethylpiperazine (1 g, 2.8 mmol, see below for preparation) in ethanol (10 mL) was treated with 10% Pd/C under an H_2 atmosphere overnight at room temperature. The mixture was filtered through celite before removing the solvent *in vacuo*, to give 480 mg (91%) of the title compound as a waxy white solid. The material was used in the next step without purification. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (3H, t, J 6.9 Hz), 1.20–1.34 (6H, m), 1.53 (2H, p, J 6.6 Hz), 2.61 (1H, dd, J 1.3 Hz, 11.2 Hz), 2.84 (1H, m), 3.01–3.16 (5H, m), 3.28 (1H, dd, J 2.2 Hz, 7.0 Hz), 3.35–3.43 (3H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.47, 23.05, 26.15, 29.90, 31.99, 44.85, 45.49, 47.55, 54.39, 72.08, 72.48; m/z 201.1954 (expected 201.1967).

1,4-Dibenzyl-2-hexoxymethylpiperazine. To a suspension of sodium hydride (134 mg, 1.8 mmol) in ether at 0 °C was added, dropwise, a solution of 1-4-dibenzyl-2-(hydroxymethyl) piperazine (0.5 g, 1.6 mmol, see below for preparation) in ether (20 ml). The crude mixture was stirred for 30 min, then the 1-bromohexane (0.45 ml, 1.8 mmol) was added dropwise at 0 °C. The solution was allowed to warm to room temperature and the reaction mixture was stirred overnight. The crude mixture was washed with aqueous sodium hydrogen carbonate (2 × 20 ml) and brine (20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a pale yellow oil purified by column chromatography using petroleum ether–ethyl acetate (9 : 1) as eluent, to give 0.438 g (72%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 (3H, t, J 7.0 Hz), 1.11–1.27 (6H, m), 1.48 (2H, m), 2.10–2.23 (3H, m), 2.45–2.49 (1H, m), 2.59–2.69 (3H, m), 3.26–3.32 (3H, m), 3.36–3.47 (3H, m), 3.59 (1H, dd, J 4.3 Hz, 10.0 Hz), 4.00 (1H, d J 13.5 Hz), 7.24–32 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.14, 23.02, 26.23, 29.95, 32.06, 51.12, 53.25, 56.80, 60.10, 63.40, 71.85, 127.16, 127.36, 128.56, 129.53, 138.56, 139.56; m/z 381.2904 (expected 381.2906); Anal. Calcd. for $C_{25}H_{36}N_2O$:C, 78.90; H, 9.53; N, 7.36%. Found C, 79.31; H, 10.50; N, 7.36%.

Piperazine-2-carboxylic acid amide (1d). A solution of 1,4-dibenzylpiperazine-2-carboxylic acid amide (1 g, 2.8 mmol, see below for preparation) in ethanol (10 mL) was treated with 10% Pd/C under an H_2 atmosphere overnight at room temperature. The mixture was filtered through celite before removing the solvent *in vacuo*, to give 350 mg (95%) of the title compound as a white powder. The material was used in the next step without purification. m.p. 144–145 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.66–2.92 (5H, m), 3.10 (1H, dd, J 3.4 Hz, 12.2 Hz), 3.28 (1H, dd, J 3.5 Hz, 12.2 Hz), 5.47 (1H, br), 6.84 (1H, br); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.69, 46.72, 49.46, 59.58, 175.34; m/z 130.0983 (expected 130.0980).

1,4-Dibenzylpiperazine-2-carboxylic acid amide. Prepared according to the procedure used by Rondu *et al.*;[18] 3 g of 2,3-dibromo propionamide (12.9 mmol) was added dropwise to a hot (80 °C) toluene solution (75 ml) of *N*,*N*′-dibenzylethylenediamine 2.98 g (12.4 mmol) and 4.24 ml of triethylamine. The reaction mixture was refluxed for 48 h and then cooled. The crude mixture was washed with aqueous sodium hydrogen carbonate (2 × 50 ml) and brine (1 × 50 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a white powder purified by recrystallisation (dichloromethane–ether) 2.83 g (74%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25–2.42 (3H, m), 2.53–2.58 (1H, m), 2.73–2.78 (1H, m), 2.88 (1H, dd, J 2.0 Hz, 11.0 Hz), 3.14 (1H, dd, J 3.4 Hz, 7.7 Hz), 3.38–3.52 (3H, m), 3.81 (1H, d, J 13.6 Hz), 7.26–7.34 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 49.73, 52.86, 56.09, 60.43, 63.18, 66.13, 174.80; m/z 310.1910 (expected 310.1919). Anal. calcd. for $C_{22}H_{29}N_3O$:C, 73.81; H, 8.36; N, 12.91%. Found: C, 73.63; H, 7.77; N, 13.63%.

Piperazine-2-carboxylic acid propylamide (1e). A solution of 1,4-dibenzylpiperazine-2-carboxylic acid propylamide (1 g, 2.8 mmol, see below for preparation) in ethanol (10 mL) was treated with 10% Pd/C under an H_2 atmosphere overnight at room temperature. The mixture was filtered through celite before removing the solvent *in vacuo*, to give 469 mg (96%) of the title compound as a white powder. The material was used in the next step without purification. m.p. 144–145 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (3H, t, J 7.5 Hz), 1.50 (2H, sextuplet, J 7.1 Hz), 2.67–2.94 (5H, m), 3.14–3.22 (3H, m), 3.30 (1H, dd, J 3.4 Hz, 8.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.80, 23.22, 41.01, 45.75, 46.66, 49.73, 59.76, 172.51; m/z 172.1440 (expected 172.1450).

1,4-Dibenzylpiperazine-2-carboxylic acid propylamide. Prepared according to the procedure used by Bihan *et al.*;[19] 0.65 ml of *n*-propylamine (7.8 mmol) in toluene (10 ml) was added dropwise to a stirred and cooled solution of 7.8 ml of $Al(CH_3)_3$ (7.8 mmol) in toluene at 0 °C, so that the temperature did not exceed 10 °C. After 1 h, a solution of 2 g of ethyl 1,4-dibenzyl-2-piperazinecarboxylate (5.9 mmol, see below for preparation) in toluene (10 ml) was added slowly at room temperature. The reaction mixture was refluxed for 4 h, then stirred overnight at room temperature. The reaction mixture was cooled and treated dropwise with 50 ml of water–MeOH (50 : 50, v/v). After filtration, the crude mixture was extracted with dichloromethane (3 × 50 ml), washed with brine (2 × 30 ml) and water (20 ml) and dried over $MgSO_4$. Evaporation of the solvents gives a waxy white solid, which was purified by column chromatography using petroleum ether–ethyl acetate (8 : 2) as eluent, to give 1.51 g (74%) of a white powder. m.p. 119–120 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (3H, t, J 7.5 Hz), 1.56 (2H, sextuplet, J 7.1 Hz), 2.26–2.36 (3H, m), 2.39 (1H, d, J 1.9 Hz), 2.60 (1H, m), 2.62 (1H, d, J 3.5 Hz), 2.74–3.50 (6H, m) 3.81 (1H, d, J 13.5 Hz), 7.29–7.34 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.95, 23.41, 41.02, 50.04, 52.99, 56.55, 60.79, 63.18, 66.29, 127.70, 128.83, 129.11, 129.62, 137.86, 138.34, 172.08; m/z 352.2381 (expected 352.2389); Anal. calcd. for $C_{22}H_{29}N_3O$:C, 75.18; H, 8.32; N, 11.96%. Found C, 75.00; H, 8.40; N, 12.01%.

2-Hydroxymethylpiperazine (1f)[18]. A solution of 1–4-dibenzyl-2-(hydroxymethyl)piperazine (1 g, 3.3 mmol, see below for preparation) in ethanol (10 mL) was treated with 10% Pd/C under an H_2 atmosphere overnight at room temperature. The mixture was filtered through celite before removing the solvent *in vacuo*, to give 392 mg (95%) of the title compound as an off-white powder The material was used in the next step without purification. m.p. 95–96 °C; ^{1}H NMR (300 MHz) δ 3.38 (2H, dd, *J* 2.2 Hz, 7.0 Hz), 2.94–2.68 (7H, m), 2.45 (1H, t, *J* 7.0 Hz) ^{13}C NMR (75 MHz) δ 46.7 (2C), 49.0, 57.6, 64.4. Spectroscopic data and melting point are in line with that previously reported.[18]

1-4-Dibenzyl-2-(hydroxymethyl)piperazine[18]. Prepared by modification to the procedure of Rondu *et al.*;[18] A stirred suspension of $LiAlH_4$ (7.5 g, 22 mmol) in dry ether (30 mL) was cooled to 0 °C and 3.34 g (88 mmol) of ethyl 1,4-dibenzylpiperazine-2-carboxylate (see below for preparation) in ether (30 mL) was added slowly. The mixture was stirred overnight at room temperature, then cooled to 0 °C and treated carefully with aqueous sodium hydrogen carbonate. The solution was extracted with CH_2Cl_2 (2 × 50 mL) and the organic extract was dried over $MgSO_4$. After the solvent was removed, recrystallization of the crude product from ethyl acetate–hexane afforded 5.8 g (88%) of the title compound as a white powder. m.p. 72–73 °C; ^{1}H NMR (300 MHz) δ 7.36–7.2 (10H, m, Ar–H), 4.06 (1H, dd, *J* 11.2, 2.9 Hz), 3.95 (1H, d, *J* 13.2 Hz), 3.59 (1H, dd, *J* 11.2, 2.9 Hz), 3.48 (1H, d, *J* 13.2 Hz), 3.78 (1H, br s), 3.47 (2H, s), 2.95–2.92 (1H, m), 2.69–2.31 (6H, m); ^{13}C NMR (75 MHz) δ 50.2, 52.8, 56.4, 58.4, 58.9, 62.5, 63.6, 127.0–129.1, 137.6, 138.4. Spectroscopic data and melting point are in line with those previously reported.[18]

Ethyl 1-4-dibenzylpiperazine-2-carboxylate. Prepared according to the procedure of Rondu *et al.*;[18] 3.67 mL of ethyl 2,3-dibromopropionate (25 mmol) was added dropwise to a hot (80 °C) toluene solution (75 ml) of *N*,*N*′-dibenzylethylenediamine 6 g (24 mmol), 8.36 mL (60 mmol) of triethylamine. The reaction mixture was refluxed overnight and then cooled. The reaction mixture was washed with aqueous sodium hydrogen carbonate (2 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo* to give a red oil which was purified by column chromatography using petroleum ether–ethyl acetate (9 : 1) as eluent, to give 7.66 g (90%) of the title compound as a colorless oil. ^{1}H NMR (300 MHz), δ 4.12 (2H, q, *J* 7.0 Hz), 3.84 (1H, d, *J* 13.1 Hz), 3.52–3.58 (2H, m), 3.35 (1H, d, *J* 12.8 Hz), 3.23 (1H, dd, *J* 11.8 Hz, 6.5 Hz), 2.99 (1H, m), 2.65 − 2.24 (5H, m); ^{13}C NMR (75 MHz), δ 14.6, 49, 53.4, 55.9, 60.0, 60.8, 63.0, 63.2, 127.4–129.5, 138.3, 138.5, 172.5. Spectroscopic data are in line with those previously reported.[18]

Piperazine–C_{60} adduct 2a[4a]. Prepared by the general photochemical procedure described above, but using only 1 eq. piperazine **1a** (0.11 mmol). Irradiation period of 18 h. Yield 75%. Spectroscopic data are in line with literature values.[4a]

2′-Methylpiperazino[1′,4′:1,2][60]fullerene (2b)[8]. Prepared from diamine **1b** and C_{60} by the general photochemical procedure described above. Irradiation period of 64 h. Yield 41%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.78 (3H, d, *J* 6.8 Hz, CH_3), 3.19 (1H, dd, *J* 6.4 Hz, 13.7 Hz, $H3_{exo}$), 3.57 (1H, dddd, *J* 4.0 Hz, 8.6 Hz, 8.6 Hz, 11.5 Hz, $H5_{exo}$), 3.91 (1H, ddd, *J* 5.4 Hz, 8.6 Hz, 14.1 Hz, $H6_{exo}$), 4.45–4.60 (2H, m, $H5_{endo}$+$H6_{endo}$), 4.72 (1H, m, $H3_{endo}$), 4.94 (1H, ddd, *J* 6.4 Hz, 6.8 Hz, 13.4 Hz, $H2_{endo}$); ^{13}C NMR ($CDCl_3$/CS_2, 100 MHz) δ 19.48, 39.17, 47.08, 48.93, 55.11, 77.54, 80.53, 137.85, 137.97, 138.06, 138.28, 140.58, 140.65, 140.67, 141.72, 141.83, 141.93, 142.61, 142.64 (2C), 142.68 (2C), 143.01 (2C), 143.03, 143.42 (3C), 143.43 (3C), 143.48, 145.46 (2C), 145.51 (2C), 146.06 (3C), 146.08 (2C), 146.34 (2C), 146.42 (2C), 146.45, 146.67, 146.75, 146.79 (3C), 146.81 (2C), 146.92 (2C), 147.16 (2C), 147.18 (2C), 148.64, 148.67, 152.93, 153.20, 153.35, 153.53; *m*/*z* 818.

2′-Hexoxymethylpiperazino[1′,4′:1,2][60]fullerene (2c). Prepared from diamine **1c** and C_{60} by the general photochemical procedure described above: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (3H, t, *J* 7.1 Hz, CH_3), 1.29 (2H, br s, CH_2), 1.45 (6H, br s, 3 × CH_2), 3.31 (1H, dd, *J* 7.0 Hz, 14.0 Hz, $H3_{exo}$), 3.57 (1H, ddd, *J* 4.8 Hz, 8.9 Hz, 14.9 Hz, $H5_{exo}$), 3.84 (1H, ddd, *J* 5.3 Hz, 11.6 Hz, 14.6 Hz, $H6_{exo}$), 3.97 (2H, s, OCH_2[Hexyl]), 4.52–4.61 (2H, m, $H5/6_{endo}$), 4.70 (1H, m, $H3_{endo}$), 4.73 (1H, dd, *J* 6.0 Hz, 11.5 Hz, CH_2O), 4.93 (1H, dd, *J* 7.6 Hz, 11.5 Hz, CH_2O), 5.14 (1H, m, $H2_{endo}$); ^{13}C NMR ($CDCl_3$/CS_2, 100 MHz) δ 14.38, 23.02, 25.65, 29.85, 31.95, 40.75, 47.43, 50.48, 52.65, 66.40, 77.41, 78.06, 136.78, 137.16, 139.54, 139.59, 139.68, 139.72, 140.59, 140.82 (2C), 141.58, 141.61, 141.64, 141.68, 142.00 (2C), 142.03, 142.40, 142.42 (2C), 142.43, 142.45 (2C), 144.36 (2C), 144.40, 144.94, 144.96, 145.07 (4C), 145.11, 145.28 (2C), 145.38, 145.41, 145.43, 145.49 (2C), 145.53 (3C), 145.55, 145.83 (3C), 145.86 (3C), 146.18 (2C), 146.21 (3C), 147.69, 147.73, 150.65; *m*/*z* 919 (MH+, expected 919.2).

2′-Amidocarboxypiperazino[1′,4′:1,2][60]fullerene (2d). Prepared from diamine **1d** and C_{60} by the general photochemical procedure described above: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.47–3.74 (2H, m, $H4_{exo}$ + $H5_{exo}$), 4.10 (1H, dd, *J* 7.0 Hz, 14.0 Hz, $H3_{endo}$), 4.22 (1H, dd, *J* 7.2 Hz, 14.4 Hz, $H3_{exo}$), 4.41–4.48 (1H, m, $H5/H6_{endo}$), 4.53–4.62 (2H, m, $H5/H6_{endo}$ +NH_2), 5.28–5.35 (1H, m, $H3_{endo}$), 5.78 (1H, br, NH); ^{13}C NMR ($CDCl_3$/Cs_2, 100 MHz) δ 41.23, 42.68, 47.74, 49.31, 78.28, 79.07, 136.96, 137.03, 137.78, 137.85, 139.92, 140.04, 140.20, 140.28, 141.03, 141.11, 141.39, 141.41, 142.00, 142.05, 142.11, 142.18, 142.36, 142.42, 142.48, 142.52, 142.90 (3C), 142.92, 142.95 (2C), 144.69, 144.80, 144.87, 145.02, 145.36, 145.43, 145.56 (2C), 145.58, 145.76, 145.86 (2C), 145.90, 146.03 (2C), 146.30, 146.33 (2C), 146.36, 146.63, 146.65, 146.71 (2C), 148.14, 145.25, 150.57, 150.82, 151.76, 15194, 173.77; *m*/*z* 849 (MH+, expected 848.1).

2′-Propylamidocarboxypiperazino[1′,4′:1,2][60]fullerene (2e). Prepared from diamine **1e** and C_{60} by the general photochemical procedure described above. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (3H, t, *J* 7.3 Hz, CH_3), 1.72 (2H, sextuplet, *J* 7.4 Hz, CH_2), 3.43 (1H, q, *J* 6.5 Hz, NCH_2), 3.49–3.65 (3H, m, NCH_2 + $H5/H6_{exo}$), 4.25 (1H, dd, *J* 6.8 Hz, 13.9 Hz, $H3_{exo}$), 4.37–4.43 (1H, m, $H5/H6_{endo}$), 4.54–4.64 (2H, m, $H5/H6_{endo}$ + $H3_{endo}$), 5.31 (1H, t, *J* 7.7 Hz, $H2_{endo}$); ^{13}C NMR ($CDCl_3$/CS_2, 100 MHz) δ 11.74, 23.3, 41.43, 42.12, 46.85, 48.03, 56.71, 77.29, 78.19, 136.97, 137.03, 137.78, 137.84, 139.91, 140.03, 140.19, 140.27, 141.03, 141.10, 141.38, 141.41, 141.99, 142.04, 142.11, 142.17, 142.36, 142.41, 142.46, 142.51, 142.89 (2C), 142.91, 142.94 (2C), 144.69, 144.79, 144.85, 145.01, 145.36, 145.42, 145.55 (2C), 145.58, 145.89, 146.02 (2C), 146.04 (2C), 146.29, 146.35, 146.62, 146.64, 146.70 (2C), 148.14, 148.25, 150.57, 150.82, 151.74, 151.92, 170.58; *m*/*z* 890 (MH+, expected 890.1).

2′-Hydroxymethylpiperazino[1′,4′:1,2][60]fullerene (2f). Prepared from diamine **1f** and C_{60} by the general photochemical procedure described above: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.77 (1H, br, OH), 3.10 (1H, dd, *J* 6.8 Hz, 13.4 Hz, $H3_{exo}$), 3.52 (1H, m, $H5_{exo}$), 3.85 (1H, ddd, *J* 5.3 Hz, 11.8 Hz, 14.5 Hz, $H6_{exo}$), 4.11 (1H, m, CH_2O), 4.25 (1H, dd, *J* 10.0 Hz, 10.0 Hz, CH_2O), 4.42–4.54 (1H, m, $H5/H6_{endo}$), 4.54–4.68 (2H, $H5/H6_{endo}$+$H3_{endo}$), 5.11 (1H, m, $H2_{endo}$); ^{13}C NMR ($CDCl_3$/CS_2, 100 MHz) δ 39.44, 47.54, 50.32, 54.98, 62.38, 78.40, 80.04, 137.20 (2C), 137.33 (2C), 137.65, 137.78 (2C), 140.01, 140.08 (2C), 140.14 (2C), 140.15, 141.07 (2C), 141.17 (2C), 141.29, 142.02, 142.11(2C), 142.46, 142.88 (2C), 142.90, 142.95, 144.82 (2C), 144.92, 145.41, 145.46, 145.56, 145.63 (2C), 145.70 (2C), 145.87 (2C), 145.89, 145.93 (2C), 146.00 (2C), 146.33 (3C), 146.40, 146.64 (4C), 146.67 (2C), 151.03 (2C), 151.38, 151.76, 151.91; *m*/*z* 834 (MH+, expected 834.08).

***trans*-2′,5′-Dimethylpiperazino[1′,4′:1,2][60]fullerene (2g).** Prepared from diamine **1g** and C_{60} by the general photochemical procedure described above, but using 5 eq. diamine (0.55 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.82 (3H, d, J 6.9 Hz, CH_{3exo}), 1.97 (3H, d, J 7.1 Hz, CH_{3endo}), 3.25 (1H, dd, J 4.8 Hz, 13.9 Hz, $H3_{exo}$), 3.82 (1H, dd, J 8.0 Hz, 9.0 Hz, $H5_{exo}$), 4.15 (1H, dd, J 9.3 Hz, 14.6 Hz, $H6_{exo}$), 4.43 (1H, ddd, J 1.3 Hz, 9.5 Hz, 14.6 Hz, $H6_{endo}$), 4.76 (1H, m, $H2_{endo}$), 5.03 (1H, ddd, J 0.9 Hz, 9.3 Hz, 13.9 Hz, $H3_{endo}$); ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz) δ 20.96, 23.71, 47.36, 49.70, 54.46, 60.03, 77.23, 77.36 (part. obsc.), 136.64, 137.38 (2C), 137.42, 139.80, 139.86, 139.87, 140.02, 140.63, 140.82, 140.95, 141.23, 141.84, 141.91, 141.97, 142.03, 142.34, 142.37, 142.39, 142.72, 142.73, 142.77, 142.94, 142.99, 143.04, 144.64, 144.67, 144.91, 145.00, 145.32, 145.38, 145.41, 145.42, 145.44, 145.45, 145.50, 145.59, 145.66, 145.77 (2C), 145.80, 145.83, 145.85, 146.13 (2C), 146.20 (2C), 146.42, 146.54 (2C), 146.56 (2C), 148.03, 148.07, 151.86, 152.09, 153.33, 153.46; m/z 833 (MH+, expected 833.1).

2′-Acroylmethylpiperazino[1′,4′:1,2][60]fullerene (2h). To a solution of adduct **2f** (10.0 mg, 12 μmol), triethylamine (7 μL, 50 μmol) and DMAP (0.4 mg, 1 μmol) in a mixed solvent (1 : 1 dichloromethane–chlorobenzene) (3 mL) was added dropwise acroyl chloride (5 μL, 72 μmol). The reaction mixture was stirred overnight at room temperature and washed with aqueous sodium hydrogen carbonate (1 × 5 mL) and brine (2 × 5 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a brown solid purified by column chromatography using toluene–ethyl acetate (8 : 2) as eluent, to give 7.6 mg (71%) of the title compound **2h** as a brown powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.35 (1H, dd, J 6.8 Hz, 13.9 Hz, $H3_{exo}$), 3.56–3.63 (1H, m, $H5_{exo}$), 3.81–3.89 (1H, m, $H6_{exo}$), 4.48–4.59 (2H, m, $H5_{endo}$+ $H6_{endo}$), 4.66–4.76 (1H, m, $H3_{endo}$), 4.79 (1H, dd, J 6.6 Hz, 11.5 Hz, 1H of OCH_2), 4.90 (1H, dd, J 7.0 Hz, 11.3 Hz, 1H of OCH_2), 5.16 (1H, q, J 7.5 Hz, $H2_{endo}$), 5.94 (1H, dd, J 1.4 Hz, 10.4 Hz, $=CH_2$), 6.29 (1H, dd, 10.4 Hz, 17.2 Hz, HC=), 6.56 (1H, dd, 1.3 Hz, 17.2 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz) 40.60 (CH_2, C-6), 47.21 (CH_2, C-5), 50.82 (CH_2, C-3), 52.53 (CH, C-2), 65.32 (OCH_2), 78.00, 80.21, 128.09 (HC=), 131.66 (H_2C=), 137.24, 137.30, 137.58, 137.66, 139.95, 140.03, 140.09, 140.14, 141.08, 141.18, 141.25 (2C), 141.27, 142.03, 142.06, 142.11, 142.42 (2C), 142.45, 142.85 (2C), 142.87 (2C), 142.91 (3C), 144.82 (2C), 144.85, 144.88, 145.41, 145.53 (2C), 145.56, 145.72, 145.78, 145.85 (2C), 145.95 (2C), 145.96, 146.28 (2C), 146.29 (2C), 146.61 (2C), 146.64, 148.16, 148.20, 151.22, 151.37, 166.27; m/z 889 (expected 889.09).

2′-*p*-Bromobenzoylmethylpiperazino[1′,4′:1,2][60]fullerene (2i). To a solution of adduct **2f** (25.0 mg, 30 μmol), triethylamine (16 μL, 0.12 mmol) and DMAP (1 mg, 3 μmol) in a mixed solvent (1 : 1 dichloromethane–chlorobenzene, 3 mL) was added dropwise *p*-bromobenzoyl chloride (26 mg, 0.12 mmol). The reaction mixture was stirred for 35 h at room temperature and washed was washed with aqueous sodium hydrogen carbonate (1 × 5 ml) and brine (2 × 5 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a brown solid purified by column chromatography using toluene–ethyl acetate (9 : 1) as eluent, to give 19 mg (62%) of the title compound **2i** as a brown powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.40 (1H, dd, J 6.8 Hz, 14.2 Hz, $H3_{exo}$), 3.60–3.65 (1H, m, $H5_{exo}$), 3.87–3.93 (1H, m, $H6_{exo}$), 4.51–4.61 (2H, m, $H5_{endo}$+ $H6_{endo}$), 4.72–4.78 (1H, m, $H3_{endo}$), 4.93 (1H, dd, J 6.7 Hz, 11.2 Hz, 1H of OCH_2), 5.08 (1H, dd, J 7.0 Hz, 11.3 Hz, 1H of OCH_2), 5.22–5.29 (1H, m, $H2_{endo}$), 7.63 (2H, d, J 8.6 Hz, Ph), 8.02 (2H, d, J 8.5 Hz, Ph); ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz) 40.67 (CH_2, C6), 47.28 (CH_2, C5), 50.86 (CH_2, C3), 52.60 (CH, C2), 65.96 (OCH_2), 78.00, 80.21, 128.30 (CH, Ph), 128.4 (C, C-*ipso*), 128.75 (C, C-*ipso*), 129.11 (CH, Ph), 131.35 (CH, Ph), 131.91, (CH, Ph), 137.24, 137.30, 137.59, 137.69, 139.97, 140.07, 140.11, 140.15, 141.06, 141.48, 141.25, 141.27, 142.04 (2C), 142.07, 142.11, 142.41 (3C), 142.44, 142.86 (3C), 142.88, 142.92 (3C), 144.82 (3C), 144.85, 144.88, 145.38, 145.51 (2C), 145.54, 145.56, 145.68, 145.77, 145.86 (3C), 145.89, 145.93, 145.95, 145.96, 146.28 (2C), 146.29, 146.31, 146.62, 146.64, 148.16, 148.20, 151.18, 151.32, 151.75, 151.90, 165.98; m/z 1017 (expected 1017.02).

2′-(*tert*-Butyldimethylsiloxymethyl)piperazino[1′,4′:1,2][60]-fullerene (2j). To a solution of adduct **2f** (10.0 mg, 12 μmol) and imidazole (3 mg, 48 μmol) in a mixed solvent (1 : 1 dichloromethane–chlorobenzene) (3 mL) was added TBDMSCl (6 mg, 48 μmol). The reaction mixture was stirred overnight at room temperature and the solvent was removed *in vacuo* to give a brown solid purified by column chromatography using dichloromethane–ethyl acetate (70 : 30) as eluent, to give 7.6 mg (67%) of the title compound **2j** as a brown powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.24 (6H, s, CH_3), 1.04 (9H, s, CH_3), 3.61–3.70 (2H, m, $H3_{exo}$+ $H5_{exo}$/ $H6_{exo}$), 3.96–4.04 (1H, m, $H5_{exo}$/ $H6_{exo}$), 4.30 (1H, dd, J 5.1 Hz, 10.4 Hz, 1H of OCH_2), 4.40 (1H, dd, J 5.4 Hz, 10.3 Hz, 1H of OCH_2), 4.46–4.51 (2H, m, $H5_{endo}$+ $H6_{endo}$), 4.56–4.62 (1H, m, $H6_{exo}$), 4.87 (1H, q, J 7.5 Hz, $H2_{endo}$); ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz) 14.14 (CH_3), 26.02 (CH_3), 41.88 (CH_2, C-6), 47.20 (CH_2, C-5), 49.99 (CH_2, C-3), 54.97 (CH, C-2), 65.60 (OCH_2), 78.14, 80.54, 137.27, 137.33, 137.66, 139.93, 139.97, 140.08, 140.11, 141.09, 141.21, 141.27 (2C), 141.28, 142.01, 142.03 (2C), 142.05, 142.08, 142.40 (2C), 142.43, 142.82 (3C), 142.90 (2C), 144.82, 144.85 (2C), 144.88 (2C), 145.45, 145.50 (3C), 145.53, 145.74, 145.81, 145.82, 145.87, 145.90 (2C), 145.94 (2C), 145.97 (2C), 146.25 (2C), 146.27 (2C), 146.59 (2C), 146.61 (2C), 146.63 (2C), 148.13, 148.17, 151.65, 151.72; m/z 949 (expected 949.17).

2′-*p*-Toluenesulfonylmethylpiperazino[1′,4′:1,2][60]fullerene (2k). To a solution of adduct **2f** (10.0 mg, 12 μmol), triethylamine (8 μL, 60 μmol) in a mixed solvent (1 : 1 dichloromethane–chlorobenzene, 3 mL) was added tosyl chloride (11 mg, 60 μmol). The reaction mixture was stirred for 48 h at room temperature and the solvent removed *in vacuo* to give a brown solid, which was purified by column chromatography using toluene–ethyl acetate (70 : 30) as eluent, to give 6.4 mg (54%) of the title compound **2k** as a brown powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.51 (3H, s, CH_3), 3.28 (1H, dd, J 6.6 Hz, 13.9 Hz, H3), 3.45–3.53 (1H, m, H5/6), 3.61–3.69 (1H, m, H5/6), 4.37–4.57 (3H, m, H5 + H6 + H3), 4.62 (1H, dd, J 6.5 Hz, 10.4 Hz, 1H of OCH_2), 4.69 (1H, dd, J 6.8 Hz, 10.3 Hz, 1H of OCH_2) 4.93–5.00 (1H, m, H2), 7.39 (2H, d, J 8.0 Hz, Ar), 7.90 (2H, d, J 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz) δ 21.99, 41.07 (CH_2, C-5/6), 47.37 (CH_2, C-5/6), 50.35 (CH_2, C3), 52.65 (CH, C2), 70.31 (OCH_2), 78.06, 80.18, 128.21 (CH, Ar), 129.95 (CH, Ar), 137.14, 137.35, 137.65, 138.11, 139.75, 139.99 (2C), 140.17, 140.19, 140.20, 141.05, 141.18, 141.20, 141.28, 142.11 (2C), 142.14 (2C), 142.14, 142.20, 142.21, 142.48, 142.49, 142.52, 142.53, 142.93 (4C), 142.93 (2C), 144.87 (2C), 144.94 (2C), 145.43, 145.45, 145.55 (2C), 145.58, 145.69, 145.72, 145.78, 145.92, 145.97 (2C), 146.01 (2C), 146.10, 146.31 (2C), 146.34 (2C), 146.66, 146.67 (3C), 146.70 151.22, 151.35; m/z 989 (expected 989.08).

2′-Methylsulfonylpiperazino[1′,4′:1,2][60]fullerene (2l). Adduct **2l** was prepared from the adduct **2f** (10 mg) by the same procedure as used for the tosylate adduct **2k**, using 5 eq. of methanesulfonyl chloride (5 μL, 60 μmol). The reaction mixture was stirred for 48 h at room temperature and the solvent removed *in vacuo* to give a brown solid, which was purified by column chromatography using toluene–ethyl acetate (80 : 20) as eluent, to give 5 mg (46%) of the title compound **2l** as a brown powder. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz) δ 3.24–3.31 (4H, m), 3.53–3.60 (1H, m), 3.80–3.88 (1H, m), 4.50–4.76 (4H, m), 4.68 (1H, m), 4.95–5.00 (1H, m), 5.14–5.25 (1H, m); m/z 913 (expected 913.06). A ^{13}C NMR spectrum of adduct **2l** could not be obtained due to the relative insolubility of the mesylate adduct in all common deuterated solvents, including admixtures with CS_2.

2′-Iodomethylpiperazino[1′,4′:1,2][60]fullerene (2m). To a solution of mesylate **2l** (20 mg, 21 μmol) in chlorobenzene (3 mL) was added a solution of sodium iodide (15 mg, 0.1 mmol)

in acetone (2 mL). The reaction mixture was heated to refluxed for 48 h and the solvents removed *in vacuo* to give a brown solid, which was purified by column chromatography using dichloromethane–ethyl acetate (90 : 10) as eluent, to give 9 mg (44%) of the title compound **2m** as a brown powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ ^{1}H NMR 3.30 (H, dd, *J* 6.5 Hz, 14.0 Hz), 3.49–3.59 (1H, m), 3.69–3.83 (3H, m,), 4.38–4.56 (2H, m), 4.70–4.79 (1H, m), 5.05 (1H, q, *J* 8.1 Hz); *m*/*z* 945 (expected 944.98). A ^{13}C NMR spectrum of adduct **2m** could not be obtained due to the relative insolubility of the mesylate adduct in all common deuterated solvents, including admixtures with CS_2.

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