One-pot synthesis of new thio-derivatives of C_{60} with the unexpected formation of a thiazolidine-fulleropyrrolidine†

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One-pot Prato reactions of C_{60} with amino acids and aldehydes afford five new fullerene derivatives, including two unexpected thiazolidine and oxazolidine fulleropyrrolidines. In particular, L-cysteine (**1**), paraformaldehyde and C_{60} in refluxing toluene solution affords an unexpected new thiazolidine-fulleropyrrolidine derivative **3** (instead of **2**) *via* 1,3-dipolar cycloaddition, whose structure was characterized in detail. A possible reaction mechanism for the formation of **3** is proposed. These suggest that the active hydrogen of S–H in **1** is essential for the formation of the thiazolidine ring in **3**. To confirm further this conclusion, reactions of C_{60} with different amino acids (**5**, **7**) and aldehydes (3-(methylthio)proplonaldehyde (**9**) and 2-thiophenaldehyde (**11**)) were also studied, resulting in the synthesis of other three new thio-derivatives of C_{60} (**6**, **10**, **12**) as well as an oxazolidine fulleropyrrolidine (**8**).

Introduction

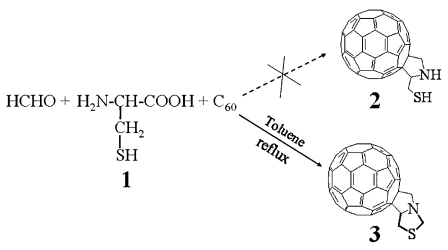
Chemical derivatization of fullerenes is crucial for the applications of fullerenes in materials science and medicinal chemistry *etc.*[1,2] Numerous reactions have been reported for fullerenes because of their unique spherical structure.[1] In particular, cycloaddition reactions of C_{60}, for which the [6,6] double bonds of C_{60} exhibit a dienophilic character, are particularly important and promising because almost any functional group can be covalently linked to C_{60} *via* the cycloaddition of suitable addends.[1–3] Among the fullerene adducts reported so far, sulfur-containing (thio) derivatives are of high importance due to their interesting electronic properties.[4] Using versatile sulfur-containing reagents, a number of thio-derivatives of fullerenes have been synthesized.[4–12] While sulfones[5] and sultines[6] were used as the main sulfur-containing reagents for the synthesis of C_{60}–chlorin dyads[7] and C_{60}–porphyrin hybrids,[5] other sulfur sources (such as sulfonium ylides,[8] *o*-thioquinone methides,[9] α,β-unsaturated thiocarbonyl compounds,[10] thiocarbonyl ylides,[11] and the heterocyclic masked 1,3-dipole 5-imino-1,2,4-thiadiazolidine-3-one[12]) have also been applied for the synthesis of thio-derivatives of fullerenes. Despite the versatility of these syntheses, it is noted that in general most of them are rather complicated. Thus it remains a challenge to design new and simpler synthetic protocols for thio-fullerene derivatives.

In this paper, we report the one-pot synthesis of four new thio-fullerene derivatives *via* the Prato reactions of C_{60} with different sulfur-containing amino acids and aldehydes, including in particular an unexpected thiazolidine-fulleropyrrolidine derivative, for which the possible reaction mechanism has been proposed. To confirm this proposed reaction mechanism, we also carried out a reference synthesis, which resulted in a new oxazolidine fulleropyrrolidine derivative.

Results and discussion

The Prato reaction[3a] established by Prato and Maggini has become one of the most commonly used methods for fullerene derivatization because of its good selectivity and the ease of adding a wide range of functional groups.[2c,3,13] Using this reaction, we have managed to synthesize new thio-fullerene derivatives *via* the Prato reactions of C_{60} with sulfur-containing amino acids. The reaction of L-cysteine (**1**), paraformaldehyde and C_{60} in refluxing toluene for 3 hours afforded a novel C_{60} derivative *via* a 1,3-dipolar cycloaddition reaction (Scheme 1, see also Figs. S1–S4 or ESI-S1 (a section containing four figs.)†).

The new C_{60} derivative was characterized by mass, ^{1}H and ^{13}C NMR spectroscopies to elucidate its molecular structure. In light of the reported 1,3-dipolar cycloaddition of azomethine ylides to C_{60},[2c,3,13] a similar fulleropyrrolidine



Scheme 1 Synthesis of the new thio-derivative of C_{60} **3** *via* 1,3-dipolar cycloaddition.

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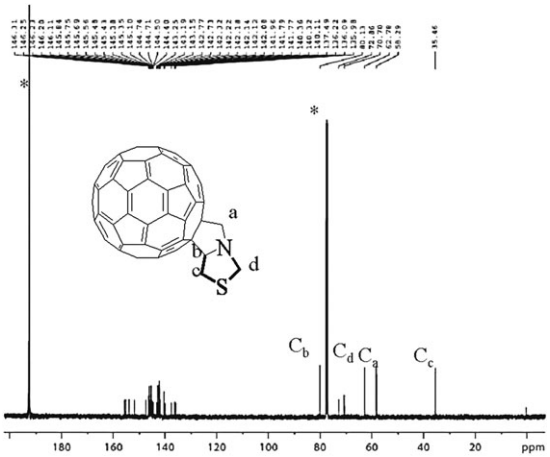


Fig. 1 The ^{13}C NMR spectrum of compound **3** in CS_2–$CDCl_3$. The asterisks represent solvent lines.

product **2** was predicted, which would exhibit m/z 809 and two active hydrogen atoms (N–H, S–H). However, the laser desorption time-of-flight (LD-TOF) MS analysis of the synthesized C_{60} derivative showed a peak at m/z = 821 as the base peak (see Fig. S1), suggesting that it was not the predicted compound **2**. Further evidence came from the detailed analysis of its ^1H and ^{13}C NMR spectra (see Fig. 1 and Fig. S2), which were not consistent with the predicted structure **2**. For instance, considering the ^{13}C NMR spectrum of structure **2**, five sp^3-C peaks (including two derived from the C_{60} cage) are expected, but six lines were observed. Together with the MS result, the formation of compound **2** is ruled out.

Given that there are two active hydrogen atoms (N–H, S–H) in the compound **2**, compound **2** may undergo subsequent reaction under the conditions employed. In the presence of paraformaldehyde, a ring-closing reaction of **2** by removal of a molecule of water is possible, leading to compound **3**. The m/z calculated for **3** is 821, coinciding with the value measured.

In the ^{13}C NMR spectrum of the new C_{60} derivative taken in CS_2–$CDCl_3$ (Fig. 1), the six sp^3-C lines (including two derived from the C_{60} cage) could be clearly seen in the 30–90 ppm regions. In addition, more than 48 partially overlapped lines were present in the 135–156 ppm range, which can be assigned to the 58 sp^2 carbon atoms of the C_{60} cage. Accordingly, the observed number of sp^3-C lines of the new C_{60} derivative is consistent with that expected for the compound **3**. In the ^1H NMR spectrum (see Fig. S2), the protons of the pyrrolidine ring were present, as expected, in the 4.67–5.05 ppm region. The coupling between them is evident in the COSY spectrum (see Fig. 2A). The signals for the pyrrolidine geminal protons (H_a) appear as doublets at 4.67 and 4.85 ppm (J = 9.0 Hz) and are separated by 0.18 ppm. Another pyrrolidine proton (H_b) gives the signal at 5.05 ppm. Furthermore, the characteristic proton signals resulting from the formation of thiazolidine in compound **3** are also clearly identified. For instance, the methylene protons of –CH–CH_2–S– (H_c) were observed at 3.60 and 3.99 ppm (doublet) and those of –N–CH_2–S– (H_d) lie at 4.56 and 4.59 ppm (see Fig. S2). Based on the above analysis, the new C_{60} derivative synthesized was unambiguously determined to be **3**.

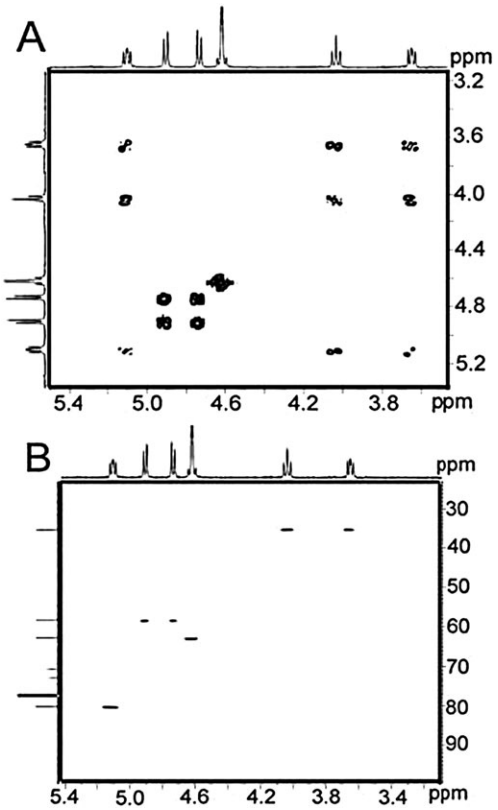
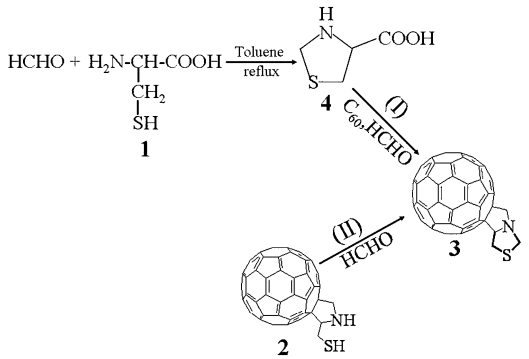


Fig. 2 COSY (A) and HSQC (B) spectra of compound **3**.

Fig. 2B shows the HSQC spectrum of compound **3**, which allowed us to assign the observed ^{13}C NMR lines. Based on the correlations of H_a (4.67 and 4.85 ppm) and H_b (5.05 ppm) with the carbon lines at 58.3 and 80.1 ppm, respectively, these two carbon lines are assigned to the two carbon atoms (C_a and C_b) within the pyrrolidine ring (see Fig. 1). Likewise, the two carbon lines at 62.8 and 35.5 ppm are assigned to –N–CH_2–S– (C_d) and –CH–CH_2–S– (C_c) within the thiazolidine ring, respectively. Finally, the other two carbon lines at 70.7 and 72.9 ppm are due to the two sp^3 carbons resulting from addition to the C_{60} cage (see Fig. 1).

Product **3** was then characterized by UV-Vis and FTIR spectroscopies. The UV-Vis spectrum of product **3** shows characteristic absorption peaks at 312, 432 and 704 nm (see Fig. S3a), exhibiting the common feature of a cycloaddition adduct of C_{60} at the [6,6] junction.[2c,3,13] In the FTIR spectrum of product **3** (see Fig. S4a), the vibrational lines at 1050 and 1321 cm^{-1} are assigned to C–N stretching and C–S deformation vibrational modes, respectively. The intense vibrational band at 1220–1370 cm^{-1} is due to the C–H stretching vibrations of –N–CH_2–S– and another intense vibrational band in 2841–2923 cm^{-1} are attributed to the stretching modes of the two C–H bonds within the pyrrolidine ring attached to C_{60} cage. Clearly, the four characteristic lines of the pristine C_{60} skeleton (1428, 1183, 576, 527 cm^{-1})[1a] are also observed in product **3** (see Fig. S4a). These spectroscopic data support strongly the elucidated structure of product **3**.

Two reaction pathways are proposed for the formation of compound **3**. The most likely reaction mechanism, which comprises two steps is shown in Scheme 2(I). In the first step,

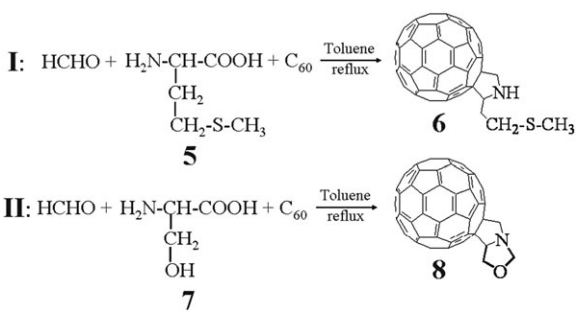


Scheme 2 Two possible reaction pathways for the formation of compound **3**.

because of the presence of the two active hydrogens (N–H, S–H) within **1**, a ring-closing reaction by removal of a molecule of water is expected upon reaction of **1** with paraformaldehyde, leading to the formation of thiazolidine-4-carboxylic acid **4**. This proposed reaction has already been reported in the literature.[14] In the subsequent Prato reaction step, **4** and paraformaldehyde react (through their *in situ*-generated 1,3-dipoles) with C_{60}, affording the thiazolidine-fulleropyrrolidine **3** *via* a second ring-closing reaction for which a similar reaction of 1-aryl-2-propen-1-ones has already been reported by Makata *et al.*[15] To confirm this reaction pathway, we reacted C_{60} and paraformaldehyde and **4** directly, and the product was found to be **3** (data not shown). The second possible pathway proceeds by a reaction of **2** with paraformaldehyde. However, in this case C_{60} itself would not participate in the follow-up step (Scheme 2(II)). Further detailed study on the reaction mechanism is underway in our laboratory.

To confirm the thiazolidine-fulleropyrrolidine structure of **3** and the reaction mechanism discussed above, we next studied the following two reference reactions, focussing on the ring-closing reaction between the active hydrogens, by a judicious choice of two specific amino acids. The first was L-methionine (**5**), chosen because there is only one type of active hydrogen (N–H), and the another active hydrogen of S–H in **1** is replaced by a methyl. The second was L-serine (**7**), which has a similar active hydrogen (O–H) like that of S–H in **1**, in addition to N–H.

The reaction of **5** with paraformaldehyde and C_{60} afforded **6** (Scheme 3I), as established by ^{1}H and ^{13}C NMR, FTIR, and UV-Vis spectroscopies. In the ^{1}H NMR spectrum of **6**, in



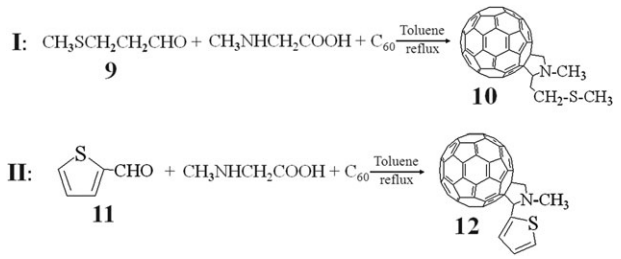
Scheme 3 Synthesis of new thio-derivatives of C_{60} **6** (I) and **8** (II).

addition to the signals for the pyrrolidine proton and methine groups, a singlet –S–CH_3 group at 2.2 ppm can be clearly seen (see Fig. S5). In its ^{13}C NMR spectrum, in addition to the two sp^3-C lines derived from the C_{60} cage, there are five lines for the other sp^3 carbons at 15–75 ppm (see Fig. S6). The UV-Vis spectrum of product **6** looks quite similar to that of **3**, exhibiting characteristic absorption peaks at 312, 432 and 704 nm (see Fig. S3b) originating from the [6,6] junction of the C_{60} adduct. However, we found that the C–H stretching vibrations of –N–CH_2–S– (present in **3** at 1220–1370 cm^{-1}) were absent in **6** (see Fig. S4b), indicating clearly that no thiazolidine ring was formed, because of absence of an S–H hydrogen. As a result, a conventional fulleropyrrolidine **6** is obtained.

The analogous reaction of L-serine (**7**) with C_{60} and paraformaldehyde led to an oxazolidine-fulleropyrrolidine product **8** (Scheme 3II). The MALDI-TOF mass spectrum of **8** showed a peak at m/z = 806 (see Fig. S7), while its FTIR spectrum exhibited the characteristic vibrational line at 1510 cm^{-1} due to the C–H deformation vibrations of the –CH_2–O–CH_2– group. Three intense vibrational lines at 1183, 576 and 526 cm^{-1} are apparently the characteristic lines of the pristine C_{60} skeleton[1a] (see Fig. S4c). The UV-Vis spectrum displays characteristic absorptions at 312, 432 and 704 nm (see Fig. S3c), which are typical for a [6,6] adduct of C_{60} and same as those in **3** and **6**.[2c,3,13] In the ^{1}H NMR spectra of **8** (see Fig. S8), the protons of the pyrrolidine (H_a, H_b) and oxazolidine (H_c, H_d) rings could be clearly seen in the 4.95–5.3 and 4.4–4.95 ppm regions, respectively. In addition (and similarly to **3**), six sp^3-C lines (including the two sp^3 carbons of the C_{60} cage) were observed in the 30–90 ppm region of the ^{13}C NMR spectrum, and other lines attributed to the sp^2 carbon atoms of the C_{60} cage could be seen in 135–156 ppm range (see Fig. S9). The HSQC spectrum of **8** further confirmed the structure of the compound **8** (see Fig. S10). These results indicate that, by replacing the active hydrogen of S–H in **1** with that of O–H in **7**, the O–H hydrogen plays the same role as that of S–H, and as a result the oxazolidine ring was formed in a similar way to **3**, leading to the formation of oxazolidine-fulleropyrrolidine **8**. A similar reaction has been recently reported by Martin *et al.*[16]

Finally, in order to investigate further the effect of the aldehyde on the formation of the fulleropyrrolidine, we carried out two similar reactions by replacing paraformaldehyde with 3-(methylthio)proplonaldehyde (**9**) or 2-thiophenaldehyde (**11**), leading to two new thio-derivatives of C_{60}, **10** and **12** (Scheme 4).[17] Interestingly, in contrast to the case with **3** and **6**, for which the thio groups were introduced in the amino acids, the synthesis of thio-derivatives of **10** and **12** was achieved by using the sulfur-containing aldehydes. These results demonstrate once more the versatility of the Prato reaction for the synthesis of fulleropyrrolidines.[3a]

The structure of **10** was conclusively established by ^{1}H NMR, ^{13}C NMR, FTIR, and UV-vis spectroscopies. In the ^{1}H NMR spectrum of **10** (see Fig. S11), in addition to the signals for the pyrrolidine proton and methane groups at 4.0–4.8 ppm, two peaks at 2.96 and 2.10 ppm for the –N–CH_3 and –S–CH_3 groups were obvious. In the ^{13}C NMR spectrum of **10** (see Fig. S12), eight sp^3-C lines



Scheme 4 Synthesis of new thio-derivatives of C_{60} **10** (I) and **12** (II).

(including the two sp^3 carbons of the C_{60} cage) were observed at 15–80 ppm, and other lines attributed to the sp^2 carbon atoms of the C_{60} cage were clearly observed at 135–157 ppm. By comparison with the NMR spectra of the analogous structure **6**, the additional ^1H and ^{13}C NMR lines assigned to –N–CH_3 (H_e and C_e) could be identified, while the other lines exhibit slight shifts, indicating their structural similarity (see Fig. S5 and S11). Furthermore, the UV-vis spectrum of **10** displays characteristic absorptions at 432 and 704 nm, which are almost identical to that of **6** (see Fig. S3b,d). The FTIR spectrum of **10** exhibited almost the same pattern as that of **6**, except for the absorption at 2776 cm^{-1} resulting from the CH_3 stretching vibrations of the –N–CH_3 (see Fig. S4b,d). Apparently (and similar to the case of **6**), because of the absence of both S–H and N–H, no thiazolidine ring is formed.

The new thio-derivative **12** was synthesized by reaction of 2-thiophenaldehyde (**11**), sarcosine, and C_{60} in refluxing toluene solution (Scheme 4II). To our knowledge, this is one of the few reports on integrating the thiophene ring into a fulleropyrrolidine.[18] In the ^1H NMR spectra of **12** (see Fig. S13), the lines for the pyrrolidine proton and methane groups were seen at 4.0–5.3 ppm, and those for the thiophene ring were observed at 7.34 and 7.00 ppm. In the ^{13}C NMR spectra of **12** (see Fig. S14), in addition to the sp^3-C lines for the two sp^3 carbons of the C_{60} cage and for the addends, two lines at 128.34 and 127.15 ppm for the thiophene group of **12**, and about 43 partially overlapped peaks at 135–157 ppm due to the sp^2 carbons of the C_{60} skeleton, were clearly observed, confirming its proposed structure. In the FTIR spectrum of **12** (see Fig. S4e), in addition to the vibrational line at 2780 cm^{-1} for the CH_3 stretching vibrations of the –N–CH_3 (as for **10**), the new vibrational line at 1630 cm^{-1} was assigned to the –C=C– stretching vibrations within the thiophene ring.

Conclusions

In summary, we have successfully synthesized five new fullerene derivatives *via* the one-pot Prato reactions of C_{60} with amino acids and aldehydes. The reaction of **1** with C_{60} and paraformaldehyde results in the formation of an unexpected new thiazolidine-fulleropyrrolidine **3**, whose structure was characterized in detail by mass, ^1H and ^{13}C NMR, FTIR and UV-vis spectroscopies. A possible reaction mechanism for the formation of **3** was proposed, and confirmed by replacing **1** with **5** or **7**. Reaction of **5** with C_{60} and paraformaldehyde afforded a conventional fulleropyrrolidine **6** without the thiazolidine ring, whereas the analgous reaction of **7** led to the formation of the oxazolidine fulleropyrrolidine **8**. These results demonstrate that the active hydrogen of S–H in **1** is essential for the formation of the thiazolidine ring in **3**.

To investigate further the effect of the aldehyde on the formation of the fulleropyrrolidine, similar reactions of C_{60} with different aldehydes (**9**, **11**) were also studied, resulting in the synthesis of other two new thio-derivatives of C_{60}, **10** and **12**. While **10** has an analogous structure to **6**, **12** is one of the few compounds reported that integrates a thiophene ring into a fulleropyrrolidine. In addition to the synthesis of five new fullerene derivatives, the finding of the unexpected formation of the thiazolidine and oxazolidine rings provides a new insight to fullerene chemistry. Further functionalization studies of the new fullerene derivatives for constructing hybrid nanostructures is underway.

Experimental

The synthesis of C_{60} fulleropyrrolidine derivative 3

A C_{60} solution (100 mg, in 40 mL of toluene) was prepared in a 100 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer bar under nitrogen atmosphere. To this solution, 20 mg of paraformaldehyde and 45 mg of L-cysteine (**1**) were added and the mixture was refluxed for 3 h. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (100–200 mesh) using a mixture of toluene and hexane (v/v 1:3) as eluent, and 15 mg (13%) of compound **3** was obtained. ^1H NMR (500 MHz, $CDCl_3$ + CS_2): δ 5.05 (dd, J = 10.5, 7.0 Hz, 1H), 4.85 (d, J = 9.0 Hz, 1H), 4.67 (d, J = 9.0 Hz, 1H), 4.56 (d, J = 10 Hz, 1H), 4.59 (d, J = 10 Hz, 1H), 3.99 (t, J = 10.5 Hz, 1H), 3.60 (dd, J = 10.5, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$ + CS_2): δ 155.65, 155.20, 153.91, 151.83, 147.41, 147.38, 146.42, 146.38, 146.37, 146.31, 146.25, 146.23, 146.20, 146.11, 145.84, 145.75, 145.69, 145.56, 145.48, 145.43, 145.38, 145.35, 145.10, 144.74, 144.71, 144.50, 144.40, 143.25, 143.19, 142.77, 142.73, 142.32, 142.22, 142.18, 142.14, 142.12, 142.08, 141.96, 141.79, 141.77, 140.36, 140.32, 140.11, 137.49, 136.22, 136.09, 135.98, 80.13, 72.86, 70.70, 62.78, 58.29, 35.46. FTIR (KBr) ν (cm^{-1}) 2923, 2841, 1428, 1370–1220, 1321, 1183, 1050, 576, 527, UV-Vis (toluene) λ_{max} (nm) 312, 432, 704. MS (MALDI-TOF) m/z 821.

The synthesis of C_{60} fulleropyrrolidine derivative 6

A mixture of C_{60} (72.0 mg), paraformaldehyde (9 mg) and L-methionine (**5**) (12 mg) in toluene (30 mL) was refluxed for 1 h under nitrogen atmosphere. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (100–200 mesh), first using CS_2 as eluent to remove the unreacted fullerene, and then using $CHCl_3$ as eluent to obtain 40 mg (47%) of compound **6**. ^1H NMR (500 MHz, $CDCl_3$ + CS_2): δ 4.88 (d, J = 11.9 Hz, 1H), 4.77 (dd, J = 10.9, 2.9 Hz, 1H), 4.66 (d, J = 11.9 Hz, 1 H), 3.10 (ddd, J = 13.0, 8.0, 5.1 Hz, 1H), 3.06–2.97 (m, 1H), 2.92–2.82 (m, 1H), 2.36 (ddd, J = 17.3, 12.2, 5.5 Hz, 1H), 2.20 (d, J = 1.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$ + CS_2): δ 155.85, 154.31,

154.10, 152.55, 147.11, 146.33, 146.27, 146.11, 146.05, 145.69, 145.49, 145.43, 145.40, 145.31, 145.26, 144.65, 144.49, 144.40, 143.31, 143.17, 142.79, 142.74, 142.45, 142.30, 142.26, 142.12, 142.02, 141.93, 141.88, 140.46, 140.35, 140.05, 136.69, 135.96, 135.83, 135.57, 129.14, 128.41, 78.30, 75.66, 73.47, 63.15, 33.58, 33.35, 16.29. FTIR (KBr) ν (cm^{-1}) 2915, 2850, 1428, 1315, 1183, 576, 526, UV-Vis (toluene) λ_{max} (nm) 312, 432, 704.

The synthesis of C_{60} fulleropyrrolidine derivative 8

A mixture of C_{60} (72.0 mg), paraformaldehyde (17 mg) and L-serine (**7**) (18 mg) in toluene (30 mL) was refluxed for 1 h under nitrogen atmosphere. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The residue was chromatographed over silica gel (100–200 mesh), first using CS_2 as eluent to remove unreacted fullerene, and then using $CHCl_3$ as eluent to obtain 30 mg (37%) of compound **8**. ^{1}H NMR (500 MHz, $CDCl_3$ + CS_2): δ 5.20 (t, J = 8.1 Hz, 1H,), 5.13 (d, J = 6.1 Hz, 1H), 4.92 (d, J = 6.1 Hz, 1H), 4.81 (d, J = 9.9 Hz, 1H), 4.73 (d, J = 10.0 Hz, 1H), 4.66 (t, J = 8.4 Hz, 1H), 4.41 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$ + CS_2): δ 154.50, 151.56, 147.43, 147.38, 146.46, 146.40, 146.38, 146.32, 146.29, 146.23, 146.20, 146.14, 146.05, 145.85, 145.77, 145.69, 145.56, 145.52, 145.45, 145.40, 145.38, 145.31, 145.20, 144.74, 144.6, 144.60, 144.37, 143.31, 143.24, 142.78, 142.42, 142.23, 142.17, 142.08, 142.06, 141.91, 141.80, 140.41, 140.35, 140.13, 137.38, 135.99, 135.54, 86.19, 75.71, 71.78, 71.64, 66.79, 64.04. FTIR (KBr) ν (cm^{-1}), 2924, 2847, 1510, 1183, 576, 526, UV-Vis (toluene) λ_{max} (nm) 312, 432, 704. MS (MALDI-TOF) m/z 806.

The synthesis of C_{60} fulleropyrrolidine derivative 10

A mixture of C_{60} (120.0 mg), 3-(methylthio)proplonaldehyde (**9**) (16 mg) and sarcosine (18 mg) in toluene (40 mL) was refluxed for 0.5 h under nitrogen atmosphere. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The residue was chromatographed over silica gel (200–300 mesh), first using CS_2 as eluent to remove unreacted C_{60}, then using $CHCl_3$ as eluent to obtain 57 mg (40%) of compound **10**. ^{1}H NMR (400 MHz, $CDCl_3$ + CS_2): δ 4.76 (1 H, dd, J 9.6, 2.4), 4.15 (1 H, dd, J 9.6, 2.9), 4.07–4.02 (1 H, m), 3.03–2.97 (2 H, m), 2.96 (3 H, d, J 2.9), 2.80–2.58 (2 H, m), 2.10 (3 H, d, J 2.7). ^{13}C NMR (125 MHz, $CDCl_3$ + CS_2): δ 156.35,154.38, 154.16, 153.02, 147.31, 147.27, 146.41, 146.31, 146.18, 146.14, 146.08, 145.82, 145.51, 145.39, 145.32, 144.84, 144.66, 144.51, 144.44, 143.30, 143.19, 142.76, 142.27, 142.17, 142.08, 141.99, 141.86, 140.45, 140.35, 140.09, 139.84, 137.44, 136.34, 136.03, 135.62, 77.73, 77.41, 76.89, 70.35, 40.03, 32.05, 30.93, 16.13. FTIR (KBr) ν (cm^{-1}), 2948, 2919, 2847, 2780, 1509, 1343, 1183, 576, 526, UV-Vis (toluene) λ_{max} (nm) 432, 704.

The synthesis of C_{60} fulleropyrrolidine derivative 12

A mixture of C_{60} (120.0 mg), 2-thiophenaldehyde (**11**) (38 mg) and sarcosine (18 mg) in toluene (40 mL) was refluxed for 1 h under nitrogen atmosphere. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The residue was chromatographed over silica gel (100–200 mesh) using CS_2 as eluent first to remove unreacted C_{60}, then obtain 60 mg (42%) of compound **12**. ^{1}H NMR (400 MHz, $CDCl_3$ + CS_2): δ 7.34 (2 H, t, J 4.6), 7.00 (1 H, dd, J 5.0, 3.6), 5.25 (1 H, d, J 7.3), 4.96–4.91 (1 H, m), 4.23 (1 H, d, J 9.5), 2.88 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$ + CS_2): δ 156.30, 154.24, 153.58, 153.52, 147.77, 147.32, 146.82, 146.75, 146.69, 146.66, 146.60, 146.57, 146.42, 146.24, 146.09, 145.88, 145.81, 145.73, 145.64, 145.19, 145.15, 144.85, 143.65, 143.49, 143.19, 143.09, 142.75, 142.65, 142.62, 142.54, 142.46, 142.39, 142.16, 142.10, 141.21, 140.72, 140.68, 140.43, 140.13, 137.51, 137.19, 136.36, 136.14, 128.34, 127.15, 79.62, 78.12, 77.81, 70.53, 40.81. FT-IR (KBr) ν (cm^{-1}), 2948, 2919, 2847, 2780, 1630, 1183, 576, 526, UV-Vis (toluene) λ_{max} (nm) 432, 704.

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References

1 (*a*) A. Hirsch and M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, 2005; (*b*) C. Thilgen and F. Diederich, *Chem. Rev.*, 2006, **106**, 5049; (*c*) F. Giacalone and N. Martın, *Chem. Rev.*, 2006, **106**, 5136.
2 (*a*) M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097; (*b*) M. Prato, *Top. Curr. Chem.*, 1999, **199**, 173; (*c*) M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.
3 (*a*) M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798; (*b*) T. Da Ros and M. Prato, *Chem. Commun.*, 1999, 663.
4 (*a*) L. Sánchez, M. Á. Herranz and N. Martín, *J. Mater. Chem.*, 2005, **15**, 1409; (*b*) G. W. Wang, J. X. Li, Y. J. Li and Y. C. Liu, *J. Org. Chem.*, 2006, **71**, 680; (*c*) G. W. Wang, J. X. Li and Y. Xu, *Org. Biomol. Chem.*, 2008, **6**, 2995.
5 (*a*) J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell and C. Rovira, *Chem. Commun.*, 1997, 659; (*b*) M. Ohno, N. Koide, H. Sato and S. Eguchi, *Tetrahedron*, 1997, **53**, 9075; (*c*) N. Watanabe, N. Kihara, Y. Furusho, T. Takata, Y. Araki and O. Ito, *Angew. Chem., Int. Ed.*, 2003, **42**, 681; (*d*) A. Rieder and B. Kräutler, *J. Am. Chem. Soc.*, 2000, **122**, 9050.
6 (*a*) B. M. Illescas, N. Martín, C. Seoane, E. Orti, P. M. Viruela, R. Viruela and A. de la Hoz, *J. Org. Chem.*, 1997, **62**, 7585; (*b*) J. H. Liu, A. T. Wu, M. H. Huang, C. W. Wu and W. S. Chung, *J. Org. Chem.*, 2000, **65**, 3395.
7 F. P. Montforts and O. Kutzki, *Angew. Chem., Int. Ed.*, 2000, **39**, 599.
8 (*a*) Y. Wang, J. Cao, D. I. Schuster and S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843; (*b*) T. Hino, K. Kinbara and K. Saigo, *Tetrahedron Lett.*, 2001, **42**, 5065.
9 M. Ohno, S. Kojima, Y. Shirakawa and S. Eguchi, *Tetrahedron Lett.*, 1995, **36**, 6899.
10 M. Ohno, S. Kojima and S. Eguchi, *J. Chem. Soc., Chem. Commun.*, 1995, 565.
11 (*a*) H. Ishida and M. Ohno, *Tetrahedron Lett.*, 1999, **40**, 1543; (*b*) H. Ishida, K. Itoh and M. Ohno, *Tetrahedron*, 2001, **57**, 1737.
12 W. Duczek, F. Tittelbach, B. Costisella and H. J. Niclas, *Tetrahedron*, 1996, **52**, 8733.
13 (*a*) A. de la Escosura, M. V. Martinez-Diaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112; (*b*) A. Gouloumis, A. de la Escosura, P. Vazquez, T. Torres, A. Kahnt, D. M. Guldi, H. Neugebauer, C. Winder, M. Drees and N. S. Sariciftci, *Org. Lett.*, 2006, **8**, 5187; (*c*) T. Nakanishi, N. Miyashita, T. Michinobu, Y. Wakayama, T. Tsuruoka, K. Ariga and D. G. Kurth, *J. Am. Chem. Soc.*, 2006, **128**, 6328.
14 (*a*) R. Sarah and H. T. Clarke, *J. Am. Chem. Soc.*, 1937, **59**, 200; (*b*) P. Albert, E. F. Glen, R. G. John, M. K. Venkatramanan and S. K. W. George, *J. Org. Chem.*, 1989, **54**, 644.

15 S. Mataka, H. Kitagawa, T. Tsukinoki, M. Tashiro, K. Takahashi and K. Kamata, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1969.
16 (*a*) M. Izquierdo, S. Osuna, S. Filippone, A. Martin-Domenech, M. Sola and N. Martin, *J. Org. Chem.*, 2009, **74**, 6253; (*b*) M. Izquierdo, S. Osuna, S. Filippone, A. Martin-Domenech, M. Sola and N. Martin, *J. Org. Chem.*, 2009, **74**, 1480.
17 Sarcosine was used in these two reactions as one of the common amino acids because there is only one active hydrogen (N–H) which was essential for the ring-closing reaction whereas another active hydrogen (N–H) was replaced by N–CH_3.
18 B. W. Boudouris, F. Molins, D. A. Blank, C. D. Frisbie and M. A. Hillmyer, *Macromolecules*, 2009, **42**, 4118.

