Pergamon

Tetrahedron, Vol. 52, No. 14, pp. 5221-5234, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00126-3

Synthesis and Electrochemical Properties of Substituted Fulleropyrrolidines

Maurizio Prato,[a]* Michele Maggini,[b]* Cristina Giacometti,[b] Gianfranco Scorrano,[b] Giancarlo Sandonà,[c] and Giuseppe Farnia[c]

[a] Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy
[b] Centro Meccanismi di Reazioni Organiche del CNR, Dipartimento di Chimica Organica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy
[c] Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, 35131 Padova, Italy

Abstract: A systematic investigation of the synthesis and electrochemical behavior of a series of fullerene derivatives containing an additional electroactive group, such as ferrocene and tetrathiafulvalene, is reported. The influence of the structure on the cyclic voltammetry is discussed.

Introduction

Considerable interest has followed the detection and isolation of bulk quantities of [60]fullerene.[1,2] Among the several reasons for such a scientific excitement are the very interesting solid state properties of C_{60}, which range from superconductivity in M_3C_{60} salts[3,4] to magnetism in TDAE-C_{60}.[5] In solution, C_{60} can accept, reversibly, up to six electrons,[6,7] whereas its chemical reactivity is typical of an electron-deficient olefin.[8] All these properties are indicative of a strong electron-acceptor character, as it was already anticipated by theoretical calculations.[9]

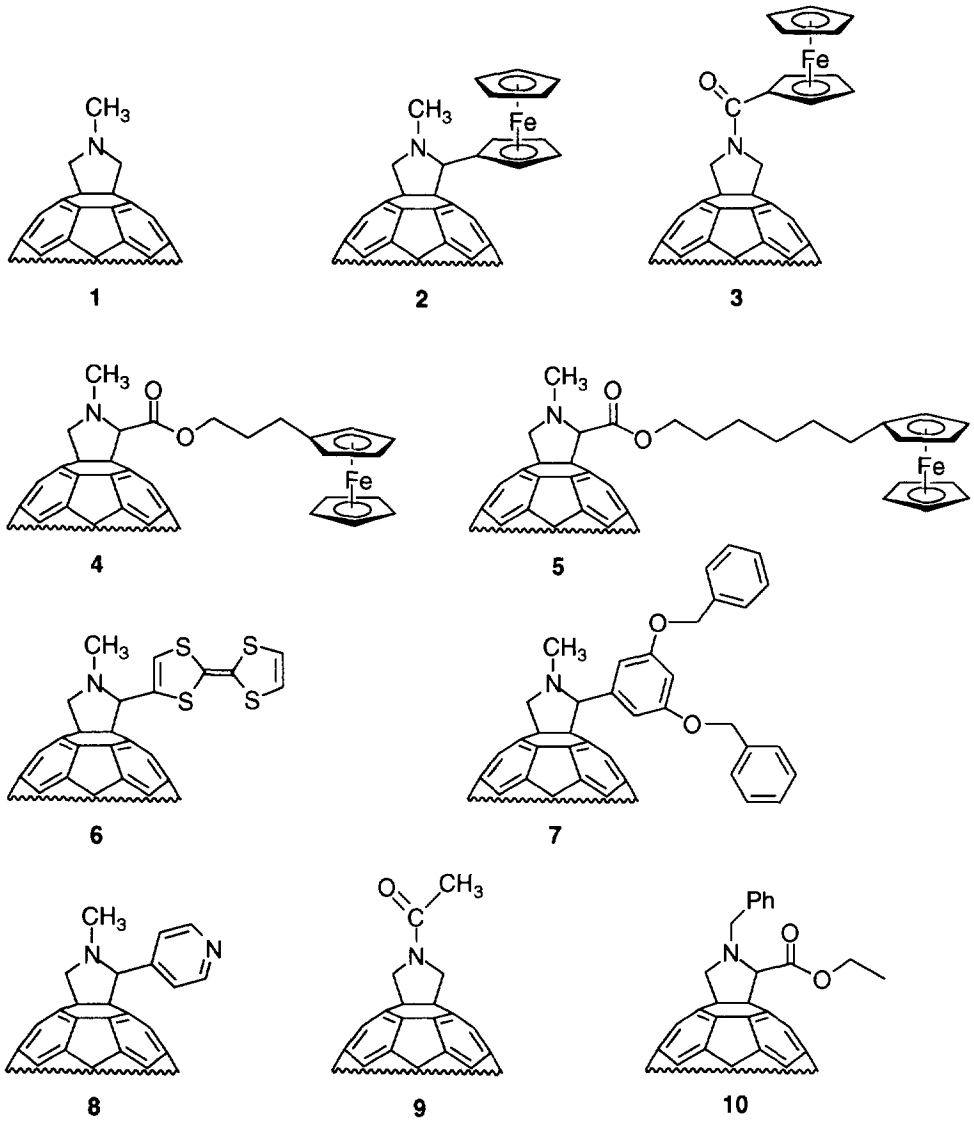
Once the reactivity pattern of C_{60} has been established,[10-12] there have remained two main tasks for the organic functionalization of this new form of carbon: the modification of some of the fullerene properties for easier handling (e.g., higher solubility) and the combination of the fullerene properties with those of other classes of materials, such as photo- and/or electroactive compounds. This latter aspect relates to a particularly appealing and widely investigated field, i.e., the design and construction of molecular assemblies where electronic interactions take place between covalently linked components.[13-15] In this context, the determination of the redox properties is a task of fundamental importance for establishing the interest for the new materials.

In this paper we describe the synthesis and electrochemical behavior of a series of compounds containing C_{60} and an additional electroactive group (ferrocene, Fc, and tetrathiafulvalene, TTF) covalently attached.

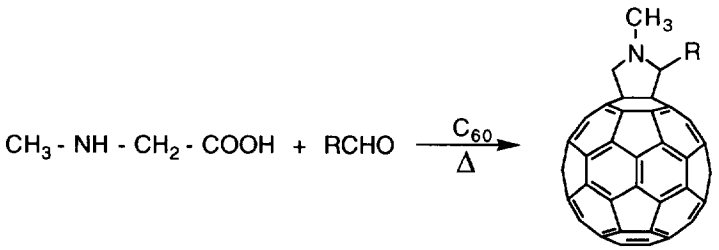
Results and Discussion

Several approaches to the functionalization of fullerenes have followed the pioneering work of Wudl with diazomethanes.[11,12] Among these methodologies,[8] one of the most versatile and more thoroughly investigated is

the cycloaddition of azomethine ylides to C_{60}.[16] This reaction leads to fulleropyrrolidines, derivatives in which a pyrrolidine ring is fused with a 6,6 ring junction of C_{60}.[17] Due to the large variety of substituted azomethine ylides that can be generated from readily accessible starting materials, highly functionalized pyrrolidine rings in fulleropyrrolidines can be relatively easily obtained.[16,18-21]

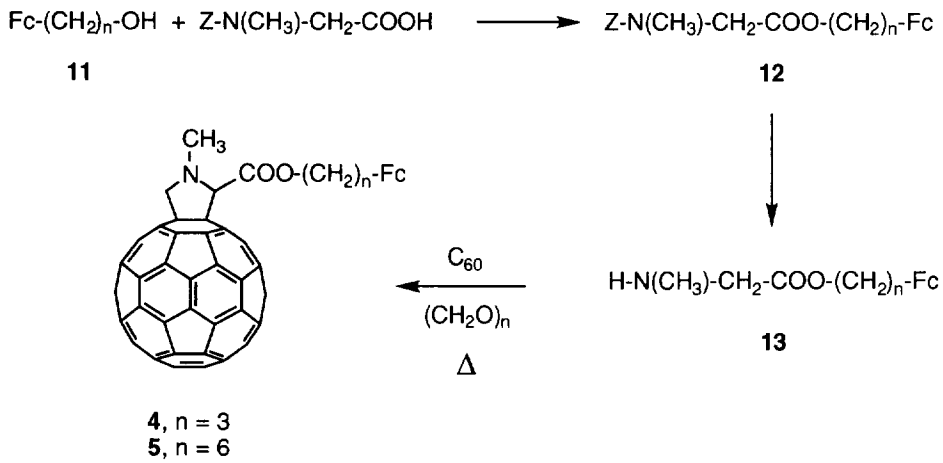


Compounds **1-10** were prepared by reaction of the appropriate azomethine ylide precursors with C_{60}. The reactive 1,3-dipoles were generated as shown below. Compounds **1**, **2**, **6**, **7**, and **8** were synthesized according to eq. 1, via the "decarboxylation approach",[22] using N-methyl glycine (sarcosine) and a substituted aldehyde.



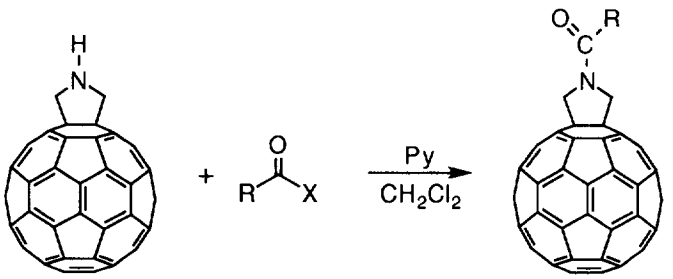
(1)

Fulleropyrrolidines **4** and **5** were prepared via the "tautomerization route",[22] by condensing the suitably functionalized ester of sarcosine and paraformaldehyde (eq. 2).



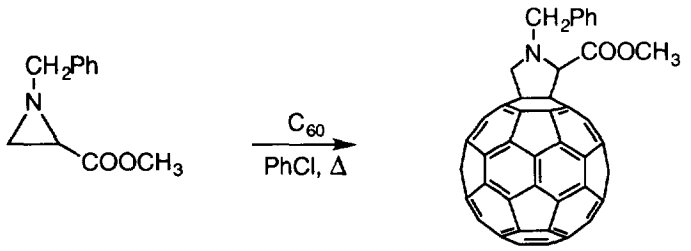
(2)

N-Acylated derivatives **3** and **9** were obtained by allowing N-H fulleropyrrolidine[16,20] to react with ferrocene carboxylic acid chloride and acetic anhydride, respectively (eq. 3).



(3)

Finally, compound **10** was prepared by thermal ring-opening of the corresponding aziridine (eq. 4).



(4)

All the desired products **1-10** were purified by flash chromatography on silica gel column, using mixtures of toluene and petroleum ether or ethyl acetate (see Experimental). Derivative **6** was particularly labile on silica columns and was obtained in pure form by gel-permeation chromatography (GPC, see Experimental).

Derivatives **1-10** possess different structural features that are important for a complete electrochemical investigation of the fulleropyrrolidines. Compound **1** is the simplest fulleropyrrolidine and is taken as a model. Derivatives **2-5** contain a ferrocenyl moiety attached in different positions, whereas **6** has a TTF fragment. Host-guest complexes of C_{60} with ferrocene[23] and BEDT-TTF[24,25] have been prepared and crystallized. Their interactions in the solid state have also been shown by X-ray crystallographic analysis. The influence of the electropositive ferrocene in **2-5** or the strong TTF donor in **6** on the cyclic voltammetry might give useful indications on the possible interactions with the electronegative fullerene moiety in solution. Whereas **2** has a relatively rigid array, **4** and **5** have flexible arms which can potentially let the ferrocene end approach the ideal position for spatial interactions with the C_{60} moiety. Also **7** has electron-rich phenyl groups that, in principle, might chelate the fullerene spheroid,[26] thus influencing its reduction potentials.

Pyrrolidine **8** has an electron-poor pyridine ring and the resulting electron-attracting effect is expected. Compounds **9** and **10** bear a carbonyl function in different positions that can help the interpretation of data for **3** and **4** and **5** respectively.

The voltammetric behavior of C_{60} and substrates **1-10** (0.1 - 0.3 mM) was investigated at -45 °C in 3:1 toluene/acetonitrile solutions, containing tetra-*n*-butyl ammonium perchlorate (TBAP, 0.1 M) as supporting electrolyte, with glassy carbon (GC, approximate area 5 mm^2) as the working electrode, a Pt counter electrode and a silver wire as a quasi-reference electrode. Each solution was dried over dry neutral alumina and purged with nitrogen. $E_{1/2}$ values for compounds **1-10**, reported in Table 1, are referred to the potential of the Fc^+/Fc redox couple utilized as an internal standard. CVs of C_{60} and of compounds **4**, **6** and **10** are reported in Figure 1 as representative examples.

As can be seen from Figure 1 and from Table 1, the observed reduction potentials of **1-10** are shifted to more negative values when compared to those of pristine C_{60}. This is expected on the basis of saturation of a double bond in C_{60}. Due to this effect, only five reduction peaks for the C_{60} moiety in **1-10** are detected in the accessible potential range. Whenever present, the additional redox center causes one (Fc) or two (TTF) oxidation processes.

The model compound **1** shows the first two reduction peaks at potentials about 110 mV more negative than C_{60}. The remaining three peaks are even more shifted ($\Delta E_{1/2}$ = 180, 140 and 380 mV for the third, forth and fifth peak, respectively). The ferrocenyl moiety seems to act as a weak donor only in **2**. In the other ferrocenyl derivatives **3-5**, the presence of the electron-attracting carbonyl group appears to prevail, as can be inferred from comparison with model compounds **9** and **10**. The amide group may be responsible for the sixth peak observed

at $E_{1/2}$ = - 3.22 V in the CV of **3** and of **9** as the same peak at the same potential was observed in the CV of N-ferrocenylcarboxamido-pyrrolidine. The strong donor TTF does not seem to have any interaction with the C_{60} spheroid. The reduction potentials of compound **6** are very similar to those of **1**. The peak at -2.99 V is very likely due to the TTF fragment. This chemically irreversible peak was observed at the same potential in the CV of unsubstituted TTF. Also compound **7** has peak potentials very close to those of **1**. A very weak acceptor effect is observed in the case of the pyridine derivative **8**, comparable to the carbonyl group.

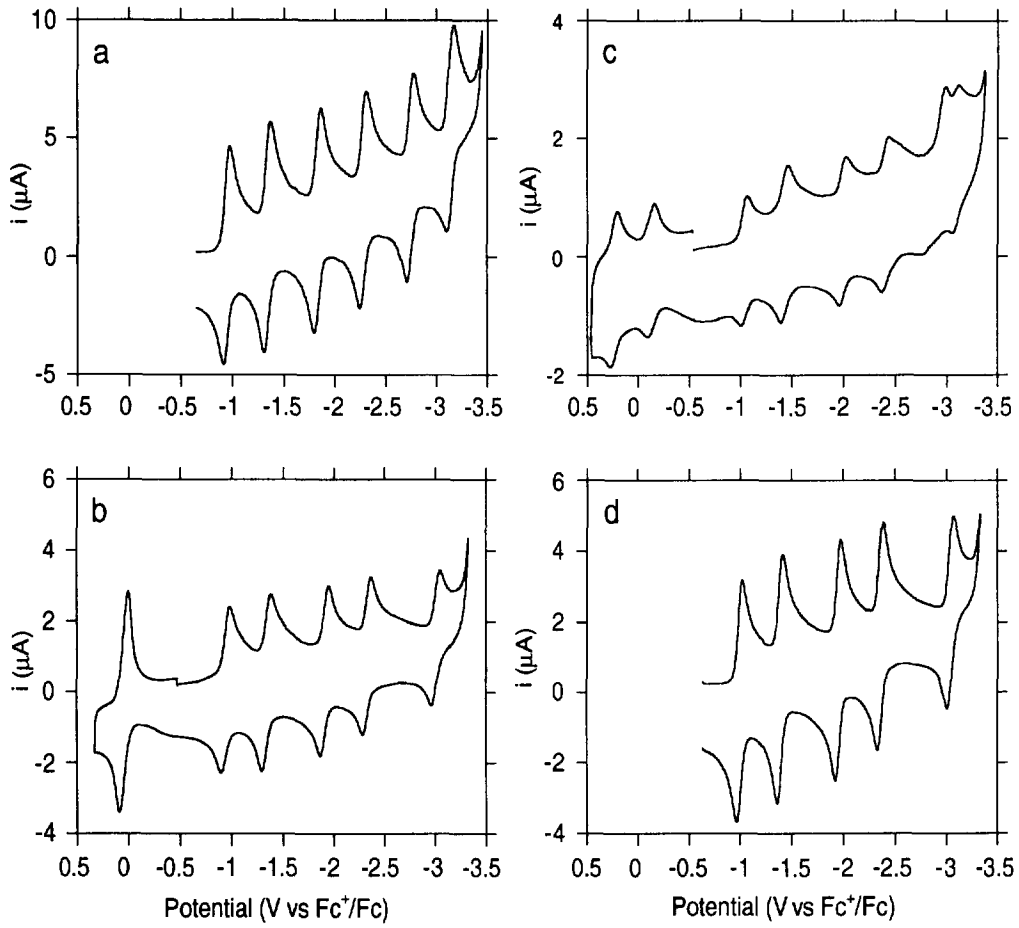


Figure 1. CVs (sweep rate 0.1 V s^{-1}) of C_{60} (a) and substrates **4** (b), **6** (c) and **10** (d) on GC electrode in 3:1 toluene/acetonitrile solutions (0.1 M TBAP), at -45 °C.

In conclusion, in solution and in the ground state, the effect of a potential donor like ferrocene or tetrathiafulvalene on the electrochemical properties of C_{60} is very weak, and barely outside the experimental error. Experiments are needed to define the possibility of energy transfer in the excited state.

	$E^{0/1-}$	$E^{1-/2-}$	$E^{2-/3-}$	$E^{3-/4-}$	$E^{4-/5-}$	$E^{5-/6-}$	$E^{1+/0}$	$E^{2+/1+}$
C_{60}	- 0.94	- 1.33	- 1.83	- 2.28	- 2.74	- 3.14		
1	- 1.05	- 1.44	- 2.01	- 2.42	- 3.12			
2	- 1.08	- 1.47	- 2.03	- 2.44	- 3.14		+ 0.05	
3	- 1.00	- 1.38	- 1.95	- 2.36	- 3.05	- 3.22	+ 0.16	
4	- 0.99	- 1.40	- 1.91	- 2.32	- 3.00		0.0	
5	- 1.00	- 1.39	- 1.97	- 2.37	- 3.05		0.0	
6	- 1.03	- 1.43	- 1,99	- 2.41	- 3.09		- 0.12	+ 0.24
7	- 1.04	- 1.43	- 1.99	- 2.41	- 3.09			
8	- 1.01	- 1.41	- 1.98	- 2.38	- 3.06			
9	- 1.00	- 1.38	- 1.95	- 2.36	- 3.05	- 3.22		
10	- 0.99	- 1.39	- 1.95	- 2.36	- 3.04			

Table 1. $E_{1/2}$ values (V vs Fc^+/Fc) of the redox couples of C_{60} and compounds **1-10**, detected by CV (sweep rate 0.1 V/s) in 3:1 toluene-acetonitrile solutions (0.1 mol/L TBAP), at - 45°C. Errors are estimated at ± 5 mV. $E_{1/2} = (E^{an}_{peak} + E^{cat}_{peak})/2$. Cathodic to anodic differences lie between 45 and 55 mV.

From the beginning of the fullerene era, the electrochemistry of C_{60} derivatives has been systematically explored by the Wudl group. They found that both fulleroids and methanofullerenes essentially retain the electronic properties of C_{60}.[11,12,27-33] An extensive investigation of the redox properties of several variously functionalized organofullerenes has been recently reported by Suzuki et al., who studied the influence of the groups attached directly to C_{60} on CV potentials.[34]

However, only recently, after Echegoyen's work,[6] has a wider cathodic window become accessible and five reduction waves for C_{60} derivatives have been detected.[19,35-37] Although the electrochemical reduction of

fulleroids and methanofullerenes is complicated by chemical processes[33,35-37] and although the data available for these compounds at very low potentials are not exhaustive, it looks as the three-membered ring (or the open [10]-annulene system) in these C_{60} derivatives causes only a minor perturbation in the electronic structure of the pristine fullerene. The reduction waves are rather regularly spaced as it happens in C_{60}. In the case of fulleropyrrolidines, the reduction peaks seem to range in groups of two, with the first two waves well differentiated from the second two waves, and the fifth wave still further away. This might mean that the energy levels of the three LUMO's of the fulleropyrrolidines are well separated, and that the dianion and the tetraanion are diamagnetic. However, much work, especially the detection of the sixth reduction wave in fulleropyrrolidines as well as quantum chemical calculations, is still required to confirm this hypothesis.

EXPERIMENTAL SECTION

Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane. UV-Vis spectra were taken on a Perkin-Elmer Lambda 5 spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer 1720 X spectrophotometer. GC-MS analyses were performed on a Hewlett-Packard electron impact mass spectrometer 5070 coupled with a gas chromatograph 8890 equipped with a 15 m x 0.25 mm column; stationary phase: SE-30, film thickness: 0.25 μ. A PL-GEL 1210-6120 column (300 x 25 mm) filled with polystyrene-divinylbenzene gel (10 μm, 100 Å) from Polymer Laboratories Ltd. was used in the GPC purification of fulleropyrrolidine **6**. Isocratic elution was performed on a LC pump unit Shimadzu LC-8A at a flow rate of 8 ml min^{-1} with HPLC-grade toluene as the mobile phase. The elution was monitored with a Shimadzu SPD-6A UV spectrophotometric detector (0.65 μl cell; light path 0.5 mm) at 340 nm. The purity of all C_{60} derivatives was checked by spectroscopic means (^{13}C and ^1H NMR) and by GPC using an analytical Phenogel™ column from Phenomenex (600 x 7.8 mm) filled with polystyrene-divinylbenzene gel (5 μm, 100 Å) mounted on the Shimadzu HPLC station previously described (toluene as eluant at a flow rate of 0.7 ml min^{-1}). FAB mass spectra were obtained on a VG-ZAB-2F mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. MALDI mass spectra were obtained in positive linear mode at 15 Kv acceleration voltage on a mass spectrometer Reflex™ time of flight (Bruker), using 2,5-dihydroxybenzoic acid as matrix. Melting points were determined with a Büchi apparatus and are uncorrected. Reactions were monitored by thin layer chromatography using Merck precoated silica gel 60-F_{254} (0.25 mm thickness) plates. Flash column chromatography was performed employing 230-400 mesh silica gel (ICN Biomedicals). Reaction yields were not optimized and refer to pure, isolated products. Unreacted C_{60} (usually ca. 50%) was always recovered and recycled in successive runs. Cyclic voltammograms were taken on a AG & G PAR potentiostat/galvanostat, model 273A using the program Model 270 (AG & G).

Materials

C_{60} was purchased from Hoechst A. G. (gold grade). Tetra-*n*-butyl ammonium perchlorate (TBAP) was crystallized from ethanol and dried in vacuo (0.01 mmHg) at 70 °C for 2 days before use. Neutral alumina (Merck, activity I) was dried under vacuum (0.01 mmHg) at 350 °C overnight before use. The solvent/supporting electrolyte system (toluene/CH_3CN 3:1, 0.1 M TBAP, 30 ml) was first treated with neutral dry alumina (5 g) and

decanted. Then 9 ml of that solution was introduced into the electrochemical cell and further 0.2 g of dry alumina was added under nitrogen. The appropriate substrate, in 1 ml of the above solvent/TBAP system, was introduced into the cell by a syringe. N-methylbenzyloxycarbonyl glycine was purchased from Bachem. All other reagents were used as purchased from Fluka. Ferrocenecarbonyl chloride,[38] tetrathiafulvalene carboxaldehyde,[39] 3-ferrocenyl-1-propanol,[40] N-benzyl-2-carbomethoxy aziridine[41] and N-(triphenylmethyl)-5-oxazolidinone[42] were prepared by standard procedures. All solvents were distilled prior to use. Acetonitrile and toluene, employed for electrochemical experiments and cyclohexane, for UV measurements, were commercial spectrophotometric grade solvents.

N-methyl-3,4-fulleropyrrolidine 1. A solution of 100 mg (0.14 mmol) of C_{60}, 25 mg (0.28 mmol) of N-methyl glycine (sarcosine) and 20 mg (0.67 mmol) of paraformaldehyde in 100 ml of toluene was stirred at reflux temperature for two hours, then the solvent was removed in vacuo. The residue was purified by flash chromatography (eluant: toluene) affording 45 mg (41%) of **1** along with 50 mg (50%) of unreacted C_{60}. ^{1}H NMR (200 MHz, $CS_2/CDCl_3$ 2:1): δ 2.98 (s, 3H), 4.38 (s, 4H). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1): δ 41.48, 69.97, 71.07, 136.22, 140.14, 141.83, 142.02, 142.16, 142.58, 143.04, 144.48, 145.21, 145.40, 145.60, 145.93, 145.98, 146.17, 147.20, 154.72. FAB MS m/z 778 ($MH^{+\cdot}$, 58%); 720 (C_{60}, 100%). UV-VIS λ_{max} (cyclohexane) 214, 254, 306, 322, 429.

N-methyl-2-ferrocenyl-3,4-fulleropyrrolidine 2. A solution of 100 mg (0.14 mmol) of C_{60}, 60 mg (0.28 mmol) of ferrocene carboxaldehyde and 25 mg (0.28 mmol) of N-methyl glycine in 100 ml of toluene was stirred at reflux temperature overnight then the solvent was removed in vacuo. The solid residue was purified by flash chromatography (eluant: toluene) affording 77 mg (57%) of **2** and 35 mg (35%) of unreacted C_{60}. ^{1}H NMR (250 MHz, $CS_2/CDCl_3$ 2:1) δ 3.40 (s, 3H), 4.16 (m, 1H), 4.21 (m, 1H), 4.31 (d, 1H, J = 9.5 Hz), 4.25 (s, 4H), 4.43 (m, 1H), 4.52 (m, 1H), 4.79 (s, 1H), 4.85 (d, 1H, J = 9.5 Hz). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1): δ 41.85, 67.21, 67.25, 67.79, 68.23, 68.45, 69.54, 71.08, 78.15, 88.58, 135.85, 135.75, 136.29, 136.48, 138.90, 139.39, 140.02, 140.14, 141.33, 141.54, 141.89, 141.78, 141.97, 142.08, 142.52, 142.60, 142.82, 143.01, 144.30, 144.58, 144.81, 145.05, 145.10, 145.18, 145.40, 145.48, 145.70, 145.81, 145.95, 146.02, 146.10, 146.13, 146.22, 146.38, 147.00, 147.14, 147.39, 147.49, 153.18, 153.59, 153.95, 156.01. FAB MS m/z 961 ($MH^{+\cdot}$, 26%), 720 (C_{60}, 100%). UV-VIS λ_{max} (cyclohexane) 211, 256, 308, 327, 429.

Synthesis of N-ferrocenylcarboxamido-3,4-fulleropyrrolidine 3. A solution of 100 mg (0.14 mmol) of C_{60} and 54 mg (0.16 mmol) of N-(triphenylmethyl)-5-oxazolidinone in 130 ml of chlorobenzene was heated to reflux overnight. The solvent was removed in vacuo and the residue purified by flash chromatography (eluant: petroleum ether/toluene 8:2) yielding 55 mg (39%) of N-(triphenylmethyl)-3,4-fulleropyrrolidine and 46 mg (46%) of unreacted C_{60}. ^{1}H-NMR (250 MHz, $CS_2/CDCl_3$ 2:1) δ 4.13 (broad s, 4H), 7.24 (m, 3H), 7.37 (m, 6H) 7.82 (broad d, 6H, J = 7.02). ^{13}C-NMR (62.9 MHz, $CS_2/CDCl_3$ 2:1) δ 60.66, 69.32, 73.93, 126.90, 128.17, 129.15, 136.44, 140.16, 141.68, 141.81, 141.96, 142.25, 142.56, 142.97, 144.46, 145.18, 145.39, 145.52, 145.98, 146.02, 146.16, 147.15. FAB MS m/z 720 (C_{60}, 100%). UV-VIS λ_{max} (cyclohexane) 211, 254, 306, 323, 429.

To a suspension of 15 mg (0.015 mmol) of N-(triphenylmethyl)-3,4-fulleropyrrolidine in 5 ml of dichloromethane 50 μl of trifluoromethansulfonic acid was added and the mixture was stirred at room temperature

for 1h. The resulting precipitate was centrifuged, washed several times with wet diethyl ether and then dried under reduced pressure. This brownish solid was subsequently suspended in dichloromethane (5ml), treated at room temperature with pyridine (0.3 ml) and 4-dimethylamino pyridine (3 mg) followed by an excess (3 eq.) of ferrocene carbonyl chloride. After one hour at ambient temperature (TLC, toluene) the clear solution was concentrated in vacuo and purified by flash chromatography (eluant: toluene/petroleum ether 1:1 then toluene) yielding 10 mg (68%) of pure **3**. ^{1}H NMR (250 MHz, $CS_2/CDCl_3$ 2:1) δ 4.32 (s, 5 H), 4.46 (m, 2 H), 4.92 (m, 2 H), 5.62 (s, 4H). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1) δ 59.16, 70.40, 70.47, 70.54, 70.96, 135.84, 140.24, 141.89, 142.04, 142.18, 142.64, 143.07, 144.43, 145.27, 145.41, 145.46, 145.56, 146.06, 146.26, 147.26, 153.45. MALDI MS m/z 976 (MH^+). UV-VIS λ_{max} (cyclohexane) 211, 254, 309, 428.

N-methylbenzyloxycarbonylglycine 3-ferrocenyl-*n*-propylester 12 (n = 3). A solution of 0.360 g (1.48 mmol) of 3-ferrocenyl-1-propanol, 0.096 g (0.79 mmol) of 4-dimethylaminopyridine and 0.340 g (1.52 mmol) of N-benzyloxycarbonyl-N-methylglycine in 3 ml of CH_2Cl_2 was cooled on an ice bath. 0.281 g (1.47 mmol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) was added and the mixture was stirred at 0 °C for 2 h and for 18 h at ambient temperature (TLC, toluene/ethyl acetate 7:3). The solvent was removed under reduced pressure and the residue purified by flash chromatography (eluant: toluene/ethyl acetate 9:1) affording 0.56 g (85%) of pure **12** (n = 3) as an orange, oily compound. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.85 (m, 2H), 2.38 (m, 2H), 3.04 (s, 3H), 4.02-4.19 (m, 13H), 5.17 (d, J = 6.6 Hz, 2H), 7.35-7.40 (m, 5H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.77, 29.77, 35.27, 35.99, 50.51, 50.67, 64.72, 67.21, 67.26, 67.37, 67.93, 68.42, 87.57, 87.70, 127.67, 127.70, 127.91, 128.38, 128.92, 169.44, 169.49. FT-IR (KBr) cm^{-1} 1210 (s), 1699 (s), 1732 (s). Anal. Calcd. for $C_{24}H_{27}FeNO_4$ (449.33): C 64.15, H 6.06, N 3.12. Found: C 63.92, H 6.30, N 3.07.

N-methylglycine 3-ferrocenyl-*n*-propylester 13 (n = 3). A solution containing compound **12** (n = 3) (0.56 g, 1.25 mmol) and 50 mg of Pd/C (10%) was stirred in 20 ml of methanol at room temperature under hydrogen atmosphere. After 1 h (TLC, toluene/ethyl acetate 8:2), the solution was purged with nitrogen and the catalyst removed by filtration over a pad of celite. The solvent was removed under reduced pressure and the residue purified by flash column chromatography (eluant: chloroform, then chloroform/methanol 9:1) yielding 0.17 g (43%) of pure **13** (n = 3) as a red oily compound. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.87 (m, 2H), 2.39 (m, 2H), 2.51 (s, 3H), 3.44 (s, 2H), 4.10 (m, 9H), 4.17 (t, J = 6.58 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.78, 29.75, 35.18, 51.36, 64.79, 67.17, 67.90, 68.38, 87.58, 170.54. FT-IR (KBr) cm^{-1} 1664 (s), 1740 (s). Anal. Calcd. for $C_{16}H_{21}FeNO_2$ (315.20): C 60.97, H 6.72, N 4.44. Found: C 61.01, H 6.89, N 4.20.

Synthesis of 6-ferrocenyl-1-hexanol 11 (n = 6). A solution of monoethyladipate (0.94 g, 5.4 mmol) in 5 ml of thionyl chloride was heated to 55 °C for 4 h. The excess of $SOCl_2$ was removed under reduced pressure and the resulting acid chloride was used without further purification. In a 100 ml flask fitted with two addition funnels, under nitrogen atmosphere, $AlCl_3$ (0.85 g, 6.4 mmol) was introduced. Ferrocene (1.0 g, 5.4 mmol) in 5 ml of CH_2Cl_2 and freshly prepared monoethyl adipate carboxylic acid chloride in 5 ml of CH_2Cl_2 were separately introduced in the two funnels and added simultaneously to the solid $AlCl_3$ over a period of 15 min. After two hours (TLC, toluene/ethyl acetate 9:1) the reaction mixture was diluted with 10 ml of CH_2Cl_2, washed with a saturated solution of Na_2HCO_3 and then with brine. The organic layer, dried over Na_2SO_4, was evaporated

under reduced pressure. The residue was purified by flash column chromatography (eluant: toluene/ethyl acetate 95:5) affording 0.47 g (26%) of ethyl 6-ferrocenyl-6-oxo-hexanoate as a red oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.26 (m, 3H), 1.74 (m, 2H), 2.75 (m, 2H), 4.14 (m, 2H), 4.19 (m, 9H), 4.50 (m, 2H), 4.78 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 16.36, 23.81, 24.71, 34.11, 39.16, 60.17, 69.20, 69.65, 72.07, 79.01, 173.36, 203.92. FT-IR (KBr) cm^{-1} 1668 (s), 1731 (s). To a 3 ml of 1M solution of $LiAlH_4$ in THF (3.0 mmol) 0.20 g (1.5 mmol) of $AlCl_3$ was added at room temperature. Then 0.42 g (1.23 mmol) of ethyl 6-ferrocenyl-6-oxo-hexanoate in 4 ml of THF was added over a period of 15 min and the reaction mixture was stirred at room temperature for 18 h. Excess $LiAlH_4$ was quenched with careful addition of water (2ml). The slurry was then diluted with 10 ml of water and extracted with diethyl ether (2 x 20 ml). The organic phase, washed with brine and dried over Na_2SO_4, was concentrated under reduced pressure and the crude alcohol **11** (n = 6) purified by flash column chromatography affording 0.20 g (57%) of 6-ferrocenyl-1-hexanol as an orange, oily compound. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36, (m, 2H), 1.54 (m, 4H), 2.31 (m, 3H), 3.43 (m, 3H), 4.11 (m, 9H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.55, 29.30, 29.44, 30.99, 32.64, 62.88, 67.15, 68.19, 68.64, 89.62. Anal. Calcd. for $C_{16}H_{22}FeO$ (286.20): C 67.51, H 7.75. Found: C 67.61, H 7.84.

N-methylbenzyloxycarbonylglycine 6-ferrocenyl-*n*-hexylester 12 (n = 6). The synthesis was carried out as described for compound **12** (n = 3), starting from 6-ferrocenyl-1-hexanol (0.17 g, 0.59 mmol). Derivative **12** (n = 6): 0.26 g (90%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.73 (m, 8H), 2.31 (m, 2H), 3.00 (s, 3H), 3.14 (s, 2H) 3.88-4.17 (m, 11H), 5.14 (d, J = 6.6 Hz, 2H), 7.34 (m, 5H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.69, 28.46, 29.09, 29.46, 30.94, 35.30, 50.60, 50.72, 65.23, 66.33, 67.13, 67.31, 67.42, 68.14, 68.26, 68.57, 69.08, 127.75, 127.95, 128.40, 128.43, 169.55. FT-IR (KBr) cm^{-1} 1710 (s), 1750 (s). Anal. Calcd. for $C_{27}H_{33}FeNO_4$ (491.41): C 65.69, H 6.77, N 2.85. Found: C 65.48, H 6.80, N 2.75.

N-methylglycine 6-ferrocenyl-*n*-hexylester 13 (n = 6). Removal of the benzyloxycarbonyl protecting group was carried out as described for compound **13** (n = 3), starting from 0.23 g (0.46 mmol) of N-methylbenzyloxycarbonylglycine 6-ferrocenyl-*n*-hexylester **12** (n = 6). Derivative **13** (n = 6): 0.103 g (0.288 mmol, 63%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (m, 4H), 1.49 (m, 2H), 1.63 (m, 2H), 1.94 (s, 1H), 2.31 (m, 2H), 2.44 (s, 3H), 3.36 (s, 2H), 4.02-4-15 (m, 11H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.73, 28.51, 29.10, 29.44, 30.95, 36.02, 52.47, 64.80, 66.96, 67.96, 68.38, 89.14, 172.29. FT-IR (KBr) cm^{-1} 1662 (s), 1740 (s). Anal. Calcd. for $C_{19}H_{27}FeNO_2$ (357.28): C 63.87, H 7.62, N 3.92. Found: C 63.89, H 7.68, N 4.01.

N-methyl-2-[carbo-*n*-propyloxy-(3'-ferrocenyl)]-3,4-fulleropyrrolidine 4. A solution of 108 mg of C_{60} (0.15 mmol), 52 mg (0.16 mmol) of **13** (n = 3) and 16 mg (0.53 mmol) of paraformaldehyde in 150 ml of toluene was heated to reflux for 1 h. The toluene was evaporated under reduced pressure and the crude product purified by flash column chromatography. Elution with toluene and then toluene/ethyl acetate 9:1 gave 73 mg (46%) of **4**. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.85 (m, 2H), 2.34 (m, 2H), 3.03 (s, 3H), 3.99 (m, 9H), 4.20-4.40 (m, 3H) 4.83 (s, 1H), 4.97 (d, J = 9.5 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.98, 29.87, 39.70, 65.42, 67.55, 68.09, 68.55, 68.75, 69.44, 73.09, 79.18, 87.60, 125.18, 128.10, 128.88, 135.36, 135.95, 136.40, 137.64, 139.48, 139.55, 140.15, 140.21, 141.59, 141.64, 141.71, 141.78, 141.96, 142.01, 142.54, 142.58, 142.94, 143.01, 144.23, 144.34, 144.56, 145.13, 145.16, 145.25, 145.39, 145.43, 145.56, 145.70,

145.89, 145.93, 146.10, 146.14, 146.18, 146.28, 146.43, 147.14, 147.25, 150.81, 152.68, 153.47, 154.48, 169.05. MALDI MS m/z 1047 (M^+). UV-VIS λ_{max} (cyclohexane) 207, 254, 308, 327, 430. Anal. Calcd. for $C_{77}H_{21}FeNO_2$ (1047.88): C 88.26, H 2.02, N 1.34. Found: C 88.05, H 2.05, N 1.12.

N-methyl-2-[carbo-*n*-hexyloxy-(6-ferrocenyl)]-3,4-fulleropyrrolidine 5. The synthesis was carried out as described for compound **4**. Starting materials: C_{60} (120 mg, 0.17 mmol), paraformaldehyde (18 mg, 0.60 mmol), N-methylglycine derivative **13** (n = 6) (65 mg, 0.18 mmol). Flash column chromatography: eluant toluene, then toluene/ethyl acetate 9:1. Derivative **5**: 79 mg (43%). ^1H NMR (250 MHz, $CDCl_3$) δ 1.27 (m, 4H), 1.43 (m, 2H), 1.60 (m, 2H), 2.24 (m, 2H), 3.02 (s, 3H), 4.00 (s, 4H), 4.05 (s, 5H), 4.24 (d, J = 9.5 Hz, 1H), 4.33 (m, 2H), 4.80 (s, 1H), 4.96 (d, J = 9.5 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.92, 28.65, 29.13, 29.49, 30.94, 40.03, 66.00, 68.48, 68.52, 68.80, 69.59, 73.26, 79.52, 125.27, 128.20, 129.01, 135.48, 136.06, 136.53, 137.75, 139.57, 139.66, 140.24, 140.31, 141.72, 141.76, 141.85, 141.88, 141.91, 142.08, 142.16, 142.63, 142.70, 143.04, 143.12, 144.35, 144.46, 144.50, 144.69, 145.28, 145.37, 145.48, 145.52, 145.57, 145.68, 145.73, 145.76, 145.88, 146.03, 146.07, 146.24, 146.27, 146.31, 146.40, 146.64, 147.29, 147.40, 150.97, 152.71, 153.75, 154.66, 169.51. MALDI MS m/z 1089 (M^+). UV-VIS λ_{max} (cyclohexane) 214, 254, 308, 327, 429. Anal. Calcd. for $C_{80}H_{27}FeNO_2$ (1089.96): C 88.16, H 2.50, N 1.29. Found: C 88.05, H 2.48, N 1.07.

N-methyl-2-tetrathiafulvalenyl-3,4-fulleropyrrolidine 6. A solution of 31 mg (0.043 mmol) of C_{60}, 15 mg (0.065 mmol) of tetrathiafulvalene carboxaldehyde and 33 mg (0.37 mmol) of N-methyl glycine in 100 ml of toluene was heated to reflux temperature under nitrogen and in the dark. After 20 h (TLC, toluene/petroleum ether 2:8) the solution was concentrated to half volume on the rotary evaporator (water bath temperature = 30 °C), poured on top of a SiO_2 pad and quickly eluted (toluene) with the aid of a stream of nitrogen in order to remove most of unreacted C_{60} and tetrathiafulvalene carboxaldehyde. The fractions containing the product were concentrated to ca. 20 ml and compound **6** was purified from residual C_{60} and from trace of higher molecular weight material by preparative HPLC (GPC, see instrumentation) affording 12 mg (29%) of a greenish black solid. ^1H NMR (250 MHz,CS_2/$CDCl_3$ 2:1) δ 2.97 (s, 3H), 4.16 (d, J = 9.7 Hz, 1H), 4.82 (s, 1H), 4.90 (d, J = 9.7 Hz, 1H), 6.28 (s, 2H), 6.67 (s, 1H). ^{13}C NMR (62.5 MHz, CS_2/$CDCl_3$ 2:1) δ 40.20, 68.58, 69.43, 75.37, 79.29, 115.59, 118.62, 118.86, 119.15, 128.57, 134.92, 135.07, 136.46, 137.02, 139.99, 141.45, 141.62, 141.85, 141.90, 141.94, 142.39, 142.41, 142.74, 144.10, 144.98, 145.07, 145.29, 145.50, 145.67, 145.71, 145.81, 145.90, 145.95, 146.03, 147.04, 152.32, 153.66, 154.85. MALDI MS m/z 980 $(MH)^+$. UV-VIS λ_{max} (cyclohexane) 212, 256, 306, 323, 429.

N-methyl-2-[(3',5'-dibenzyloxy)phenyl]-3,4-fulleropyrrolidine 7. A solution of 30 mg (0.042 mmol) of C_{60}, 15 mg (0.047 mmol) of 3,5-dibenzyloxyphenyl benzaldehyde and 15 mg (0.17 mmol) of N-methylglycine in 30 ml of toluene was stirred at reflux temperature overnight then the solvent was removed in vacuo. The solid residue was purified by flash column chromatography (eluant: toluene/petroleum ether 8:2 then toluene) affording 13 mg (29%) of **7**. ^1H NMR (250 MHz, CS_2/$CDCl_3$ 2:1) δ 2.83 (s, 3H), 4.26 (d, J = 9.4 Hz, 1H), 4.85 (s, 1H), 4.98 (d, J = 9.4 Hz, 1H), 5.06 (m, 4H), 5.56 (m, 1H), 7.08 (m, 2H), 7.22-7.48 (m, 10H). ^{13}C NMR (62.5 MHz, CS_2/$CDCl_3$ 2:1) δ 39.93, 68.83, 69.80, 70.01, 76.74, 83.37, 126.94, 127.31, 127.87, 127.92, 128.11, 128.47, 128.57, 135.63, 136.64, 136.51, 136.59, 139.49, 139.76, 140.00, 140.08, 141.51,

141.54, 141.70, 141.92, 141.99, 142.03, 142.08, 142.46, 142.86, 144.24, 144.57, 145.03, 145.06, 145.13, 145.22, 145.39, 145.43, 145.82, 145.90, 145.99, 146.03, 146.13, 146.19, 147.15, 153.18, 153.83, 155.87, 159.91. MALDI MS m/z 1065 (M^+). UV-VIS λ_{max} (cyclohexane) 216, 254, 308, 325, 429.

N-methyl-2-(4'-pyridyl)-3,4-fulleropyrrolidine 8. A solution of 100 mg (0.14 mmol) of C_{60}, 75 mg (0.70 mmol) of pyridine-4-carboxaldehyde and 31 mg (0.35 mmol) of N-methylglycine in 90 ml of toluene was stirred at reflux temperature for 8 h then the solvent was removed in vacuo. The solid residue was purified by flash column chromatography (eluant: toluene, then toluene/ethyl acetate 9:1) affording 53 mg (44%) of **8**. ^1H NMR (250 MHz, $CS_2/CDCl_3$ 2:1) δ 2.84 (s, 3H), 4.21 (d, J = 9.5 Hz, 1H), 4.94 (s, 1H), 5.01 (d, J = 9.5 Hz, 1H), 7.74 (m, 2H), 8.67 (m, 2H). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1) δ 39.77, 68.77, 69.81, 76.15, 82.12, 123.80, 135.35, 135.80, 136.12, 136.83, 139.34, 140.05, 141.35, 141.47, 141.57, 141.63, 141.71, 141.91, 142.36, 142.39, 142.50, 144.16, 144.46, 144.99, 145.09, 145.19, 145.31, 145.37, 145.41, 145.74, 145.88, 145.93, 145.98, 146.09, 147.06, 150.05, 151.67, 152.16, 153.19, 155.36. MALDI MS m/z 855 $(MH)^+$. UV-VIS λ_{max} (cyclohexane) 216, 254, 308, 323, 429.

N-acetyl-3,4-fulleropyrrolidine 9. The synthesis was carried out as described for compound **3**. Excess (1 ml) acetic anhydride was used as the acylating agent. Derivative **9**: 10 mg (83%). ^1H NMR (250 MHz, $CS_2/CDCl_3$ 2:1) δ 2.55 (s, 3H), 5.38 (s, 2H), 5.45 (s, 2H). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1) δ 22.23, 56.84, 59.78, 69.58, 70.84, 125.22, 128.14, 128.93, 135.58, 136.10, 140.12, 140.25, 141.86, 142.09, 142.62, 143.04, 144.29, 144.47, 145.27, 145.43, 145.53, 146.06, 146.30, 147.32, 152.77, 153.47, 168.70. MALDI MS m/z 806 (MH^+). UV-VIS λ_{max} (cyclohexane) 211, 254, 311, 429.

N-benzyl-2-carbomethoxy-3,4-fulleropyrrolidine 10. A solution of 100 mg (0.14 mmol) of C_{60} and 53 mg (0.28 mmol) of N-benzyl-2-carbomethoxy aziridine in 100 ml of *o*-dichlorobenzene was heated at 150 °C overnight. The solvent was distilled in vacuo and the crude purified by flash chromatography (eluant: toluene/petroleum ether 1:1, then toluene) affording 51 mg (40%) of pure **10** along with 45 mg (45%) of unreacted C_{60}. ^1H NMR (250 MHz,$CS_2/CDCl_3$ 2:1) δ 3.81 (s, 3H), 4.06 (d, 1H, J = 13.2 Hz), 4.25 (d, 1H, J = 9.5 Hz), 4.56 (d, 1H, J = 13.2 Hz), 4.90 (d, 1H, J = 9.5 Hz), 5.05 (s, 1H), 7.28-7.45 (m, 3H), 7.60 (d, 2H, J = 6.6 Hz). ^{13}C NMR (62.5 MHz, $CS_2/CDCl_3$ 2:1v) δ 51.82, 56.07, 64.68, 69.15, 72.58, 127.85, 128.78, 128.98, 135.42, 136.04, 136.48, 136.91, 137.71, 139.61, 139.79, 140.22, 140.27, 141.73, 141.80, 141.79, 141.93, 142.04, 142.15, 142.19, 142.56, 142.59, 143.01, 144.34, 144.41, 144.46, 144.57, 145.17, 145.21, 145.36, 145.38, 145.44, 145.49, 145.59, 145.63, 145.76, 145.96, 145.98, 146.16, 146.18, 146.20, 146.29, 147.18, 147.28, 150.89, 153.41, 154.44, 169.47. FAB MS m/z 912 ($MH^{+\cdot}$, 15%), 720 (C_{60}, 100%). UV-VIS λ_{max} (cyclohexane) 212, 254, 310, 429.

Acknowledgement. This work was in part developed within the *Progetto Strategico Materiali Innovativi* of the C.N.R.

REFERENCES AND NOTES

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
(3) Hebard, A. F.; Rosseinski, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.
(4) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154.
(5) Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.
(6) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.
(7) Ohsawa, Y.; Saji, T. *J. Chem. Soc, Chem. Comm.* **1992**, 782.
(8) Hirsch, A. *The Chemistry of Fullerenes*; Thieme: Stuttgart, 1994.
(9) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459.
(10) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. In *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*; G. S. Hammond and V. J. Kuck, Eds.; American Chemical Society: Washington, DC, 1992; ACS Symposium Series 481; p 161.
(11) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186.
(12) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157.
(13) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(14) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: London, 1991.
(15) *Supramolecular Chemistry*; Balzani, V.; De Cola, L., Eds.; Kluwer Academic: Dordrecht, 1992; NATO-ASI Series C: Mathematical and Physical Sciences, Vol. 371.
(16) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
(17) The term *fulleropyrrolidines* is a general short term for C_{60}-fused pyrrolidine rings. Chemical Abstract name for N-methyl-3,4-fulleropyrrolidine (**1**) is: 2'H-[5,6]fullereno-C_{60}-I_h-1',5'-dihydro-1'-methyl-[1,9-c]pyrrole. Pyrrolidino-fullerenes (another short name for these compounds) would emphasize the fullerene part, but would not follow Chemical Abstract nomenclature.
(18) Maggini, M.; Scorrano, G.; Bianco, A.; Toniolo, C.; Sijbesma, R. P.; Wudl, F.; Prato, M. *J. Chem. Soc., Chem. Comm.* **1994**, 305.
(19) Maggini, M.; Karlsson, A.; Scorrano, G.; Sandonà, G.; Farnia, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1994**, 589.
(20) Maggini, M.; Karlsson, A.; Pasimeni, L.; Scorrano, G.; Prato, M.; Valli, L. *Tetrahedron Lett.* **1994**, *35*, 2985.
(21) Maggini, M.; Donò, A.; Scorrano, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1995**, 845.
(22) Tsuge, O.; Kanemasa, S. *Adv. Heterocyclic Chem.* **1989**, *45*, 231.
(23) Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Comm.* **1993**, 1764.
(24) Izuoka, A.; Tachikawa, T.; Sugawara, T.; Suzuki, Y.; Konno, M.; Saito, Y.; Shinohara, H. *J. Chem. Soc., Chem. Comm.* **1992**, 1472.
(25) Izuoka, A.; Tachikawa, T.; Sugawara, T.; Saito, Y.; Shinohara, H. *Chem. Lett.* **1992**, 1049.
(26) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455.
(27) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *J. Am. Chem. Soc.* **1992**, *114*, 7300.

(28) Wudl, F.; Suzuki, T.; Prato, M. *Synthetic Metals* **1993**, *59*, 297.
(29) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
(30) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594.
(31) González, R.; Knight, B. W.; Wudl, F.; Semones, M. A.; Padwa, A. *J. Org. Chem.* **1994**, *59*, 7949.
(32) Hummelen, J. C.; Knight, B. W.; Lepeq, F.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 532.
(33) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364.
(34) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.
(35) Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388.
(36) Arias, F.; Echegoyen, L.; Wilson, S. R.; Lu, Q.; Lu, Q. *J. Am. Chem. Soc.* **1995**, *117*, 1422.
(37) Paolucci, F.; Marcaccio, M.; Roffia, S.; Orlandi, G.; Zerbetto, F.; Prato, M.; Maggini, M.; Scorrano, G. *J. Am. Chem. Soc.* **1995**, *117*, 6572.
(38) Lau, H. H.; Hart, H. *J. Org. Chem.* **1959**, *24*, 280.
(39) Green, D. C. *J. Org. Chem.* **1979**, *44*, 1476.
(40) Schlögl, K. *Monatsch. Chem.* **1957**, *88*, 601.
(41) Stolberg, M. A.; O'Neill, J. J.; Wagner-Jauregg, T. *J. Am. Chem. Soc.* **1953**, *75*, 5045.
(42) Tsuge, O.; Kanemasa, S.; Ohe, M.; Takenaka, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4079.

(*Received* 28 *July* 1995)