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New π-extended tetrathiafulvalene-containing fulleropyrrolidine dyads endowed with vinyl spacers

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Abstract

The synthesis of novel C_{60}-donor dyads in which the fulleropyrrolidine moiety is covalently attached to an π-extended tetrathiafulvalene analogue through an ethylenic spacer is described. The cyclic voltammetry confirms the redox reactivity of both donor and acceptor chromophores and the semiempirical PM3 theoretical calculations predict the existence of two conformational isomers. In the ground state, no evidence of charge transfer interaction was observed in solution. Upon excitation, the fullerene singlet excited state in C_{60}-donor dyads is subject to a solvent-dependent, rapid fluorescence quenching, suggesting an intramolecular electron transfer. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: [60]Fullerene; π-Extended tetrathiafulvalenes; Donor–acceptor dyads; Cyclic voltammetry; Fluorescence; Electron transfer

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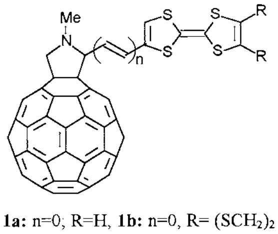
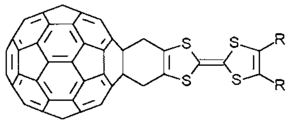
1. Introduction

A large effort has been recently devoted to the synthesis of new C_{60}-donor dyads due to the interesting photophysical properties they exhibit. The concept of these systems relies on a photoinduced *intra*molecular energy- and/or electron-transfer process from the donor unit to the adjacent fullerene cage [1].

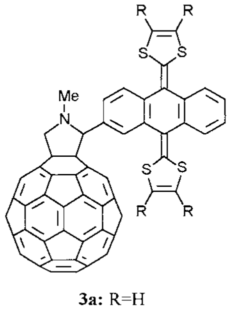
A wide variety of electron donor molecules have been covalently attached to the C_{60} cage to activate *intra*molecular charge-transfer (CT) interactions. These CT interactions take place either in the ground or in the excited state generating charge-separated species, which open potential application in the preparation of artificial photosynthetic systems [2]. Representative examples of photoinduced *intra*molecular electron-transfer processes have been reported in [60]fullerene–ferrocene dyads [3] or carotene–porphyrin–fullerene triads [4]. A direct observation of an *intra*molecular CT interaction as a band in the electronic spectra has also been reported [5]. In the search for new C_{60}-donor dyads bearing stronger electron donor moieties, differently substituted tetrathiafulvalene (TTF) molecules (**1**, **2**) have been bound to the C_{60} core. For the synthesis of the latter either 1,3-dipolar cycloadditions [6,7] following Prato's procedure [8] or Diels–Alder reactions from *o*-quinodimethane analogues of TTF have been pursued [9,10].



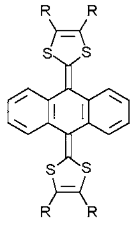
1a: n=0; R=H, **1b:** n=0, R= (SCH₂)₂
1c: n=1; R=H; **1d:** n=1; R= (SCH₂)₂



2a: R=H
2b: R=Me
2c: R= CO_2Me
2d: R= SMe



3a: R=H
3b: R=SMe
3c: R=$(SCH_2)_2$



4 (R=H, SMe, $(SCH_2)_2$)

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In our group we have recently reported the synthesis of dyads **3a–c** in which the C_{60} cage is covalently attached to highly conjugated TTF analogues with a *p*-quinodimethane structure (**4**) [11]. Interestingly, these π-extended TTF are known to form stable dication species upon oxidation. This leads to CT complexes with electrical and magnetic properties [12]. In this regard, compounds **3a–c** exhibit a paramagnetic behavior according to their molar magnetic susceptibility measurements [11].

Considering the striking influence that the spacer, connecting both donor and acceptor moieties, has on the efficiency of the electron-transfer process in these donor–spacer–acceptor systems, we describe in this paper the synthesis, electrochemistry, and fluorescence measurements of the novel dyads (**7**). In the latter the donor fragment is covalently linked to the fulleropyrrolidine moiety through an ethylenic spacer. In order to rationalize the experimental findings, theoretical calculations at the semiempirical PM3 level have been carried out on these C_{60}-donor dyads (**7**).

2. Results and discussion

Compounds **7a–c** were prepared in moderate yields (32–38%) by in situ generation of the respective azomethine ylides, formed from sarcosine (*N*-methylglycine) and the corresponding aldehyde (**6a–c**), followed by 1,3-dipolar cycloaddition to C_{60} [8]. Compounds **6a–c** were in turn prepared by a Wittig reaction from the respective 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**5a–c**) [11] and (triphenylphosphoranylidene)acetaldehyde (Scheme 1).

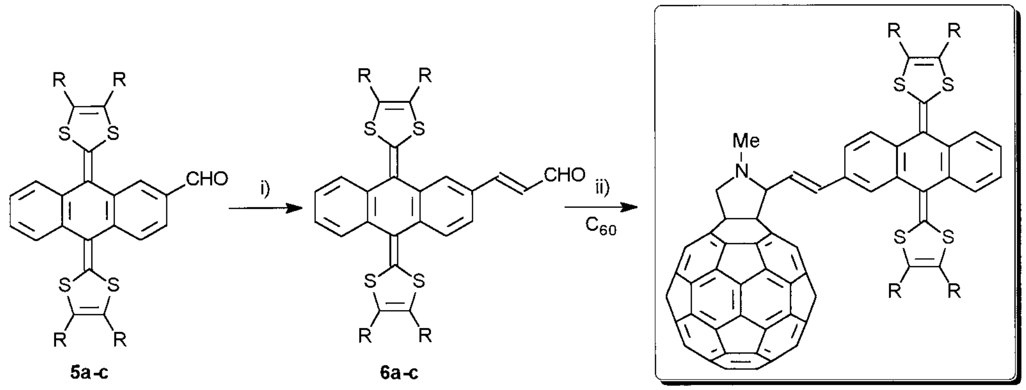
It has been previously shown that 1,3-dipolar cycloadditions of azomethine ylides to C_{60} occur at the 6,6-ring junction of the C_{60} cage [13]. The structural assignment of novel compounds **7a–c** was supported by their analytical and spectroscopic data. ^{1}H-NMR spectra of organofullerenes **7a–c** showed the presence of a mixture of isomers. This is probably due to the existence of a conformational equilibrium between two isomers (see below). A thermal isomerization of the starting *trans*-α,β-unsaturated carbonylic compounds (**6a–c**) to the *cis* isomer can be ruled out, since performing the reaction in toluene at a lower temperature (90°C) and/or using a shorter period of time (5 h), afforded only the *trans* isomer ($J_{H,H} = 15.3$ Hz).

Compounds **7** showed a poor solubility in most common organic solvents, thus preventing the collection of the ^{13}C-NMR spectra of dyads **7a** and **7c**. Compound **7b** presented a slightly better solubility, which allowed its ^{13}C-NMR spectrum to be recorded. In addition to the N-Me group at δ 39.8, compound **7b** shows the presence of the sp^3 carbons at the 6,6-ring junction and the remaining pyrrolidine carbons at δ 68.5, 69.9, 77.1 and 81.2.

Interestingly, the electronic spectra of **7a–c** show an absorption band at around 440 nm corresponding to the donor moiety [12,14], which prevents the observation of the characteristic band at around 430 nm of dihydrofullerenes. In agreement with these findings, organofullerrenes **7a–c**, show a yellow–brown color in the solid state and in solutions of different solvents.

The electrochemical properties of dyads **7a–c** were studied by cyclic voltammetry (CV) in solution at room temperature and the corresponding data are collected in Table 1. For illustration we added the data for C_{60} and the parent unsubstituted donor molecule [9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] (**4**) as reference compounds.

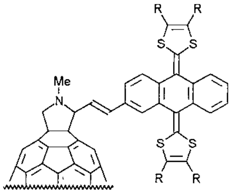
Compounds **7a–c** show the presence of four quasi-reversible reduction waves corresponding to the first four reductions of the C_{60} moiety. As expected, these reduction waves are slightly shifted towards more negative values due to the saturation of a double bond of the C_{60}



7a: R = H
7b: R = SMe
7c: R = $(SCH_2)_2$

Scheme 1. Reagents: (i) $Ph_3P{=}CHCHO$/toluene/Δ; (ii) sarcosine/toluene/90°C/5 h.

Table 1
Redox potentials of novel dyads **7a–c**

Compound		E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^1_{oxd}
	**7a:** R=H	-0,65	-1,05	-1,62	-1,90	0,50
	7b: R=SMe	-0,70	-1,10	-1,70	-2,06	0,71
	7c: R=$(SCH_2)_2$	-0,66	-1,07	-1,64	-1,93	0,61
	C_{60}	-0.60	-1.07	-1,.64	-1.93	—
	4 (R=H)^b	—	—	—	—	0.45[12]

^{a} In V *vs* SCE; GCE; $Bu_4N^+ClO_4^-$ (0,1 M); Tol:MeCN (4:1); 200 mV/s;
^{b} in V *vs* SCE; GCE; $Bu_4N^+ClO_4^-$ (0,1 M); CH_2Cl_2; 200 mV/s

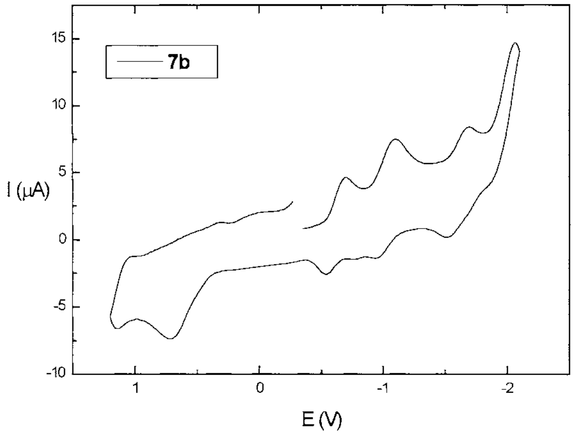


Fig. 1. Cyclic voltammogram of **7b** at 200 mV s^{-1}.

cage [15]. On the oxidation side, compounds **7a–c** exhibit the presence of a single oxidation wave, involving two electrons, to form the TTF dication species. This redox behavior is characteristic for these π-extended systems with *p*-quinonoid structure [12,14b] (see Fig. 1).

We have determined the structure of compound **7a** by molecular geometry optimization at the semiempirical PM3 level (Hyperchem 3.0). The geometries of the minimum-energy configurational and conformational isomers are shown in Fig. 2.

In good resemblance to previous observations regarding compounds **3a–c**, the calculated geometry of the donor fragment in **7a** is highly distorted from planarity. This is clearly a consequence of the strong steric hindrance between the sulfur atoms of the 1,3-dithiole rings and the CH units in *peri* positions. The theoretical predictions compare quite well with the X-ray data found for the unsubstituted parent donor moiety [16].

The distortion from planarity of the donor unit in **7a** has been described in terms of the angles α and γ. α is the angle formed by the 'wings of the butterfly' (dihedral angle C2–C1–C4–C5), and angle γ is the tilting of the 1,3-dithiole rings with respect to the C2–C3–C5–C6 plane (dihedral angle C6–C1–C2–C3). The calculated values for these angles are α = 138.6° and γ = 38.8°. These values are almost identical to those calculated for the related structure **3a** [11] and those obtained from the X-ray data for the isolated donor moiety (γ = 34.9°) [16].

Depending upon the orientation of the dithiole rings (e.g. up and down), two isomers are possible. We have calculated the relative stabilities of the minimum-energy conformations for both isomers of **7a** (*Z* and *E*). Theoretical calculations predict that the A_E conformation (*E* isomer with the dithiole rings pointing upward) is 4.11 kcal mol^{-1} more stable than the B_E isomer (*E* isomer with the dithiole rings pointing downward). As ex-

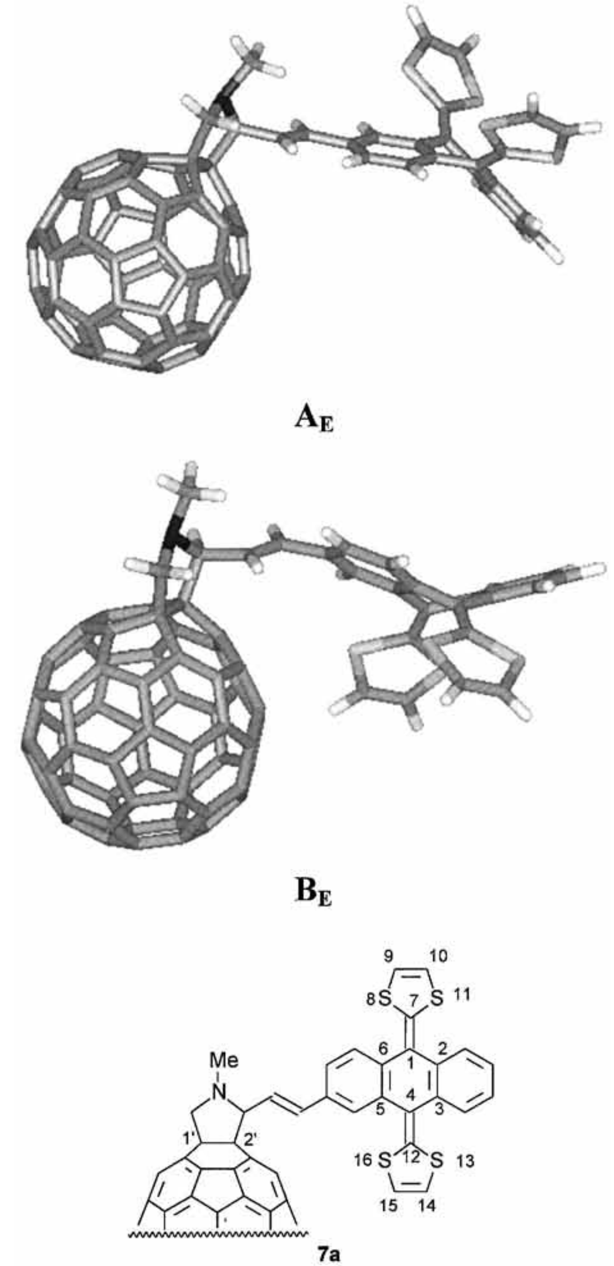
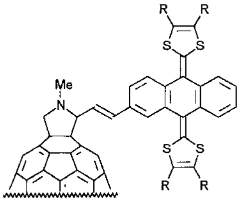


Fig. 2. Minimum-energy conformations (**A** and **B**) calculated for **7a** and aleatory atom numbering used in the text for this compound.

Table 2
Photophysical properties of dyads **7a–c** in different solvents

Compound		solvent	ΔG°	Φ_{FL}	τ_{FL}
	**7a**: R=H	toluene	-0.11	3.5	0.626
		CH_2Cl_2	-0.76	2.16	0.383
		PhCN	-0.92	1.14	0.26
	7b: R=SMe	toluene	+0.1	4.9	0.839
		CH_2Cl_2	-0.55	2.4	0.576
		PhCN	-0.71	1.6	0.467
	7c: R=$(SCH_2)_2$	toluene	0	4.2	0.79
		CH_2Cl_2	-0.65	2.16	0.512
		PhCN	-0.81	1.4	0.41

pected, the energy of the *Z* isomers is higher than that of the most stable A_E isomer, thus confirming the ^1H-NMR assignments.The distance between the closest sulfur atom of the donor moiety and the surface of the sphere in conformation B_E (3.87 Å) is too long to support a CT interaction. These data are in agreement with the absence of a CT band from the HOMO of the donor unit to the LUMO of the C_{60} cage. These results are thus quite similar to that found for the related structures **3a–c**.

It is important to note that, in contrast to the previously reported C_{60}-based dyads bearing a TTF unit, [6,7,10] the geometrical features of *p*-quinodimethane analogues of TTF [14c] have a strong impact on the stabilization of the charge-separated state. In addition to the gain of aromaticity of the 1,3-dithiole units, a further aromatization process occurs upon oxidation leading to planar aromatic arenes that possess larger aromatic stabilization energies than the heteroaromatic rings.

Considering the redox activities of the two components, e.g. the electron-accepting nature of the fullerene and the electron-donating properties of the TTF moieties employed, photoexcitation of dyads **7a–c** should possibly activate an intramolecular electron-transfer event. This assumption is further supported by calculations regarding the thermodynamic driving force ($\Delta G°$) associated with an electron transfer in dyads **7a–c**. For example, ($\Delta G°$) for dyad **7a** is -0.11, -0.76, and -0.92 eV in toluene, dichloromethane, and benzonitrile, respectively.

A powerful tool to probe the excited-state properties of a chromophore, such as the fullerene moiety, is time-resolved and steady-state fluorescence spectroscopy. Monofunctionalized fullerene derivatives give rise to singlet excited-state emissions near 700 nm with, however, moderate fluorescence quantum yields (e.g. 6.0×10^{-4}). Accordingly, the energy of the fullerene singlet excited state lies around 1.77 eV. In weak polar toluene, all the investigated dyads reveal a markedly quenching of the fluorescence quantum yield relative to the fullerene reference model compound employed, e.g. a *N*-methyl fulleropyrrolidine. Furthermore, changing the solvent polarity from non-polar toluene via dichloromethane to polar benzonitrile led to an additional enhancement of the fluorescence quenching. It is notable that in the fullerene reference the solvent polarity has a negligible impact on the fluorescence quantum yield. The only observable effect is a red shift of the fluorescence transition in polar solvents (benzonitrile) versus non-polar solvents (toluene), in accordance with the nature of the singlet excited-state emission, e.g. a $\pi^*-\pi$ transition. The rigidity of the dyad structures should be noted, which, in turn, suggests interpretation of the fluorescence quenching in terms of an intramolecular 'through-bond' electron-transfer process.

To confirm the qualitative fluorescence quantum yields, we probed the fluorescence lifetimes of the fullerene singlet excited states in dyads **7a–c** under similar conditions to those employed in the steady-state experiments. In general, the steady-state and time-resolved techniques results are in excellent agreement with each other (see Table 2).

An interesting observation is the fact that the extent of quenching follows mainly the type of TTF functionalization and, in turn, the oxidation potential of the donor moiety. This fact has been previously observed for dyads of type **2** for which the presence of different substituents on the TTF moiety allows the tuning of the HOMO–LUMO gap, which has a direct impact on the photophysical properties [10b]. In this context, replacement of the hydrogens with the electron-withdrawing S–Me or $(SCH_2)_2$ groups, alters the oxidation potential of the TTF moieties (see Table 1). In line with the unfavorably shifted oxidation potential, the quenching efficiency of the S–Me and $(SCH_2)_2$ derivatives diminishes. Similarly, a comparison between the parent TTF and extended TTF donor reflects the impact of the weaker electron-donating ability of the extended TTF derivatives on the singlet excited-state quenching.

3. Summary and conclusions

We report the synthesis of novel C_{60}-donor dyads, in which both donor (π-extended TTF derivative) and acceptor (C_{60}) moieties are connected through a pyrrolidine ring attached to an ethylene bridge. The CV measurements clearly indicate the presence of both donor and acceptor chromophores. The double bond present in compounds **7a–c** in comparison with the previously reported related compounds **3a–c** has no influence on the electrochemical behavior. Theoretical calculations predict a highly distorted structure for the electron-donor moiety and a higher stability for the *trans* isomer with the two 1,3-dithiole rings pointing upwards. Steady-state and time-resolved fluorescence measurements indicate a rapid deactivation of the fullerene singlet excited state, whose efficiency depends mainly on the oxidation strength of the TTF donor moiety. We are currently probing these dyads by time-resolved transient absorption spectroscopy to further unravel the dynamics and mechanism of the intramolecular deactivation and to shed light onto the involvement upon excitation of the radical cation of the extended TTF species as well as the stability of the charge-separated radical pairs formed.

4. Experimental

4.1. Synthesis of aldehydes ***6a–c****. General procedure*

A solution of (triphenylphosphoranyliene)acetaldehyde (1 mmol) and the corresponding aldehyde **5a–c** (0.5 mmol) was refluxed in toluene (20 ml) under argon atmosphere for 12 h. The mixture was cooled at room temperature and hexane (30 ml) was added. The triphenylphosphine oxide precipitated was removed by filtration, the solvent was removed and the crude product was purified by flash chromatography by using CH_2Cl_2 as eluent.

*4.1.1. 2(E-2′-formylvinyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**6a**)*

58% yield; m.p.: 265–267°C (dec.); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.71 (1H, d, $J = 7.7$ Hz), 7.89 (1H, d, $J = 1.5$ Hz), 7.70 (1H, d, $J = 9.2$ Hz), 7.72–7.69 (2H, m), 7.47 (1H, d, $J = 16.1$ Hz), 7.44 (1H, dd, $J_1 = 9.2$, $J_2 = 1.5$ Hz), 7.31–7.28 (2H, m), 6.75 (1H, dd, $J_1 = 16.1$, $J_2 = 7.7$ Hz), 6.30 (4H, d, $J = 6.6$ Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 193.5, 152.3, 138.1, 136.9, 136.0, 134.8, 131.3, 128.1, 126.3, 126.2, 126.1, 125.4, 124.9, 124.8, 124.6, 121.3, 121.0, 117.4, 117.2, 116.8; IR (KBr, cm^{-1}): 1675 (CHO), 1625, 1600, 1545, 1505, 1450, 1420, 1130, 975, 805, 760, 655; UV–vis (CH_2Cl_2) λ_{max} (nm) (log ε): 234 (4.98), 270 (4.96), 306 (5.02), 398 (4.87), 456 (4.74); MS (m/z): 434 [M$^+$]; Elemental analysis: Calc. for $C_{23}H_{14}OS_4$, C, 63.56%, H, 3.25%. Found, C, 63.33%, H, 3.87%.

*4.1.2. 2(E-2′-formylvinyl)-9,10-bis (1,3-dithiol-4,5-methylthio-2-ylidene)-9,10-dihydroanthracene (**6b**)*

72% yield; m.p.; 270–272°C (dec.); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.75 (1H, d, $J = 7.2$ Hz), 7.74 (1H, d, $J = 1.2$ Hz), 7.64 (1H, d, $J = 7.8$ Hz), 7.58 (1H,d, $J = 15.9$ Hz), 7.60–7.56 (2H, m), 7.52 (1H, dd, $J_1 = 7.8$, $J_2 = 1.2$ Hz), 7.36–7.33 (2H, m), 6.78 (1H, dd, $J_1 = 15.9$, $J_2 = 7.5$ Hz), 2.41 (12H, s); ^{13}C-NMR ($CDCl_3$, 62 MHz) δ: 193.9, 152.3, 137.5, 136.0, 134.2, 133.0, 131.7, 128.6, 126.7, 126.1, 125.6, 125.5, 125.4, 123.0, 19.4, 19.2; IR (KBr, cm^{-1}): 1675 (CHO), 1625, 1600, 1530, 1500, 1455, 1425, 1130, 975, 900, 815, 760; UV–vis (CH_2Cl_2) λ_{max} (nm) (log ε): 234 (5.12), 268 (5.09), 308 (5.04), 406 (4.85), 462 (4.80); MS (m/z): 618 [M$^+$]. Elemental analysis: Calc. for $C_{27}H_{22}OS_8$, C, 52.39%, H, 3.58%. Found, C, 52.73%, H, 3.63%.

*4.1.3. 2(E-2′-formylvinyl)-9,10-bis(1,3-dithiol-4,5-ethylendithio-2-ylidene)-9,10-dihydroanthracene (**6c**)*

56% yield; m.p.: 265–267°C (dec.); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.74 (1H, d, $J = 7.7$ Hz), 7.69 (1H, d, $J = 1.5$ Hz), 7.57 (1H, d, $J = 8.0$ Hz), 7.52 (1H, d, $J = 15.9$ Hz), 7.54–7.50 (2H, m), 7.51 (1H, dd, $J_1 = 8.0$, $J_2 = 1.5$ Hz), 7.49–7.32 (2H, m), 6.79 (1H, dd, $J_1 = 15.9$, $J_2 = 7.7$ Hz), 3.29 (8H, s); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 193.5, 151.9, 137.3, 135.3, 134.2, 134.1, 132.0, 131.7, 131.1, 126.5, 126.0, 125.5, 125.2, 123.1, 122.9, 111.1, 110.9, 29.6, 29.4; IR (KBr, cm^{-1}): 1675 (CHO), 1625, 1600, 1545, 1505, 1455, 1420, 1290, 1125, 975, 925, 815, 760; UV–vis (CH_2Cl_2) λ_{max} (nm) (log ε): 244 (5.36), 272 (5.37), 310 (5.37), 420 (5.13), 476 (5.14); Elemental analysis: Calc. for $C_{27}H_{18}OS_8$, C, 52.74%, H, 2.95%. Found, C, 53.20%, H, 3.17%.

4.2. Synthesis of fulleropyrrolidines ***7a–c****. General procedure*

A toluene solution containing C_{60} (0.14 mmol), *N*-methylglycine (0.70 mmol) and the appropriate aldehyde (**6a–c**) (0.14 mmol) was heated to 90°C for 5 h. The solvent was then evaporated and the crude material was carefully chromatographed on a silica gel column (cyclohexane and cyclohexane–toluene mixtures). Further purification was accomplished by repetitive precepitation and centrifugation in cyclohexane, methanol and diethyl ether.

*4.2.1. N-Methyl-2-[(9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl)ethenyl]-3,4-fulleropyrrolidine (**7a**)*

34% yield; ^{1}H-NMR (300 MHz, $CDCl_3$:CS_2, 1:1) 7.80 (1H, s), 7.68 (1H, d, $J = 9.2$ Hz), 7.61 (2H, q, Syst. AA′XX′), 7.31 (1H, d, $J = 9.2$ Hz), 7.23 (2H, q, Syst. AA′XX′), 7.10 (1H, d, $J = 15.3$ Hz), 6.76 (1H, dd, $J_1 = 15.3$, $J_2 = 8.7$ Hz), 6.22 (4H, m), 4.91 (1H, d, $J = 9.6$ Hz), 4.52 (1H, d, $J = 8.7$ Hz), 4.20 (1H, d, $J = 9.6$ Hz), 2.95 (3H, s); FT-IR (KBr, cm^{-1}): 1540, 1522, 1492, 1411, 1329, 1281, 1260, 1177, 1122, 1030, 969, 887, 752, 553, 525; UV–vis (CH_2Cl_2) λ_{max} (log ε): 248 (2,67); 440 (4,32); MS (FAB$^+$): 1182.

*4.3. N-Methyl-2-[(9,10-bis(1,3-dithiol-4,5-methylthio-2-ylidene)-9,10-dihydroanthracenyl)ethenyl]-3,4-fulleropyrrolidine (**7b**)*

38% yield; ^{1}H-NMR (300 MHz, $CDCl_3$:CS_2, 1:1) 7.65 (1H, s), 7.53 (1H, d, $J = 9.3$ Hz), 7.50–7.41 (3H, m), 7.26 (2H, q, Syst. AA′XX′), 6.97 (1H, d, $J = 15.4$ Hz), 6.80 (1H, dd, $J_1 = 15.4$, $J_2 = 8.7$ Hz), 4.90 (1H, d, $J = 9.0$ Hz), 4.49 (1H, d, $J = 8.7$ Hz), 4.15 (1H, d, $J = 9.0$ Hz), 2.91 (3H, s), 2.35 (12H, s); ^{13}C-NMR (75 MHz, $CDCl_3$:CS_2, 1:1) δ: 145.4, 153.7, 153.1, 147.0, 146.4, 145.9, 145.8, 145.7, 145.5, 145.3, 145.0, 144.9, 144.4, 144.1, 142.8, 142.4, 142.3, 141.9, 141.8, 141.5, 140.0, 139.8, 137.4, 136.1, 135.7, 135.4, 134.8, 134.2, 134.1, 133.8, 131.7, 128.9, 128.6, 127.8, 126.0. 125.6, 125.2, 123.2, 117.2, 117.1, 81.2, 77.1, 69.9, 68.5, 39.8, 29.7; FT-IR (KBr, cm^{-1}): 1540, 1522, 1489, 1456, 1411, 1329, 1281, 1260, 1177, 1122, 1030, 964, 890, 752, 553, 526; UV–vis (CH_2Cl_2) λ_{max} (log ε): 256 (2.45); 438 (5.01); MS (FAB$^+$): 1364.

*4.4. N-Methyl-2-[(9,10-bis(1,3-dithiol-4,5-ethylendithio-2-ylidene)-9,10-dihydroanthracenyl)ethenyl]-3,4-fulleropyrrolidine (**7c**)*

32% yield; ^{1}H-NMR (300 MHz, $CDCl_3$:CS_2, 1:1) δ: 7.61 (1H, s), 7.50 (1H, d, $J = 9.2$ Hz), 7.44–7.38 (3H, m), 7.25 (2H, q, Syst. AA′XX′), 7.07 (1H, d, $J = 15.5$ Hz), 6.77 (1H, dd, $J_1 = 15.5$, $J_2 = 8.7$ Hz), 4.89 (1H, d, $J = 9.0$ Hz), 4.49 (1H, d, $J = 8.7$ Hz), 4.14 (1H, d, $J = 9.0$ Hz), 3.27 (8H, s), 2.91 (3H, s); FT-IR (KBr, cm^{-1}): 1540, 1522, 1453, 1329, 1281, 1260, 1177, 1122, 1030, 964, 819, 797, 749. 685, 553, 524; UV–vis (CH_2Cl_2) λ_{max} (log ε): 254 (2.56); 438 (4.96); MS (FAB$^+$): 1362.

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