PERKIN 2

Long-lived photoproduced radical ions in tetrathiafulvalenes covalently tethered to C_{60}

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C_{60}, or [60]fullerene, a reversible one- to six-electron acceptor with moderate first electron affinity, was covalently linked, *via* a 1,3-dipolar addition reaction using azomethine ylides and two flexible insulating σ-chains of different lengths, to a tetrathioalkyltetrathiafulvalene, a reversible one- to two-electron donor with low first ionization potential, yielding molecules **1** and **2**. The electrochemical oxidation and reduction waves are the same as those of the separate components; UV-VIS spectra indicate no appreciable charge transfer in the ground state between the donor and acceptor moieties of these D–σ–A systems **1** and **2**: there is only a weak shoulder at 800 nm ($\varepsilon \approx 200$ L mol^{-1} cm^{-1}), which could be the intervalence transfer band.

These same molecules, as well as their donor and acceptor components taken separately, were electrochemically oxidized/reduced in liquid solutions, and also irradiated with laser light in low-temperature glasses. The electron paramagnetic resonance (EPR) spectra revealed photoexcited electron transfer at 77 K, with resulting $S = 1/2$ radical cation and radical anion states. In a glass at 77 K these radical signals survive a long time (up to several days) after the end of light irradiation. This may be separately solvated pairs of long-lived radicals $D^{\bullet +}$–σ–A and D–σ–$A^{\bullet -}$ or, less likely, a long-lived excited-state zwitterionic biradical $D^{\bullet +}$–σ–$A^{\bullet -}$. With increasing temperature and the onset of diffusional motion, the EPR signals disappear.

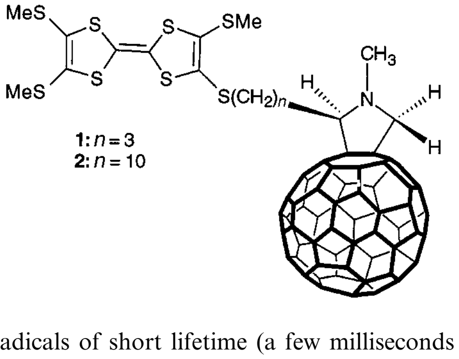
Introduction

The preparation of fullerenes in macroscopic quantities[1] and the chemical functionalization of fullerenes have generated many new fullerene-based materials.[2] The modification of fullerenes makes it possible to design new molecular assemblies with interesting physical and chemical properties on a preparative scale. Furthermore, compounds containing two different, covalently linked electroactive centers have evoked interest for potential applications (electronic devices,[3] rectifiers,[4] superconductors[5]), or for other solid state properties.[6] There has been interest in linking C_{60} to a relatively strong one-electron donor; one such set of donors is the tetrathiafulvalene (TTF) family.[7] Although crystalline 1:1 complexes between C_{60} and both tetratellurafulvalene (TTeF)[8] and bis(ethylenedithiolene)tetrathiafulvalene (BEDT-TTF)[9] have been reported, these complexes show little or no electron transfer in the ground state.[8,9]

The (3+2) cycloaddition reaction of C_{60} is one of the most important methods to obtain functionalized fullerenes. Prato *et al.* reported the 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.[10]

It is believed that long-lived intramolecular photoinduced electron transfer (charge-separated state) in molecules of the type D–σ–A (to a zwitterionic state D^+–σ–A^-) requires a saturated spacer σ between the electron donor (D) and acceptor (A) units; the molecular orbitals of the D and A moieties must be so decoupled as to prevent an immediate back electron transfer process.[11] The goal of stabilizing either the electron-transferred zwitterionic state D^+–σ–A^-, or some suitable daughter radical states, has been a long-standing goal of research leading towards artificial photosynthetic molecules.[11] Photolysis of D–σ–A molecules in a frozen glass at 77 K has produced radicals with a relatively short lifetime (up to 12.7 ms at 77 K [12] or 5 ms at 250 K,[13] which was, however, longer than the D^+–σ–A-σ′–A'^- radical lifetimes at room temperature.[14]

We report here the synthesis, electrochemistry, and photochemistry of two functionalized [60]fullerenes (**1**, and **2**) covalently linked to a tetrathiafulvalene (TTF) by a flexible insulating σ-chain; this is a covalent molecule in which the electron deficient C_{60} is tethered by a flexible chain to an electron donor derived from tetrathiafulvalene.[7] After the synthetic work described herein was completed, a TTF adduct rigidly attached to C_{60} was described, and a new flexible TTF adduct of C_{60} was reported.[15]



1: $n = 3$
2: $n = 10$

Free radicals of short lifetime (a few milliseconds at 80 K) were formed by photoinduced electron transfer for one of these supramolecules (Ru(II)-tris(bipyridine)-coupled C_{60}); their nature was inferred by their *g*-values.[16] Prato *et al.* synthesized

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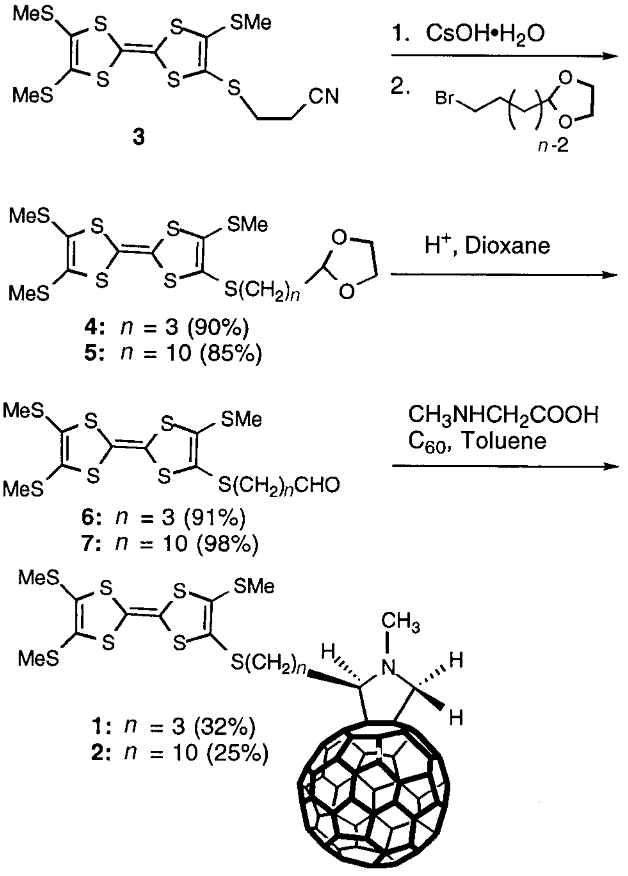
a fulleropyrrolidine, in which a stable aminoxyl (nitroxide) radical is spiro-linked to the pyrrolidine ring:[17] EPR of this compound has shown photoinduced generation of paramagnetic species produced by intramolecular interaction.[17] Photoinduced electron transfer from the excited state has been demonstrated, under steady illumination only, for a conducting polymer mixed with buckminsterfullerene.[18] Adducts of C_{60} connected by norbornylogous bridges to many weak electron donors or acceptors have also been studied.[19] For dimethylaniline linked by an 11-bond rigid bridge to C_{60}, photoexcited electron transfer yielded a charge-separated state with a lifetime of about 0.25 μs at room temperature.[20]

We report below the formation of long-lived radicals, with *g*-values characteristic of the $D^{\bullet +}$ radical cation and the $A^{\bullet -}$ radical anion, from the photoexcitation of D–σ–A molecules **1** and **2**; these radicals are stable for days in a toluene glass at 77 K.

Experimental

Synthetic methodology

The 1,3 dipolar addition of azomethine ylides to C_{60}, recently reported by Prato *et al.*, affords a very convenient way to functionalize [60]fullerenes.[10] The required azomethine ylides are generated *in situ* when *N*-methylglycine and appropriate aldehydes are refluxed in toluene. In our study, two aliphatic aldehydes derived from the readily accessible protected 4,4′,5-tris(methylthio)tetrathiafulvalene-5′-thiolate **3**[21] were used in order to incorporate the TTF unit onto the fullerene sphere. The acetal precursors **4** and **5** were prepared in excellent yield by treatment of **3** with caesium hydroxide monohydrate in *N*,*N*-dimethylformamide solution followed by the addition of 2-(3-bromopropyl)-1,3-dioxolane[22] and 2-(10-bromodecyl)-1,3-dioxolane,[23] respectively (Scheme 1). Hydrolysis of the acetals **4** and **5** in 1,4-dioxane afforded the corresponding aldehydes **6** and **7**.



Scheme 1 Synthesis of **1** and **2**.

The synthesis of the novel fulleropyrrolidine derivatives **1** and **2** was accomplished by refluxing equimolar amounts of the TTF aldehydes **6** or **7**, *N*-methylglycine and C_{60} in toluene for 3 and 8 hours, respectively. After half an hour of refluxing, the original purple C_{60} color turned dark red and finally dark brown. Chromatographic separation (silica, chloroform or toluene–chloroform 1 : 3) afforded **1** and **2** as the main products, together with more polar fractions containing double addition products, as confirmed by PDMS. The fulleropyrrolidines are stable and could be stored for several months without special precautions.

Other experimental procedures

Fresh samples of C_{60} (99.98% pure) were used as received from MER Corp. All reactions were carried out in dry solvents. DMF was allowed to stand over molecular sieves (3 Å) for three days and toluene was distilled from P_2O_5 under an atmosphere of nitrogen.

NMR spectra were obtained using a Bruker Model AM360 NMR spectrometer. UV-VIS spectra were recorded on a Perkin-Elmer Model Lambda 4B spectrophotometer, and also on a Shimadzu 1601 spectrophotometer. Cyclic voltammograms were measured using a PAR 273 potentiostat, in CH_2Cl_2 under nitrogen at room temperature, employing 0.1 M Bu_4NPF_6 (TBAHFP) as supporting electrolyte with a sweep rate of 100 mV s^{-1}. Counter and working electrodes were made of platinum and the reference electrode was SCE. Molecular modeling calculations were performed using HyperChem software (version 4.0, HyperCube, Inc., Waterloo, Ontario) on a Gateway 2000 P5/60 computer: using the AM1/RHF semi-empirical molecular orbital algorithm. Radical cations and radical anions were separately generated electrochemically at room temperature in a small EPR cell[24] placed in the microwave cavity of a Varian E-12 EPR spectrometer. The electrode potential was controlled by a Bio Analytical Systems Model BAS-100W potentiostat. Solutions in CH_2Cl_2 (Aldrich, anhydrous, 99.8%), with 0.1 M TBAHFP added, were bubbled with N_2 and then electrolyzed at the potentials 0.1 V behind the first oxidation or reduction peaks. The photochemical experiments were carried out in quartz EPR tubes, using 10^{-4} molar solutions in toluene (Sigma-Aldrich, HPLC, distilled over P_2O_5 in N_2 atmosphere) and CH_2Cl_2 (Aldrich, anhydrous, 99.8%). The sample solutions were degassed by five freeze-pump-thaw cycles and then illuminated in the rectangular TE_{103} cavity of the Varian E-12 EPR spectrometer by a Questec XeCl-laser ($\lambda = 308$ nm) at 77 K; the EPR spectrum at X-band, using 100 kHz modulation, was digitized on a IBM model XT microcomputer. The microwave frequency was read using a Hewlett Packard Model 5245 M/5255 A frequency counter.

Syntheses

5′-[3-(1,3-Dioxolan-2′-yl)propylthio]-4,4′,5-tris(methylthio)-tetrathiafulvalene (4). 5′-(2-Cyanoethylthio)-4,4′,5-tris(methylthio)tetrathiafulvalene (**3**, 0.42 g, 1.0 mmol) was dissolved in DMF (50 mL) and degassed with N_2 for 30 min. A solution of $CsOH{\cdot}H_2O$ (0.18 g, 1.1 mmol) in MeOH (3 mL) was added in one portion and the solution turned to a slightly darker orange color. After stirring for an additional 30 min, a solution of 2-(3-bromopropyl)-1,3-dioxolane[22] (0.20 g, 1.05 mmol) in degassed DMF (2 mL) was added in one portion. The reaction mixture was stirred for 2 h and the solvent removed *in vacuo*. The resulting orange compound was purified by column chromatography (silica gel, CH_2Cl_2–hexane 19 : 1, $R_f = 0.5$). Evaporation of the solvent yielded 0.43 g (90%) of **4** as an orange oil. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 4.88 (t, $J = 4.1$ Hz, 1H, CH), 3.97 (m, 2H, OCH_2), 3.85 (m, 2H, OCH_2), 2.87 (t, $J = 6.8$ Hz, 1H, SCH_2), 2.43 (s, 6H, SCH_3), 2.42 (s, 3H, SCH_3), 1.80 (m, 4H, CH_2CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 130.05, 127.57, 127.46, 125.56, 111.20, 110.47, 104.01, 64.93, 36.16, 32.41, 24.15, 19.22. MS (EI) m/z 488 (M^+, 100). HRMS: Found 487.9275, calcd. 487.9229. Anal. calcd. for $C_{15}H_{20}O_2S_8$ (488.8): C, 36.86; H, 4.12; S, 52.47. Found: C, 36.95; H, 4.16; S, 52.40%. CV (CH_2Cl_2): $E_{1/2}$ = 0.50 V, 0.85 V.

5′-[10-(1,3-Dioxolan-2-yl)decylthio]-4,4′,5-tris(methylthio)-tetrathiafulvalene (5). Chromatography (silica gel, CH_2Cl_2–hexane 3:1, R_f = 0.45), yield 0.35 g (85%) orange oil. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 4.83 (t, J = 4.7 Hz, 1H, CHO_2), 3.93 (m, 2H, OCH_2), 3.86 (m, 2H, OCH_2), 2.80 (t, J = 7.2 Hz, 2H, CH_2S), 2.42 (s, 6H, SCH_3), 2.41 (s, 6H, SCH_3), 1.60 (m, 4H, CH_2), 1.45–1.2 (m, 14H, CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 129.18, 127.46, 127.40, 126.11, 111.14, 110.21, 104.64, 64.77, 36.26, 33.86, 29.65, 29.44, 29.39 (2C), 29.37, 29.03, 28.40, 24.02, 19.13. Anal. calcd. for $C_{22}H_{34}O_2S_8$ (587.0): C, 45.02; H, 5.84; S, 43.70. Found: C, 45.14; H, 5.86; S, 43.76%. CV (CH_2Cl_2): $E_{1/2}$ = 0.53 V, 0.87 V.

5′-(4-Oxobutylthio)-4,4′,5-tris(methylthio)tetrathiafulvalene (6). The acetal **4** (0.36 g, 0.74 mmol) was dissolved in dioxane (40 mL) and 0.5 M HCl (10 mL) was added. The reaction mixture was stirred at 60 °C for 5 h. The mixture was cooled to room temperature, H_2O (50 mL) was added and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were washed with H_2O (2 × 50 mL), $NaHCO_3$ (50 mL) and NaCl (50 mL) and dried over Na_2SO_4. Removal of the solvent *in vacuo* gave 0.30 g (91%) of **6** as an orange oil, pure by TLC, ^{1}H and ^{13}C NMR for further reactions. Compound **6** is unstable and must be used immediately after preparation. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 9.80 (s, 1H, CHO), 2.85 (t, J = 6.9 Hz, 2H), 2.65 (t, J = 6.9 Hz, 2H, CH_2CHO), 2.43 (s, 9H, SCH_3), 1.96 (quintet, J = 6.9 Hz, 2H, CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 201.13, 131.18, 127.53, 127.42, 124.05, 111.09, 110.56, 42.14, 35.36, 22.94, 19.17. HRMS: Found 443.8994 [M^+]; Anal. calcd. for $C_{13}H_{16}OS_8$, 443.8967%. CV (CH_2Cl_2): $E_{1/2}$ = 0.52 V, 0.86 V.

5′-(11-Oxoundecylthio)-4,4′,5-tris(methylthio)tetraathiafulvalene (7). Chromatography (silica gel, CH_2Cl_2–hexane 3:1, R_f = 0.55), yield 0.27 g (98%) orange oil. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 9.76 (t, J = 1.6 Hz, 1H, CHO), 2.80 (t, J = 7.2 Hz, 2H, CH_2S), 2.42 (s, 9H, SCH_3), 1.60 (m, 4H, CH_2), 1.45–1.2 (m, 14H, CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 202.82, 129.24, 127.49, 127.43, 126.07, 111.11, 110.25, 43.87, 36.25, 29.64, 29.35, 29.28 (2C), 29.10, 29.00, 28.37, 22.04, 19.17 (2C), 19.14. Anal. calcd. for $C_{20}H_{30}OS_8$ (542.9): C, 44.24; H, 5.57; S, 47.24. Found: C, 44.31; H, 5.62; S, 47.33%. CV (CH_2Cl_2): $E_{1/2}$ = 0.52 V, 0.86 V.

***N*-Methyl-2-{3-[4,4′,5-tris(methylthio)tetrathiafulvalen-5′-ylthio]propyl}-3,4-fulleropyrrolidine (1).** To a mixture of **5** (80 mg, 0.18 mmol) and C_{60} (75 mg, 0.12 mmol) in dry toluene (in a 100 mL round-bottom flask equipped with condenser and nitrogen inlet) was added *N*-methylglycine (16 mg, 0.18 mmol). The reaction mixture was refluxed and followed on TLC. After three hours, all of the starting material was gone and the mixture was cooled to room temperature and concentrated to give a dark brown/black powder. The crude material was subjected to column chromatography (silica gel, $CHCl_3$) and unreacted C_{60} (25 mg) collected as the first purple band. The product was collected as a dark brown band (R_f = 0.65) and evaporation of the solvent gave 40 mg (32%) of **5** as a brown powder (48% based on unreacted C_{60}). ^{1}H-NMR (360 MHz, $CDCl_3$): δ 4.81 (d, J = 9.6 Hz, 1H, CH_AH_B in pyrrolidine), 4.12 (d, J = 9.6 Hz, 1H, CH_AH_B in pyrrolidine), 3.90 (t, J = 6.5 Hz, 1H, CH in pyrrolidine), 2.95 (s, 3H, NCH_3), 2.94 (t, J = 7.4 Hz, 2H, SCH_2), 2.54 (quintet, J = 7.4 Hz, 2H, CH_2), 2.39 (s, 3H, SCH_3), 2.35 (s, 3H, SCH_3), 2.33 (s, 3H, SCH_3), 2.25 (2H, m, CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 156.24, 154.32, 154.05, 152.95, 147.27 (2C), 146.31 (2C), 146.19, 146.13 (2C), 146.05, 145.98 (2C), 145.78, 145.73, 145.53 (2C), 145.47, 145.44, 145.41, 145.32, 145.28 (2C), 145.24 (2C), 145.21, 144.72 (2C), 144.42 (2C), 143.10 (2C), 142.99, 142.69, 142.63, 142.51, 142.44, 142.22 (2C), 142.17 (2C), 142.09 (2C), 142.07 (2C), 141.89, 141.85, 141.72, 141.53, 140.27, 140.24, 139.77, 139.67, 137.13, 136.30, 135.89, 135.51, 129.81, 127.47, 126.92, 124.89, 110.96, 110.03, 77.71, 75.76, 70.38, 69.79, 40.02, 36.19, 29.70, 27.35, 19.2, 19.01, 18.80. UV/Vis ($ClCH_2CH_2Cl$) λ_{max}/nm 225, 255, 320, 425, 700 (br). CV (CH_2Cl_2): $E_{1/2}$ = −1.11 V, −0.72 V, 0.50 V, 0.86 V. MS (PDMS): *m/z* 1192.9 [M^+]. Calcd. for $C_{75}H_{21}NS_8$, 1192.5. Bisadduct: MS (PDMS): *m/z* 1664.1 [M^+]. Calcd. for $C_{90}H_{42}N_2S_{16}$, 1664.4.

***N*-Methyl-2-{10-[4,4′,5-tris(methylthio)tetrathiafulvalen-5′-ylthio]decyl-3,4-fulleropyrrolidine (2).** The preparation of **2** was analogous to that of **1**. Upon chromatography (silica gel, $CHCl_3$–toluene 3:1), unreacted C_{60} (15 mg) was collected as the first purple band. The product was collected as a dark brown band (R_f = 0.60) and evaporation of the solvent gave 32 mg (25%) of **2** as a brown powder (31% from reacted C_{60}). ^{1}H-NMR (360 mHz, $CDCl_3$) δ 4.81 (d, J = 9.7 Hz, 1H, CH_AH_B in pyrrolidine), 4.15 (d, J = 9.6 Hz, 1H, CH_AH_B in pyrrolidine), 3.90 (t, J = 7.0 Hz, 1H, CH in pyrrolidine), 2.98 (s, 3H, NCH_3), 2.79 (t, J = 7.3 Hz, 2H, SCH_2), 2.54 (quintet, J = 7.4 Hz, 2H, CH_2), 2.44 (s, 3H, SCH_3), 2.42 (s, 3H, SCH_3), 2.41 (s, 3H, SCH_3), 1.92 (2H, m, CH_2), 1.60 (quintet, J = 7.5 Hz, 2H, CH_2), 1.47 (quintet, J = 7.4 Hz, 2H, CH_2), 1.60–1.3 (m, 12H, CH_2). ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ 156.48, 154.51, 154.43, 153.47, 147.21 (2C), 146.80, 146.51, 146.37, 146.29 (2C), 146.26, 146.16 (2C), 146.10, 146.03, 145.97 (2C), 145.93, 145.79, 145.56, 145.49 (2C), 145.39 (2C), 145.27 (2C), 145.22 (2C), 144.73, 144.56, 144.40, 143.20, 143.04, 142.68 (2C), 142.66 (2C), 142.60, 142.20 (2C), 142.16 (2C), 142.11 (2C), 142.05 (2C), 141.79, 141.72, 141.65, 140.27, 140.19, 139.71, 139.57, 137.18, 136.26, 135.84, 135.52, 128.98, 127.53, 127.39, 126.20, 111.18, 110.24, 78.21, 76.26, 70.46, 70.09, 40.06, 36.28, 30.95, 30.00, 29.68, 29.31, 29.14, 29.01, 28.44, 27.33, 27.10, 19.19, 19.16, 19.09. UV/Vis ($ClCH_2CH_2Cl$) λ_{max}/nm 225, 255, 316, 420, 650 (br). CV (CH_2Cl_2): $E_{1/2}$ = −1.08V, −0.70V, 0.51V, 0.85V.

Results

NMR Spectra

The ^{1}H-NMR spectra of **1** and **2** clearly show the formation of a fulleropyrrolidine substituted in the 3 position by the linked TTF. The CH_2 protons in the pyrrolidine ring give a nice AB pattern, and appear as two doublets at 4.81 ppm and 4.12 ppm, respectively, due to geminal coupling (J_{AB} = 9.5 Hz); the CH proton in the ring appears as a triplet at 3.90. Another interesting observation is that the resonances for the three methylthio groups in **1** and **2**, while identical in the precursor compound **5**, are split into three distinct signals in **1** and **2**.

The ^{13}C-NMR spectra of **1** and **2** are very similar. Forty-four signals are observed in the fullerene sp^2 region between 135 and 156 ppm with some lines overlapping. Due to the presence of a chiral carbon in the pyrrolidine ring, all the carbons in the sphere should ideally be nonequivalent. Indeed, this compound lacked C_{2v} symmetry, making the carbon spectra very complicated (Fig. 1). Gan *et al.* have also reported the same number of C_{60} skeleton signals for other fulleropyrrolidines containing a chiral pyrrolidine carbon.[25] The TTF unit gives rise to six signals between 110 and 130 ppm, which is comparable with the spectrum of the precursor aldehydes **6** and **7**. The fullerene sp^3 carbons appear at 76 and 70 ppm and the pyrrolidine ring carbon at 78 and 70.5 ppm for both **1** and **2**. Four and eleven lines in the 27–40 ppm region were assigned to the chain carbon and the *N*-methyl carbon for **1** and **2**, respectively. The three methylthio groups give rise to three lines around 19 ppm.

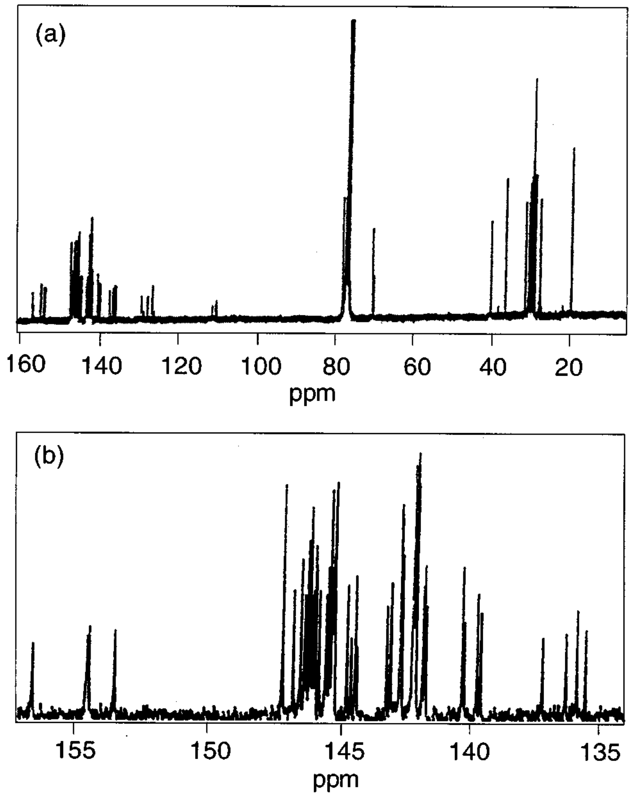


Fig. 1 ^{13}C-NMR spectrum of **2** (a) and expanded spectrum of **2** (b).

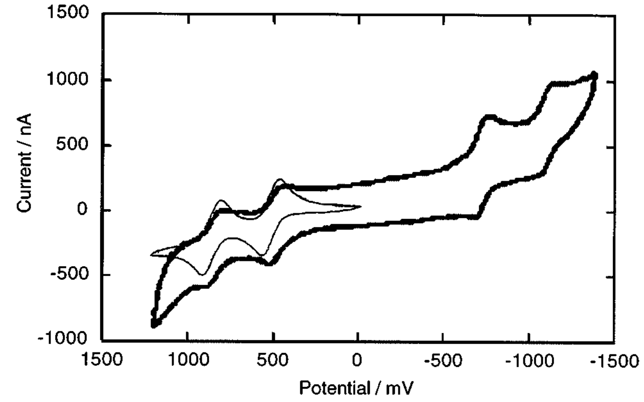


Fig. 2 Cyclic voltammograms of **1** (bold line) and **6** (thin line). For conditions see Table 1. The reversibility of the weaves is analysed in Table 2.

Cyclic voltammetry

The cyclic voltammograms (CVs) at room temperature of both **1** and **2** show four quasi-reversible one-electron redox waves, two redox waves from the TTF portion (oxidation) and two from the C_{60} portion (reduction) (Fig. 2). The half-wave potentials for all new compounds are collected in Table 1. The two reduction waves (within the range of the solvent employed) for the C_{60} unit are comparable with other functionalized [60]fullerenes[26] and C_{60};[27] the oxidation waves are comparable to those for TTF (**8**),[28] and BEDT-TTF (**9**).[29]

The halfwave potentials of the TTF moiety are very close for both the precursor TTF's **4**–**7** and for the TTF fullerenes **1** and **2**, which are seen as two redox waves at 0.50–0.53 and 0.85–0.86 V. Given the solvent used, only the first two of the six known reduction waves for the C_{60} ends of **1** and **2** could be determined. No appreciable shift of the oxidation or reduction potentials of **1** or **2** from those of the separate TTF and C_{60} components were seen.

Quantitative criteria for chemical and electrochemical reversibility for the oxidations and reductions in **1** and **6** are examined in Table 2. The criterion $\Delta E = 0.059$ for electrochemical reversibility of a one-electron oxidation or reduction is met approximately for the first and second reduction of **1**; the separation between peaks is larger for the other waves. The criterion for chemical reversibility (the equality $|i_{p,a}/i_{p,c}| = 1$ of the absolute values of the peak anodic and cathodic currents), is difficult to establish from Fig. 2, because of the large charging current: ratios $|i_{p,a}/i_{p,c}| = 0.52$ to 1.37 are measured. So the oxidations and reductions of **1** can be taken to be quasi-reversible.

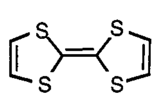
Table 1 Electrochemical cyclic voltammogram half-wave potentials[a]

Compound	$E^1_{1/2}$/V[b]	$E^2_{1/2}$/V[b]	$E^3_{1/2}$/V[b]	$E^4_{1/2}$/V[b]
C_{60}	—	—	−0.85	−1.28
TTF (**8**)	0.71	0.35	—	—
BEDT-TTF (**9**)	1.0	0.6	—	—
4	0.85	0.50	—	—
5	0.87	0.53	—	—
6	0.86	0.52	—	—
7	0.86	0.52	—	—
1	0.86	0.50	−0.72	−1.11
2	0.85	0.51	−0.70	−1.08

[a] Measured in dichloromethane under nitrogen at room temperature, employing 0.1 M Bu_4NPF_6 as supporting electrolyte with a sweep rate of 100 mV s^{-1}, Pt counter and working electrodes and an SCE reference electrode. Data for C_{60}, TTF (**8**), and BEDT-TTF (**9**) are from refs. 27, 28, and 29, respectively. [b] V *vs.* SCE.

UV-Visible spectra

Comparison of the UV-VIS spectrum of **1** with those of **10** and **11** (Fig. 3) shows that the TTF and fullerene moieties retain the electronic properties of the original molecules, with peaks around 225, 255, 320, 420 and 680 nm, and a weak peak at 700 nm, characteristic of the pyrrolidino-fullerene part of the molecule.[10] The spectrum of **1** also shows a new, broad, but weak shoulder extending from 400 nm to 1000 nm, which may be an intervalence transfer (IVT) band centered at about 800 nm ($\varepsilon \approx 200$ L mol^{-1} cm^{-1}) (Fig. 3, inset).



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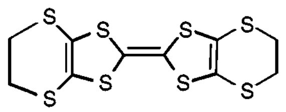

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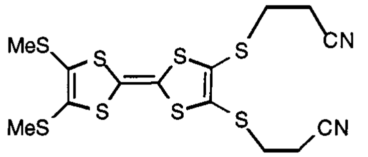

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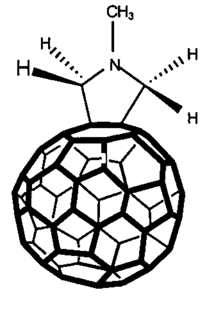

11

Calculation of molecular conformations of 1

Two conformers of **1** were obtained by AM1. A bent con-

Table 2 Analysis of reversibility of oxidations and reductions for **1** and **6**, from the CV of Fig. 1. Listed are the peak potentials E_p, their differences ΔE (which should equal 0.059 V for an electrochemically reversible wave), the peak anodic and cathodic currents i_p approximately corrected for the charging current, the ratios ($|i_{p,a}/i_{p,c}|$) (which should equal 1 for a chemically reversible wave), and the average of the peak potentials ($\approx E_{1/2}$).

	First reduction		Second reduction		First oxidation		Second oxidation	
Compound	E_p/V	i_p/nA	E_p/V	i_p/nA	E_p/V	i_p/nA	E_p/V	i_p/nA
1	−0.758	−198	−1.140	−148	0.512	−146	0.899	−73
	−0.681	145	−1.081	119	0.432	117	0.799	140
ΔE, $\|i_{p,a}/i_{p,c}\|$	0.077	1.37	0.063	1.24	0.080	1.25	0.100	0.52
$E_{1/2}$	−0.720		−1.113		0.472		0.849	
								253
6					0.565	230	−0.926	247
					0.452	262	0.803	1.02
ΔE, $\|i_{p,a}/i_{p,c}\|$					0.113	0.88	0.123	
$E_{1/2}$					0.509		0.865	

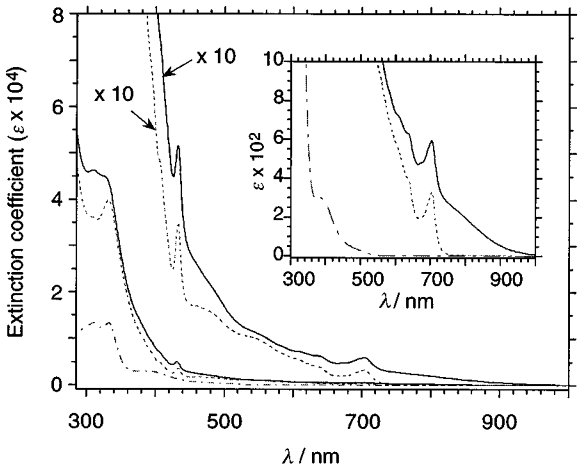

Fig. 3 UV-VIS optical absorption bands of **1** (——), **10** (–·–·–·–) and **11** (-----) in toluene solutions at 298 K, also shown in 10 × magnification for **1** and for **11**. Inset: details of all three spectra at low extinction coefficients.

former (TTF close to C_{60}) is lower in energy, with a dipole moment of 3.0 Debyes; an extended conformer is 21 kJ mol^{-1} higher, with a dipole moment of 4.0 Debyes. This suggests that at room temperature several conformers of **1** may coexist at equilibrium.

Electrogeneration of radicals of the donor

There was no EPR signal from a solution of **10** before its electrochemical oxidation. The radical cation of **10** (TTF-$(SMe)_2(SC_2H_4CN)_2{}^+$) was generated electrochemically in dichloromethane solution. Its EPR signal is narrow at room temperature ($g = 2.0079 \pm 0.0002$, linewidth $\Delta H_{p\text{-}p} = 2$ Gauss), then broadens as the solution is cooled to 77 K ($g = 2.0078 \pm 0.0002$, $\Delta H_{p\text{-}p} = 14$ G): this signal is characteristic for a tetrathiafulvalene derivative (see Table 3).

Photogeneration of radicals of the donor and the acceptor

The TTF-like cation of **10** was also generated photochemically by XeCl-laser irradiation of frozen CH_2Cl_2 solution and also a frozen toluene glass (although the yield of radicals was much less in toluene). The EPR spectrum has parameters $g = 2.0078 \pm 0.0001$ and $\Delta H_{p\text{-}p} = 14.0$ G for the CH_2Cl_2 solution frozen to 77 K (Fig. 4(a)), and a similar but slightly broader spectrum in a frozen toluene glass ($g = 2.0078 \pm 0.0002$, $\Delta H_{p\text{-}p} = 17.2$ G). These data coincide with the EPR-parameters of the $\mathbf{10}^+$ cation generated electrochemically and cooled to 77 K, and are also in close agreement with the EPR parameters in the literature for TTF^+ ($\mathbf{8}^+$)[30] and for BEDT-TTF^+ ($\mathbf{9}^+$).[31]

Irradiation of C_{60} in toluene at 77 K by XeCl-laser produced a complex spectrum (Fig. 4(b)): a narrow and intense EPR signal characteristic of fullerene anion ($g = 2.0000 \pm 0.0001$, $\Delta H_{p\text{-}p} = 3.6$ G), in agreement with earlier reports on the electrolytically generated $C_{60}{}^{-\bullet}$ radical monoanion ($g = 2.0000 \pm 0.0002$),[32] as well as two less intense lines. A triplet signal was not seen.

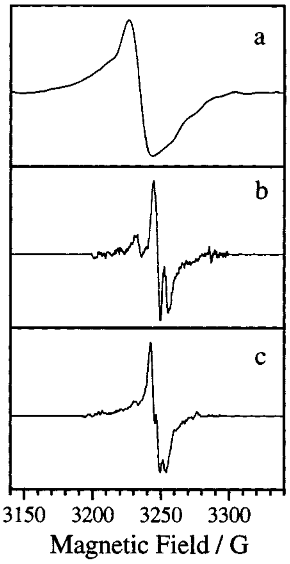

Fig. 4 EPR spectra (microwave power = 5 mW, frequency 9.0914 GHz) of (a) $(TTF(SMe)_2(SC_2H_4CN)_2{}^+)$, **10** in frozen CH_2Cl_2, (b) C_{60} in frozen toluene (c) C_{60}-$N(Me(CH_2)_2)$, **11** in frozen toluene, irradiated by a XeCl laser at 77 K (dose 20–50 J per sample), then measured at 77 K with the laser turned off.

Irradiation of **11** in toluene by XeCl-laser gave an EPR spectrum which is similar to the case of C_{60} in toluene, but the main signal ($g = 1.9998 \pm 0.0001$, $\Delta H_{p\text{-}p} = 3.0$ G) is less intense, and a second, distinctive signal ($g = 2.00223$, $\Delta H_{p\text{-}p} = 3.2$ G) is seen (Fig. 4(c)).

Photolysis of solutions of both unsubstituted C_{60} and of **11** in CH_2Cl_2 produced, instead, an EPR signal ($g = 2.0028 \pm 0.0001$, $\Delta H_{p\text{-}p} = 1.8$ G). This g-value is much greater than that of fullerene monoanion, is characteristic of π radicals with no spin-orbit coupling, and is attributable to adducts of C_{60} with free radicals produced by photolysis or radiolysis of the CH_2Cl_2 solvent molecules.[33] Therefore, further use of dichloromethane was avoided below.

Photolysis of an equimolar mixture of **10** and **11** in toluene by XeCl-laser irradiation, cooled to 77 K, produced an intense and complex EPR spectrum (Fig. 5): a broader signal ($g = 2.0078$, $\Delta H_{p\text{-}p} = 17.2$ G) is accompanied by a narrower signal ($g = 2.0035 \pm 0.0002$, $\Delta H_{p\text{-}p} = 6.4$ G), but no signal around $g = 2.0000$ was observed. This spectrum persisted several days after turning off the laser light, as long as the temperature was held at 77 K. After warming to 120 K for 10 min, the initial spectrum changed (see Fig. 4) to the spectrum typical for irradiation of pure toluene. However, to obtain the same EPR

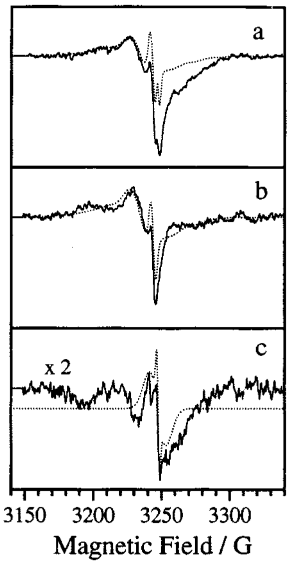

Fig. 5 EPR spectrum (microwave power = 5 mW, frequency 9.0914 GHz) of an equimolar mixture (8×10^{-5} M) of **10** and **11** in frozen toluene, irradiated by a XeCl laser at 77 K (dose 20–50 J per sample), then (a) measured at 77 K with the laser turned off; (b) EPR spectrum measured at 77 K after warming for 10 min at 120 K. (c) Difference spectrum [(a) minus (b)]. Dashed lines: simulations.

intensity in pure toluene, ten times more light exposure had to be used. Irradiation of pure toluene at the light intensities used for the mixture of **10** and **11**, negliglible toluene radical signals were observed.

Photogeneration of covalently linked donor and acceptor radicals

Photolysis of a frozen light brown toluene solution of C_{60}-$NMe(CH_2)_2$-$(CH_2)_3$-TTF (**1**) at 77 K by XeCl-laser irradiation produced five superimposed EPR signals, with an overall quantum efficiency of about 10^{-4}. Such a spectrum is shown in Fig. 6(a), and consists of the following lines: two broad ones ($g = 2.0078$, $\Delta H_{p\text{-}p} = 17.3$ G and $g = 2.0026$, $\Delta H_{p\text{-}p} = 26$ G), a narrow one ($g = 2.0001 \pm 0.0001$, $\Delta H_{p\text{-}p} = 2.6$ G), and two intermediate ones ($g = 2.0033$, $\Delta H_{p\text{-}p} = 4.2$ G and $g = 2.0023$, $\Delta H_{p\text{-}p} = 8$ G). When the laser was kept on during the EPR measurement, the signal was not appreciably larger than that shown in Fig. 6(a). The same sample was then warmed for 10 min at 120 K, then cooled back to 77 K: the narrowest high-field signal ($g = 2.0033$, $\Delta H_{p\text{-}p} = 4.2$ G) and broad signal ($g = 2.0026$, $\Delta H_{p\text{-}p} = 26$ G) disappeared, and only the TTF-like and π-radical-like broad signals remained [Fig. 6(b)]. The difference spectrum [Fig. 6(c)] shows that the signals that have decayed during the short "warming" above the softening temperature of toluene are one signal due to C_{60} ($g = 2.0001$, $\Delta H_{p\text{-}p} = 2.6$ G), plus signals due to typical π-radicals ($g = 2.0033$, $\Delta H_{p\text{-}p} = 4.2$ G and $g = 2.0026$, $\Delta H_{p\text{-}p} = 2.6$ G). A broad signal with $g = 2.0026$ gives a 92% contribution to this difference spectrum.

Photolysis of a frozen light brown toluene solution of **2** at 77 K by XeCl-laser irradiation yields four superimposed EPR signals, with an overall quantum efficiency of about 10^{-4}. The spectrum is shown in Fig. 7(a), and consists of a broad resonance line ($g = 2.0078$, $\Delta H_{p\text{-}p} = 17.2$ G), a narrow line ($g = 2.0001 \pm 0.0001$, $\Delta H_{p\text{-}p} = 2.6$ G), and intermediate lines ($g = 2.0003$, $\Delta H_{p\text{-}p} = 12$ G and $g = 2.0024$, $\Delta H_{p\text{-}p} = 3.6$ G). After warming the sample for 10 min at 120 K, then cooling back to 77 K, the signals with $g = 2.0001$ and $g = 2.0003$ disappear, and only the broad signals remain: the TTF-like signal (≈ 50%) and the "toluene" signal (≈ 50%). The difference spectrum [Fig. 7(c)] shows that the signals that have decayed are one signal due to C_{60} anion ($g = 2.0001 \pm 0.0001$, $\Delta H_{p\text{-}p} = 2.6$ G), plus a broad signal ($g = 2.0003 \pm 0.0001$, $\Delta H_{p\text{-}p} = 12 \pm 2$ G).

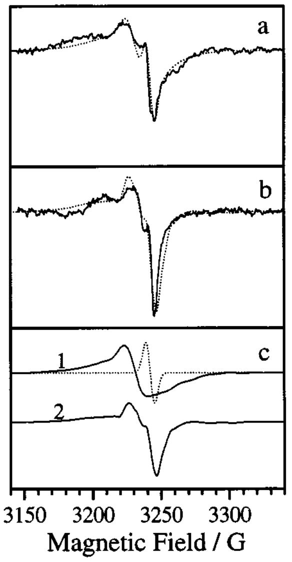

Fig. 6 EPR spectrum (microwave power = 5 mW, frequency 9.092 GHz) of **1** in frozen toluene (8×10^{-5} M), irradiated with a XeCl laser at 77 K (same conditions as for Fig. 5), then (a) measured at 77 K with the laser turned off, dashed line: simulation; (b) EPR spectrum measured at 77 K after warming for 10 min at 120 K, dashed line: simulation. (c) difference spectrum: (c2) difference [(a) minus (b)], (c1) dashed line: narrow component of (c2) due to C_{60}; (c1) solid line: π-radical signal, difference between (c2) and the dashed line of (c1).

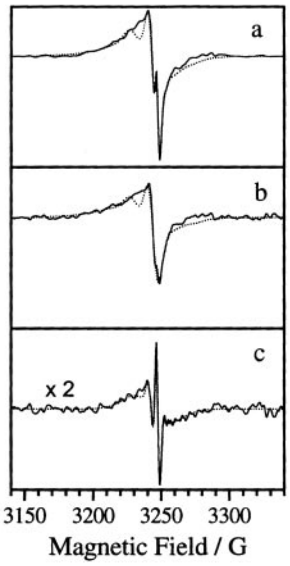

Fig. 7 EPR spectrum of **2** (8×10^{-5} M), in frozen toluene, irradiated with a XeCl laser at 77 K (same conditions as for Fig. 5), then (a) measured at 77 K with the laser turned off; (b) EPR spectrum measured at 77 K after warming for 10 min at 120 K. (c) Difference spectrum [(a) minus (b)]. Dashed lines: simulations.

Discussion

The CVs indicate that the D end and the A end of molecules **1** and **2** act independently; no new intramolecular redox peak appears, nor are the D and A peak potentials shifted appreciably, compared to the redox potentials of the separate D and A components. A large electron transfer is not observed in the ground state between the C_{60} core of **1** or **2** and the tethered tetrathioalkyl TTF donor units. In view of the modest acceptor properties of C_{60}, large electron transfer in the ground state can be expected only in analogs of **1** and **2** derived from a much stronger donor than TTF; such a donor would be exceptionally air-sensitive. In accord with our results, no ground state charge separation occurs even for "$C_{60}{}^{3}$TMPD", where TMPD (*N*,*N*,*N*′,*N*′-tetramethyl-*para*-phenylenediamine) is a stronger donor than TTF.[20]

Table 3 EPR parameters for electrogenerated (E) or photogenerated (P) signals. The relative intensities are from the spectral simulations. Numbers in parentheses are standard deviations

Compound	Solvent	P/E	T/K	g-value	$\Delta H_{p\text{-}p}$/G	Rel. intensity (%)
$TTF(SMe)_2(SC_2H_4CN)_2$ (**10**)	CH_2Cl_2	P	298	2.0079(2)	2.0	
	CH_2Cl_2	P	77	2.0078(2)	14.0	
	CH_2Cl_2	E	298	2.0079(2)	2.0	
[a]	CH_2Cl_2	E	77	2.0078(2)	14.0	
	$C_6H_5CH_3$	P	77	2.0078(2)	17.2(5)	
C_{60}	$C_6H_5CH_3$	P	77	2.0000(1)	3.6	
	CH_2Cl_2	P	77	2.0028(1)	1.8	
C_{60}–N(Me(CH_2)$_2$ (**11**)	$C_6H_5CH_3$	P	77	1.9999(1)	3.0	
				2.00223(1)	3.2	
	CH_2Cl_2	P	77	2.0028(1)	1.8	
Equimolar mixture of **10** + **11** (initial signal)	$C_6H_5CH_3$	P	77	2.0035	6.4	4.2
				(2.0078)	(17.2)	78
				2.0023		18
Equimolar mixture of **10** + **11** (difference after warming to 120 K)	$C_6H_5CH_3$	P	77	2.0035	6.4	
				2.0078	17.2	
1[b]	CH_2Cl_2	P	77	2.0032(1)	1.8	
				2.0062(5)	12	
1 (initial signal)	$C_6H_5CH_3$	P	77	2.0001(1)	2.6	0.76
				2.0023	8	10.6
				2.0026	26	16
				2.0033(5)	4.2	0.7
				(2.0078)	(17.3)	72.8
1 (difference after warming to 120 K)[c]	$C_6H_5CH_3$	P	77	2.0001(1)	2.7	4.4
				2.0026(10)	26	92
				2.0033	4.2	4.1
2 (initial signal)	$C_6H_5CH_3$	P	77	2.0001	2.6	0.2
				2.0003	12	4
				2.0024(1)	3.6	0.8
				2.0078	17.2	42
2 (difference after warming to 120 K)[c]	$C_6H_5CH_3$	P	77	2.0001(2)	2.6	0.5
				2.0003(5)	12	9.7
				2.078?	17.2?	≈90

[a] Radical generated at 298 K, then frozen to 77 K. [b] Radical adduct of C_{60} is formed with solvent, after photolysis of a solvent C–Cl bond; see ref. 33. [c] Photolysis and first EPR spectrum at 77 K are followed by warming to 120 K for 10 min, by cooling to 77 K and a second EPR spectrum, which is then subtracted from the first one.

The UV-VIS spectra of **1** and **2** (Fig. 3) show new broad shoulders in the visible region (400 to 1050 nm), that could be a weak intervalence transfer (IVT) band,[34] which should allow a very small mixing of the zwitterion state D^+–σ–A^-- with the ground state D–σ–A.

The photogeneration of $S = 1/2$ anion radicals of C_{60} and of **11** in toluene must be accompanied by the formation of appropriate solvent counterions. The assignment of $g = 2.0001(1)$ to a $S = 1/2$ anion radical $C_{60}^{-\bullet}$ is straightforward,[32] although there is some discussion about how many EPR signals, broad or narrow, exist for $C_{60}^{-\bullet}$.[35] It is interesting that an EPR signal with low g-value (close to that of $C_{60}^{-\bullet}$) is observed in **1** or **11** despite the lowering of symmetry of the C_{60} cage in the fulleropyrrolidine. No triplet signals with zero-field splittings were observed (and no $\Delta m = 2$ transition at half-field) for any of the species studied.

For solutions of C_{60} in CH_2Cl_2, a photolytic cleavage of a C–Cl bond in the solvent is followed by addition of the resulting photofragment onto the fullerene cage, as reported previously for C_{60} in dichloroethane solutions:[33] this is why the observed g-value in CH_2Cl_2 solution is no longer characteristic of $C_{60}^{-\bullet}$ ($g = 2.0000$), but is shifted to values more typical for conventional organic π-radicals ($g = 2.0028$).

During the photogeneration of $TTF^{+\bullet}$ -like radicals for **10**, the counterion radicals that may be photogenerated in the solvent were not detected, presumably because of rapid spin exchange. For molecule **10**, the identity of the EPR parameters of the photoproduced radicals with the radicals obtained by electrochemical mono-oxidation confirms the assignment of the $g = 2.0078 \pm 0.0002$ signal to the $TTF^{+\bullet}$-like radical.

When an equimolar mixture of **10** and **11** was photoirradiated, the EPR spectrum (Fig. 5) resembled more the EPR spectrum of D–σ–A molecule **2** (longer tether; Fig. 7) than the EPR spectrum of **1** (shorter tether, Fig. 6).

The flexible tethers in the D–σ–A molecules **1** and **2** may allow different conformations in solution at room temperature, including one where the TTF is directly above the C_{60} cage. In toluene at 77 K, a temperature at which diffusional motion is arrested,[36] **1** is probably a mixture of several frozen conformers; at 120 K, which is above the softening point of toluene (113 K[36]), the increased mobility of the solvent allows intermolecular approaches, chemical reactions, and maybe even a radical-assisted polymerization of the C_{60} species. The net result is a decrease of the EPR signals.

For molecules **1** and **2** there is a low quantum efficiency for radical formation (*ca.* 10^{-4} spins per photon). Table 3 shows, within the limits of EPR signal simulation, an unequal relative distribution of cation radicals $D^{\bullet +}$ (73% for **1**, 42% for **2**) *versus* anion radicals $A^{\bullet -}$ (0.8% for **1**, 4.4% for **2**). Since the EPR experiment, using 100 kHz modulation, detects radicals with relatively long lifetimes (>10 μs), one must presume that the different product intensities ($TTF^{\bullet +}$, $C_{60}^{-\bullet}$) arise either from different rates of formation for anion radicals *vs.* cation radicals at the two ends of the D–σ–A molecules, or from different decay rates for these radicals.

There seem to be two choices for the interpretation of Figs. 6 and 7: (a) assign the EPR spectra to separately solvated $D^{\bullet +}$–σ–A and D–σ–$A^{\bullet -}$ species; (b) assign the EPR spectra to some long-lived $D^{\bullet +}$–σ–$A^{\bullet -}$ species. These two choices are discussed in turn below.

(a) Solvated $D^{\bullet +}$–σ–A and D–σ–$A^{\bullet -}$ species

If anion radicals and cation radicals are formed independently of each other, then one opines eqns. (1) and (2), where (solv) is

$$\mathrm{D{-}\sigma{-}A\ (solv)} \xrightarrow{h\nu} \mathrm{D^{\bullet+}{-}\sigma{-}A\ (solv^{\bullet-})} \qquad (1)$$

$$\mathrm{D{-}\sigma{-}A\ (solv)} \xrightarrow{h\nu} \mathrm{D{-}\sigma{-}A^{\bullet-}\ (solv^{\bullet+})} \qquad (2)$$

the solvent (toluene). This first hypothesis is supported by the photoproduction of TTF-like radicals in a toluene solution of pure **10** at 77 K (Table 3 and Fig. 4(a)), and by the photoproduction of C_{60}-like radicals in a toluene solution of **11** at 77 K (Table 3 and Fig. 4(c)). The $S = 1/2$ radicals may also be formed from an initial biradical [eqn. (3)], that is followed by

$$\mathrm{D{-}\sigma{-}A\ (solv)} \xrightarrow{h\nu} \mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv)} \qquad (3)$$

either solvent-induced radical migration [eqns. (4) and (5)], or

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv) + D{-}\sigma{-}A\ (solv)} \longrightarrow \mathrm{D{-}\sigma{-}A^{\bullet-}\ (solv) + D^{\bullet+}{-}\sigma{-}A\ (solv)} \qquad (4)$$

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}} \longrightarrow \mathrm{D{-}\sigma{-}A + solvent\ radicals} \qquad (5)$$

by unequal attack by the solvent on the two ends of the molecule: [eqns. (6) and (7)].

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv)} \longrightarrow \mathrm{D^{\bullet+}{-}\sigma{-}A\ (solv^{\bullet-})} \xrightarrow{(120\ \mathrm{K})} \mathrm{solvent\ radicals} \qquad (6)$$

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv)} \longrightarrow \mathrm{D{-}\sigma{-}A^{\bullet-}\ (solv^{\bullet+})} \xrightarrow{(120\ \mathrm{K})} \mathrm{solvent\ radicals} \qquad (7)$$

If the biradical $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ is formed [eqn. (3)] "through space",[37] *i.e.* not involving the molecular orbitals of D–σ–A, then the biradical may be formed most efficiently for the fraction of the conformers of **1** and **2** for which the TTF is found relatively close to the C_{60} end: this fraction is presumably small, and would argue for low photoproduced EPR signals. If, instead, the electron transfer and formation of the biradical $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ is "through bond",[37] then this process should be easier for **1** (where there are only 6 atoms in the bridge between D and A) than for **2** (where there are 12 atoms in the bridge between D and A). The low intensity of the IVT shoulder for both **1** and **2** between 400 and 1000 nm (Fig. 3) supports a low electron transfer efficiency. When considering eqn. (4), one should remember that in these dilute solutions (10^{-4} mol L^{-1}) the average estimated isotropic distance between solute molecules **1** (or **2**) is 260 Å, or about 8 molecular diameters.

(b) Long-lived $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ species

The formation of the biradical $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ (eqn. (3)) should be an endothemic process: the LUMO of C_{60} is about 4 electron volts (eV) above the HOMO of TTF, when both molecules are at infinite separation, and, because of Coulomb attraction of the $\mathrm{D^{\bullet+}}$ end for the $\mathrm{A^{\bullet-}}$ end in the zwitterion, the ground state of $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ may still be about 2 eV above the ground state D–σ–A for molecule **1**. Unless a large reorganization of the molecular geometry occurs upon biradical formation, a biradical should rapidly (within μs to ms at 77 K, or seconds at 4 K) recombine to re-establish the neutral D–σ–A state, as in eqn. (8).

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv)} \longrightarrow \mathrm{D{-}\sigma{-}A\ (solv)} \qquad (8)$$

This biradical $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ should be then too short-lived to be observed on the EPR time scale. Since the EPR signal is the same with the laser on and the laser off, extra radicals detectable by EPR are not produced. If the EPR signal were due to the biradical $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ at 77 K, then its persistence could be due to some severe Jahn–Teller distortion, or conformational change, which would stabilize some new $\mathrm{D^{\bullet+}}$–σ–$\mathrm{^{\bullet}A^{-}}$ biradical state, eqn. (9).

$$\mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (solv)} \longrightarrow \mathrm{D^{\bullet+}{-}\sigma{-}A^{\bullet-}\ (new\ geometry;\ solv)} \qquad (9)$$

However, for the EPR study of D–σ–A = porphyrin–σ–quinone at 77 K[38] the assignment of the long-lived EPR signal to the $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ biradical[38] has been criticized;[39] this same criticism may be valid here for D–σ–A = **1** or **2**. Furthermore, in four studies, the fluorescence lifetimes τ observed for the charge-separated state are too short to yield a persistent paramagnetic resonance signal in $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$: for DMA[11]C_{60} (where DMA = dimethylaniline) at room temperature $\tau = 0.25$ μs;[20] for a carotene-C_{60} dyad at room temperature $\tau = 0.53$ ns;[40] for a carotene-porphyrin-fullerene triad at 77 K $\tau = 12$ ps to 7.43 ns;[41] for a fullerene-ferrocene dyad at 77 K $\tau = 1.8$ to 2.5 μs.[42] One should also note that the quantum efficiency for production of the radical species is quite low. A fluorescence lifetime study would determine whether eqn. (9) is applicable.

To summarize, photoexcitation of two tethered TTF–σ–C_{60} molecules **1** and **2** has yielded persistent EPR signals that can be attributed to the donor radical cation and to the acceptor radical anion; these signals are persistent at 77 K, but have unequal calculated intensities. At present one cannot claim that these signals are due to isolated and persistent $\mathrm{D^{\bullet+}}$–σ–$\mathrm{A^{\bullet-}}$ biradicals.

Conclusion

In photoirradiated TTF–σ–C_{60} molecules **1** and **2**, with a saturated bridge linking the donor (TTF) to the acceptor (C_{60}) moieties, a persistent narrow EPR signal characteristic of the $C_{60}{}^{-\bullet}$ radical monoanion ($g = 2.0001$), plus a broad line assignable to $\mathrm{TTF^{+}}$ ($g = 2.0078$) were observed in frozen toluene glass at 77 K, with different intensities. These signals are stable for several days, and can be attributed to long-lived radicals at the two ends of the molecules (radicals on the same molecule or on different molecules).

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Paper 8/03737J