Chromophore-Appended C_{60} and C_{70} Fullerenes: Anthracene and Pyrene Derivatives – Syntheses, Cyclic Voltammetry, and Spectra

Thomas Gareis, Oliver Köthe, and Jörg Daub*

Institut für Organische Chemie, Universität Regensburg,
Universitätsstraße 31, D-93040 Regensburg, Germany
Fax: (internat.) + 49(0)941/943-4984
E-mail: joerg.daub@chemie.uni-regensburg.de

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C_{60} and C_{70} adducts containing spacer-linked phenyl (**BK1**), 9-anthracenyl (**BK2**), 4-(9-anthracenyl)phenyl (**BK3**), and 1-pyrenyl groups (**BE1** and **FE1**) have been studied. Two different synthetic pathways were employed based on the [4+2] cycloaddition of fullerenes with 2-trimethylsiloxy-1,3-butadienes (**TB**). Spectroscopic data for the new compounds are given. Electrochemical and optoelectrochemical studies were undertaken by using cyclic voltammetry and spectroelectrochemical methods. The fluorescence emission spectra of **BK2**, **BK3**, **BE1**, and **FE1** are reported. Intramolecular energy transfer from the excited fluorophore to the fullerene subunit is shown to occur.

Introduction

The delocalized, highly unsaturated, and strained structure of the spheroidal-shaped fullerenes makes them candidates for a wide range of applications in chemistry, medicine, and technology[1]. After their discovery[2] and production in gram quantities by resistive evaporation of graphite[3] intensive studies, mainly with buckminsterfullerene C_{60} (I_h symmetry), were undertaken in order to determine their photophysical[4] and chemical properties[5] as well as to investigate possible biomedical perspectives[6]. Although the chemistry of buckminsterfullerene has been well exploited, the derivatization and study of C_{70} (D_{5h} symmetry) and higher fullerenes is still fragmentary[7]. Much work has been devoted to multifunctionalization routes[8], supramolecular architectures[9], ring-opening reaction sequences and synthesis of fullerenes bearing heteroatoms[10]. In addition to the chemistry of their ground states, fullerenes in excited states are attractive compounds for chemical processes due to the propensity to populate long-lived triplets by singlet−triplet intersystem crossing[11]. Access and utilization of excited-state chemistry is expected to be favored in dye-functionalized fullerenes by virtue of an “antenna effect” of the extra chromophores[12].

The present communication reports on the synthesis and characterization of fullerene derivatives appended with aryl groups as represented by **BK1**, **BK2**, **BK3**, **BE1**, and **FE1**[*] (Scheme 1). Investigations of the electrochemical and spectroscopic properties are reported. Previously, we have presented preliminary results on singlet-oxygen formation using the fullerene derivatives **BE1**, **BK3**, and **FE1** as photosensitizers[13]. The electrochemical and optical properties of the new species were investigated by cyclic voltammetry, spectroelectrochemistry, and absorption/emission spectroscopy.

Synthesis, Molecular Structure, and Spectroscopy

The synthetic pathways for the functionalization of fullerenes gain from the high electron affinity of fullerenes. Cycloadditions leading to 1,2-bridged fullerenes preferentially succeed by the use of electron-rich compounds[14]. Recently, we reported on the [8+2] cycloaddition by treating an electron-rich heptafulvene with C_{60} and C_{70}[14c][16]. Rubin et al. introduced the Diels-Alder reaction of buckminsterfullerene with electron-rich butadienes bearing trimethylsiloxy groups[15]. We now adopted this strategy by using aryl-substituted silyldienes[16]. The synthetic sequence implies the transformation of the methyl arylvinyl ketones into the silyl enole ethers **TB1**−**TB3** by the use of Danishefsky's method[17]. The reaction of **TB1**−**TB3** with buckminsterfullerene in refluxing toluene and fluoride-assisted cleavage of the trimethylsiloxy group of **BC1**−**BC3** yields the new compounds **BK1**, **BK2**, and **BK3** (Scheme 2). Structural assignment as “6,6-ring adducts” follows by analogy to the known regiochemical outcome of C_{60} cycloadditions and is in agreement with the 2-trimethylsilylbutadiene cycloaddition of C_{60}[15]. **BK1**, **BK2**, and **BK 3** are thermally stable towards retro Diels-Alder reaction. Isolation, work-up and chromatographic separation is made easier due to the better solubility compared to the parent fullerene. However, the steric congestion in the transition state caused by the covalently attached aryl groups slows down the rate of cycloaddition and lowers the yields.

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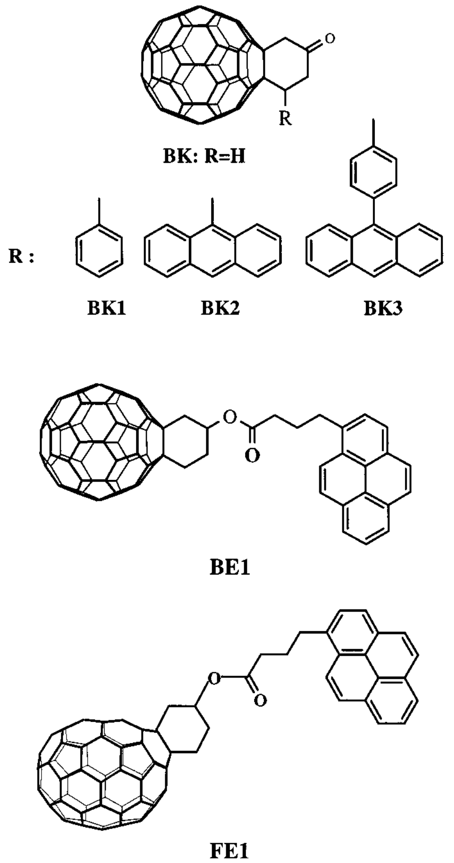
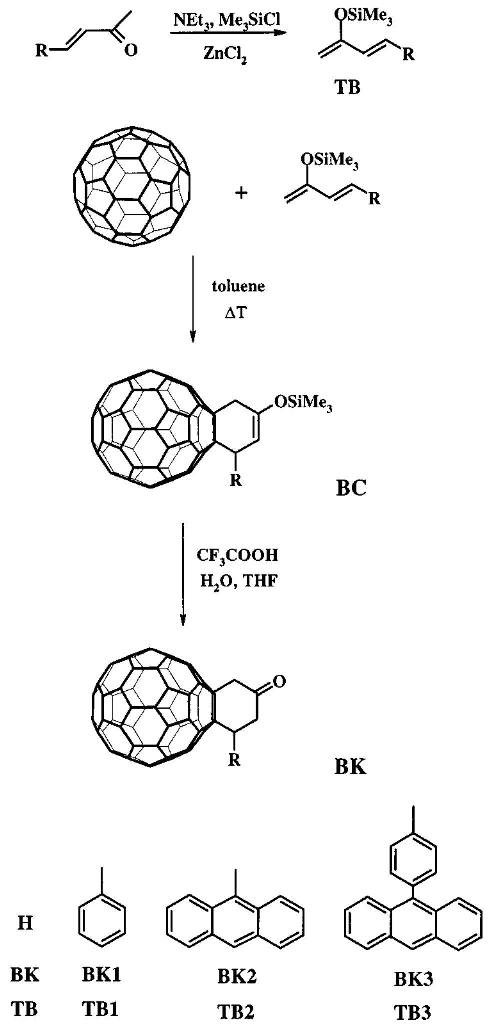
[*] The following abbreviations are used for derivatives of C_{60}: cyclohexanones, BK; esters, BE; trimethylsiloxy derivatives, BC; cyclohexanol derivative, BA; for derivatives of C_{70}: cyclohexanone derivative, FK; ester derivative, FE; cyclohexanol derivative, FA; for 1,3-butadienes: TB.

1434−193X/98/0808−1549 $ 17.50+.50/0

Scheme 1



Scheme 2

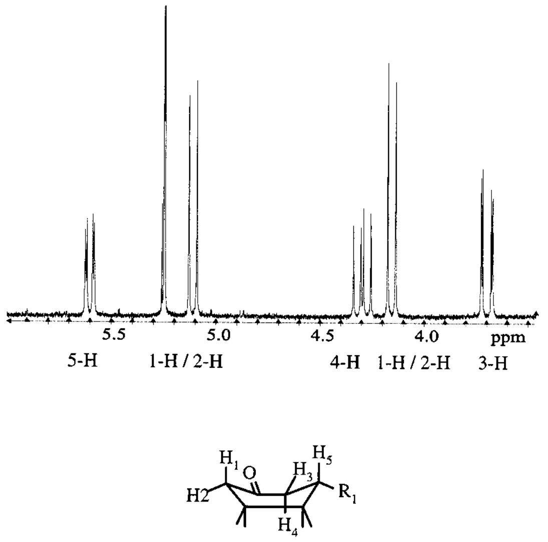


The cyclohexanone subunits in **BK1**, **BK2**, and **BK3** adopt sterically induced conformations which differ from the ideal chair conformation[18]. In Figure 1 the 400-MHz ^{1}H-NMR spectrum of **BK3** at room temperature is given. The two large coupling constants (14.1 and 15.2 Hz) are assigned to the geminal (1-H/2-H) and vicinal (5-H/4-H) protons of the CH_2 groups. A staggered conformation follows from ^3J(5-H/3-H) = 2.8 Hz. The aryl substituent must definitely be in an equatorial position. The aryl groups increase the barrier of inversion. Qualitatively, this follows from the ^{1}H-NMR spectra of **BK2−3** which show sharp lines at room temperature and whose coupling patterns are consistent with only one stable conformation. For comparison, the nonfunctionalized cyclohexanone derivative **BK1** has a barrier of inversion of 12.0 ± 0.2 kcal/mol[15][18]. Semiempirical calculations of **BK2** at the AM1 level using full geometry optimization[19] show the boat form to be the most stable conformation. The isomer with R in the equatorial position is favored by 5.9 kcal/mol[16]. The ^{13}C-NMR spectrum is also in agreement with the structure assignment. As expected for a compound with C_1 symmetry, **BK1** shows fifty-eight different signals for the sp^2-hybridized carbon atoms in the range $\delta = 134-156$ in addition to two signals at $\delta = 63.31$ and 68.87. The formation of the racemic form has also been verified by ^{1}H-NMR and chiral-shift experiments. The UV/Vis spectra of **BK1−3** exhibit the typical absorption pattern of the fullerene unit and the chromophore side groups. The low-intensity absorption band at 432 nm is characteristic of 6,6-ring-functionalized cycloadducts[20].

The ester derivatives were prepared by a second synthetic strategy (the "cyclohexanol route"[15]). The reaction of 2-trimethylsiloxy-1,3-butadiene [**TB** (R = H)] with C_{60} and C_{70} was employed followed by the reduction of the ketone group in **BK** and **FK** to the corresponding fullerene−cyclohexanols **BA** and **FA**, respectively and subsequent esterification with 1-pyrenebutanoic acid to **BE1** and **FE1** (Scheme 3).

The rugby-ball-shaped C_{70} (D_{5h} symmetry) has five nonequivalent carbon sites and eight constitutionally distinct C−C bonds as indicated in Figure 2. One main product was obtained as black crystals by the two-step process shown in Scheme 2. The assignment of the structure as **FK** is corroborated by knowing that cycloadditions of C_{70} prefer the 6,6-ring double bond nearest to the pole position which is most strained and therefore most reactive. The ^{13}C-NMR spectrum of **FK** displays thirty-five signals for sp^2-hybridized carbon sites which result from the two carbon atoms positioned on the symmetry plane and thirty-three signals for pairs of the sixty-six remaining carbon atoms. The present

Figure 1. Cyclohexanone substructure of C_{60}−ketone **BK3**: ^{1}H-NMR spectrum



[a] δ: 5.60 (dd, $^3J_{53}$ = 2.8 Hz, $^3J_{54}$ = 14.1 Hz, 1 H, H_5), 5.11 (d, $^2J_{12}$ = 15.2 Hz, 1 H, H_1 or H_2), 4.25 (dd, $^2J_{43}$ = 19.3 Hz, $^3J_{45}$ = 14.1 Hz, 1 H, H_4), 4.15 (d, $^2J_{21}$ = 15.2 Hz, 1 H, H_1 or H_2) 3.69 (dd, $^2J_{34}$ = 19.3 Hz, $^3J_{35}$ = 2.8 Hz, 1 H, H_3).

Scheme 3

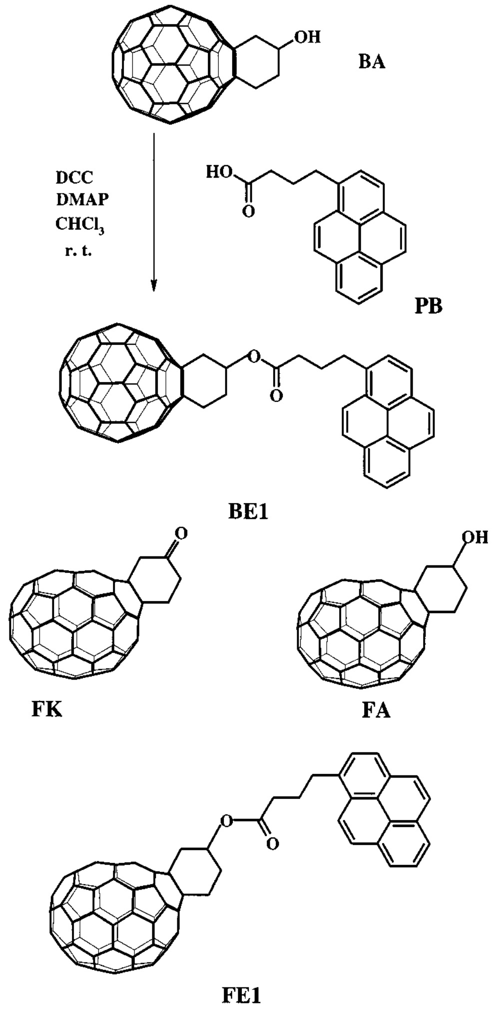
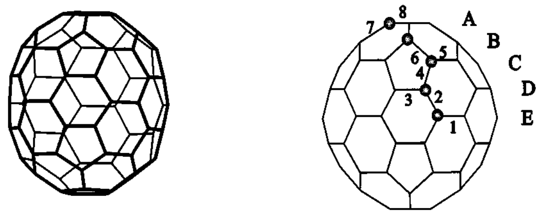


Figure 2. Geometry of C_{70} with D_{5h} symmetry



data do not allow a safe assignment of the regiochemistry of the cyclohexanone ring in **FK** resulting from the two ways of regioselective approach of **TB** at C_{70} fullerene. Quantum chemical calculations at the AM1 level, as described before, support the preferred cycloaddition at C−C bond 7 (Figure 2) and a boat conformation for the cyclohexanone subunit. The two regioisomers resulting from the "nonsymmetrically substituted" butadiene are found to have equal energy.

The ^{1}H-NMR spectrum of the C_{70}−cyclohexanone adduct **FK** shows coalescing signals of the six-membered ring proton at room temperature (400 MHz spectrum). On cooling, the band pattern sharpens and the coupling is again consistent with a nonchair conformation. At the coalescence temperature of −20°C an activation barrier of 11.9 ± 0.2 kcal/mol was calculated which is in the same range as that found for the C_{60}−cyclohexanone adduct **BK** (12.0 ± 0.2 kcal/mol)[15].

Cyclic Voltammetry and Spectroelectrochemistry

The π systems of fullerenes result in high electron affinities (EAs) as exemplified by the following data: C_{60}, EA = 2.65 eV; C_{70}, EA = 2.72 eV and due to symmetry the frontier orbitals are energetically degenerate[21]. The formation of multicharged ions, e.g. $C_{60}{}^{n-}$ and $C_{70}{}^{n-}$ is favored. C_{60} and C_{70} show six reduction waves at −10°C in toluene/acetonitrile[22]. The redox potentials strongly depend on the experimental conditions. This complicates the comparison of the electrochemical data[23]. For the derivatized fullerenes in this study we used THF as the solvent and tetrabutylammonium hexafluorophosphate (TBAHFP) as the supporting electrolyte. Measurements took place at room temperature. All potentials are referenced against ferrocene/ferrocenium (Fc). The results are listed in Table 1. The data for the parent fullerenes in 1,2-dichlorobenzene (ODCB) are also given for comparison.

The cyclic voltammograms (CVs) of **BK1**, **BK3**, **FK**, and **FE1** show four reversible waves of reduction indicating radical anion, dianion, trianion, and tetraanion formation. The pyrene esters **BE1** and **FE1** show an additional fifth reduction wave (Figure 3), possibly due to a reduction of the pyrene subunit. In **BE1** the "fullerene tetraanion" and the pyrene radical anion lead to an unresolved signal at −2640 mV.

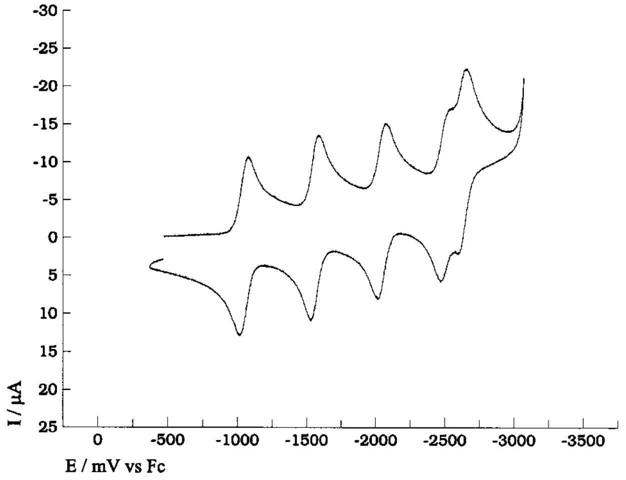
BE1 in CH_2Cl_2 gives rise to an irreversible wave at 890 mV which is assigned to the radical cation of the pyrene chromophore[24]. The cyclic voltammogram of the cyclohexanone derivative **BK2** leads to only one reversible re-

Table 1. Electrochemical data from cyclic voltammetry (in mV, referenced vs Fc)[a]

Half-wave potentials $E_{1/2}$	red. 1	red. 2	red. 3	red. 4	red. 5	ox.
C_{60} (ODCB)[b]	−1120	−1500	−1940	−2400	–	–
BK (THF)	−990	−1540	−2150	−2610	–	–
BK1 (THF)	−1040	−1600	−2200	−2650	–	–
BK2 (THF)	−1020	–	–	–	–	–
BK3 (THF)	−980	−1540	−2150	−2530	–	–
BE1 (THF)	−1040	−1580	−2190	−2640	−2640	890* in CH_2Cl_2
C_{70} (ODCB)	−1130	−1490	−1890	−2280	–	–
FK (THF)	−1010	−1520	−2020	−2470	–	–
FK (ODCB)	−1230	−1590	–	–	–	–
FE1 (THF)	−1050	−1560	−2040	−2500	−2630	–

[a] The separation of the peak potentials ΔE_p is in the range of 60 mV, the ratio of the peak currents amounts to unity – [b] ODCB: 1,2 dichlorobenzene.

Figure 3. Cyclic voltammogram of **FE1** (THF, 25°C, TBAHFP)



duction wave at −1020 mV (in THF, vs Fc). Obviously, even at this early state of reduction of **BK2**, a species is formed (tentatively assigned as anthracene radical anion) which leads to dimerization. The shape of the CV of the C_{70}–cyclohexanone adduct **FK** depends strongly on the solvent. Whereas in ODCB two reversible reduction waves are observed (−1230, −1590 mV), four reversible waves appear (−1010, −1520, −2020, and −2470 mV) in THF. In ODCB deposition on the trianion stage at the electrode may occur.

It may be concluded from the electrochemical results (Table 1) that the reduction to the radical anion of the C_{60} derivatives occurs at slightly less negative potentials compared with the C_{70} derivative. For the higher reduction steps this order is reversed.

By spectroelectrochemistry we recorded the potential-dependent electronic absorption spectra of the first two reduction waves. The data are listed in Table 2. Figure 4 displays the spectral changes of the stepwise reduction of **BE1** to the radical anion $\mathbf{BE1}^{\bullet-}$. The overall changes show the reversibility of the process; the neutral species can be regenerated by oxidation. A differential plot clearly indicates the appearance of a new band for $\mathbf{BE1}^{\bullet-}$ in the NIR at 1000 nm. Compared with the nonfunctionalized fullerene this absorption is shifted to higher energy. The absorption band of the species formed by the second wave of **BK1** is found at 870 nm and agrees with C_{60}-fullerene dianion[16][25][26].

Figure 4. Spectral changes during the reduction of **BE1** to the radical anion (solvent: THF); inset: cyclic voltammogram of **BE1** (THF, 25°C, TBAHFP, v = 250 mV/s)

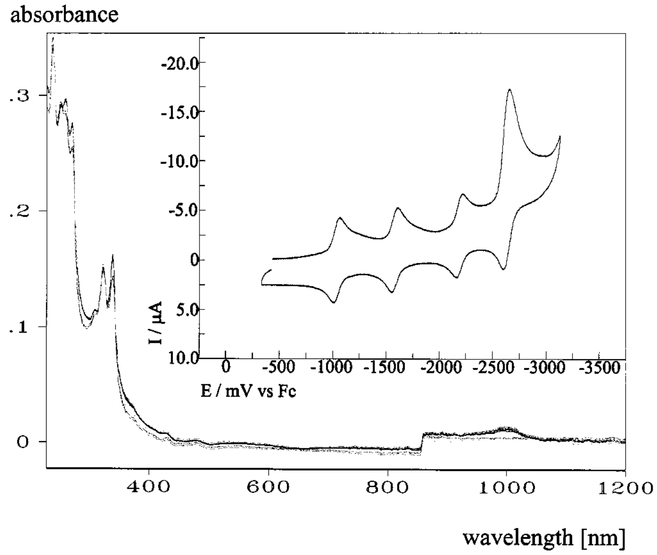


Table 2. Long-wavelength absorption bands of the radical anion and dianion species from in-situ spectroelectrochemistry evaluation by the difference-spectra approach

Compound (solvent)	Absorption maxima λ_{max} [nm] of the radical anions	Absorption maxima λ_{max} [nm] of the dianions
BK (THF)	1005	–
BK1 (THF)	1010	380, 720, 870
BK2 (THF)	1010	–
BE1 (THF)	1000	–
C_{60}[a]	1075	825, 945
C_{70}[b]	760, 790, 1370	685, 1175

[a] Toluene/acetonitrile (8:2). – [b] ODCB: 1,2-dichlorobenzene.

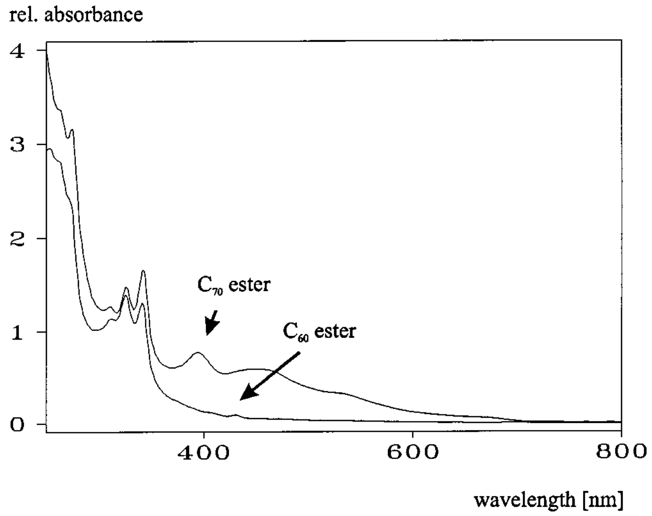
Optical Properties

The absorption spectra of fullerenes can be divided into two sections; a long-wavelength region of the symmetry-forbidden HOMO–LUMO transition, with low intensity (C_{60}, 440–700 nm) and an intense absorption pattern ($\varepsilon \approx 10^5$) in the UV/Vis (C_{60}, $\lambda \leq 440$ nm)[27]. Dihydrofullerenes exhibit long-wavelength absorption bands around 700 nm and 430 nm; the absorption at 700 nm is assigned to the $S_1 \leftarrow S_0$ transition. Details of the absorption spectra of the newly synthesized fullerene derivatives are given in Table 3. The absorption spectra of the functionalized fullerenes are composed of the individual chromophores signalling little interaction within the ground-state configuration. Figure 5 shows the electronic spectra of the esters **BE1** and **FE1**. Typical absorption bands at 430 nm for the C_{60} derivatives and 390 nm for the C_{70} derivatives are significant probes for disubstituted fullerenes[28][20]. Typical absorption bands of the pyrene moities in **BE1** and **FE1** appear at about 330 nm. This indicates that the spectra of the derivatized fullerenes **BE1** and **FE1** are composed of the individual chromophoric subunits. This finding and the lack of charge transfer bands is a good indication that there is no significant interaction of the pyrene and fullerene chromophores in the ground state.

Table 3. UV/Vis data (solvent: chloroform)

Species	abs. 1 λ [nm] log ε	abs. 2 λ [nm] log ε	abs. 3 λ [nm] log ε	abs. 4 λ [nm] log ε	abs. 5 λ [nm] log ε	abs. 6 λ [nm] log ε	abs. 7 λ [nm] log ε	abs. 8 λ [nm] log ε	abs. 9 λ [nm] log ε
C_{60}	256 4.68	–	327 4.15	–	403 3.24	–	–	–	–
BK1	253 5.01	310 4.54	–	–	–	429 3.48	–	–	–
BK2	252 5.18	310 4.56	357 4.29	374 4.23	397 4.10	429 3.64	–	–	–
BK3	–	313 4.66	345 4.52	366 4.43	387 4.29	431 3.61	–	–	–
anthracene	251 4.99	–	356 3.81	375 3.76	–	–	–	–	–
BE1	243 5.03	253 4.99	264 4.97	273 4.90	313 4.58	325 4.66	341 4.64	409 3.57	431 3.49
C_{70}	239 5.08	–	–	–	–	328 4.45	357 4.34	–	466 4.19
FK	–	–	–	–	–	–	344 4.34	393 4.35	453 4.24
FA	234 5.10	–	–	–	–	–	342 4.33	395 4.35	451 4.23
FE1	234 5.26	240 5.27	264 5.05	275 5.02	311 4.62	326 4.69	342 4.74	394 4.41	451 4.29
pyrene	239 4.71	252 4.03	261 4.28	272 4.48	319 4.35	334 4.52	–	–	–

Figure 5. UV/Vis spectra of esters **BE1** and **FE1** (solvent: chloroform)



The fluorescence spectra of **BE1**, **FE1**, **BK2**, and **BK3** at room temperature were measured in chloroform as solvent. Data from the emission spectra of the functionalized fullerenes supplemented by the emission data of pyrene and anthracene as references are summarized in Table 4. Unlike the parent C_{60} and C_{70}[11][29] which fluoresce rather weakly the functionalized fullerenes emit more strongly at about 700 nm which may be ascribed to the reduced symmetry[30]. On excitation at λ_{exc} = 553 nm the C_{60}– and C_{70}–cyclohexanone derivatives **BK** and **FK** show broad fluorescence emission at λ_{em} = 710 nm and λ_{em} = 700 nm, respectively. The photoluminescence spectra of the fluorophore-appended systems **BK2**, **BK3**, **BE1**, and **FE1** give rise to dual emission (Table 4) with a long-wavelength band at around 700 nm (peak 6) assigned to "fullerene emission" and an emission at around 400 nm with vibrational structure (peaks 1–5). A qualitative evaluation of the quantum yields of **BK2**, **BE1**, and **FE1** relative to the parent compounds C_{60}, C_{70}, pyrene, and anthracene indicates that the typical "fullerene" emission of the dihydrofullerene derivatives is increased whereas the "fluorophore emission" at about 400 nm is decreased by a factor of 10^3–10^4. We also found that the emission spectra of the pyrene derivatives **BE1** and **FE1** depend on the excitation wavelength: excitation at λ_{exc} = 320 nm leads both to a typical "pyrene" emission at 400 nm and a "fullerene" emission at 700 nm. In addition, the excitation spectra of **BE1** (λ_{de} = 380 nm) and **FE1** (λ_{det} = 380 nm) are in good agreement with the respective absorption subspectrum of the pyrene unit. Excitation of **BE1** and **FE1** at λ_{exc} = 500 nm leads exclusively to the "fullerene" emission.

Table 4. Fluorescence emission data (solvent: chloroform, $c = 1 \times 10^{-5}$ mol/l)

Species	excitation [nm]	peak 1 [nm]	peak 2 [nm]	peak 3 [nm]	peak 4 [nm]	peak 5 [nm]	peak 6 [nm]
pyrene	335	375	385	395	420	445	–
BE1	345	380	–	400	420	445	715
FE1	320	–	385	400	420	–	705
anthracene	375	385	405	430	455	–	–
BK2	375	sh	400	420	450	–	710
BK3	254	382	405	430	455	–	705

The data presented above allow to discuss the excited-state behaviour of the fluorophore-functionalized fullerenes. Unlike typical donor-functionalized fullerenes[12c] the fluorescence quenching in **BE1**, **FE1**, **BK2**, and **BK3** by intramolecular electron transfer appears to be less effective. This is in agreement with a qualitative assessment of the energetics of the photoinduced charge separation assuming infinite separation of the donor and acceptor subunits[31] and neglecting solvent effects (Eq. 1) which gives $\Delta G_{(et)} \approx 0.16$ eV and which is significantly higher than the number obtained for a dimethylanilin-appended C_{60}[12c]. Nevertheless, the intramolecular electron-transfer process may energetically be allowed in case of exciting the donor group [E_{00}(pyrene) ≈ 3.26 eV (380 nm), $\Delta G_{(et)} \approx -1.6$ eV].

$$\Delta G_{(et)} = -E_{oo}(\text{fullerene}) + E_{ox}(\text{pyrene}) - E_{red}(\text{fullerene}) \qquad (1)$$

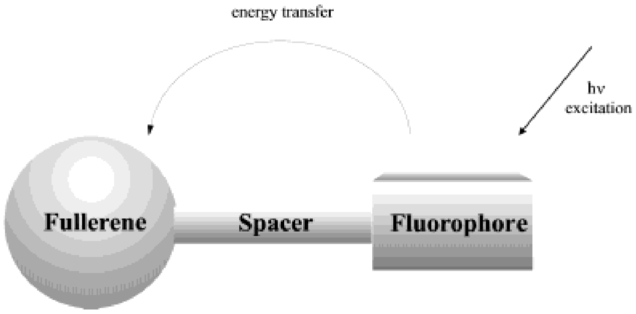
E_{oo}(fullerene) ≈ 1.75 eV (700 nm)
E_{ox}(pyrene) ≈ 910 mV[23]
E_{red}(fullerene) ≈ −1000 mV

The decrease in the intensity of the pyrene emission in **BE1** and **FE1** and the increase of the fullerene emission is consistent with energy transfer from the first excited singlet state of the fluorophore subunit [^{1}(fluorophore)*] to the S_1 state of the fullerene moiety [^{1}(fullerene)*] which either leads to fluorescence or intersystem crossing to the triplet state [^{3}(fullerene)*][12b]. Although unlikely, on the basis of an approximate Rehm-Weller-type calculation, the photoinduced electron-transfer quenching[32] cannot be completely excluded. Photophysical investigations on the nature of the excited-state behavior are in progress.

Summary and Conclusions

Fluorophore−fullerene adducts have been prepared based on the carbon Diels-Alder transform[33] employing electron-rich silylbutadienes and fullerenes as precursor compounds. Investigations by cyclic voltammetry and spectroelectrochemistry reveal intramolecular interaction in the ground state of the bichromophoric systems to be neglegible. In the excited-state domain, however, energy transfer appears to be likely. This makes fluorophore-attached fullerenes of the general formula given in Scheme 4 attractive compounds for the application in photostimulated processes such as singlet-oxygen[13] generation or in energy-transport systems.

Scheme 4



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Experimental Section

General: Melting points (uncorrected): Büchi SMP 20 and Reichert THERMOVAR. − UV/Vis: Perkin Elmer LAMBDA 9 UV/Vis/NIR spectrophotometer, on-line data acquisition using PECSS 4.0 on PC Acer 486/33 or PC Acer 910, respectively. − IR: Biorad FT-IR-Spectrometer FTS 155, on-line data acquisition using Bio-Rad Win-IR 3.02 on PC Acer 486/33. − MS: Finnigan MAT 95. − NMR: Bruker ARX-400 spectrometer at frequencies of 400 and 101 MHz for proton and carbon NMR, respectively. TMS (^{1}H and ^{13}C) was used as the reference sample. − Emission spectra: Hitachi F-4500 fluorometer, on-line data acquisition with PC Acer 1120. The solvents used were not degassed. Measurements were made without exclusion of atmospheric oxygen. Prior to the measurements the samples were purified by gel-permeation chromatography. − Cyclic voltammetry: A standard one-compartment, three-electrode arrangement was used with a platinum disc as the working electrode, a platinum wire as the counterelectrode and a pseudo Ag/AgCl reference electrode. The reversible oxidation signal of ferrocene/ferrocenium (Fc) was used as the internal standard. The solvents and the supporting electrolyte (tetrabutylammonium hexafluorophosphate, TBAHFP) were purified according to standard procedures[34], except for 1,2-dichlorobenzene, which was used as purchased from Aldrich. All measurements were carried out under nitrogen and the exclusion of moisture. − Spectroelectrochemistry: After the measurements by cyclic voltammetry, the solutions were transferred with a syringe to the spectroelectrochemical cell. The Vis/NIR spectra were recorded using the Perkin Elmer LAMBDA 9 spectrophotometer.

Syntheses: Solvents and reagents were used as purchased without further purification unless stated otherwise. Toluene was dried with Na. THF was dried and stored over Na and benzophenone under nitrogen. $CHCl_3$ was dried with P_2O_5. The course of the reactions was monitored by TLC. Buckminsterfullerene and C_{70} fullerene were obtained from the HOECHST AG.

1,2-(4-Oxo-6-phenylcyclohexano)buckminsterfullerene (**BK1**): Under nitrogen, 510 mg (0.71mmol) of C_{60} was dissolved in 550 ml of dry toluene and the magenta solution was refluxed. Within 2.5 h, a solution of 310 mg (ca. 0.71 mmol) of 1-phenyl-3-trimethylsiloxy-1,3-butadiene (**TB1**)[35] in 50 ml of dry toluene was added dropwise and the reaction mixture was refluxed for 14 h. After cooling to 50°C, the black reaction mixture was added to 350 ml of THF, 150 ml of CH_3OH, 10 ml of CH_3COOH, 2.0 g of KF and was stirred at room temperature for 4 h. After washing with 1.3 l of H_2O, drying with Na_2SO_4 and filtration, the solvent was removed. By flash chromatography on silica gel with toluene as eluent, black crystals were obtained (374 mg, 61%). − M.p. > 360°C. − IR (KBr): ν = 1715 cm^{-1} (C=O), 1705, 1415, 1405, 1185, 1175, 755, 730, 680. − UV (chloroform): λ_{max} (lg ε) = 692 nm (2.51), 629 (sh, 2.59), 603 (sh, 2.67), 545 (sh, 2.92), 478 (sh, 3.14), 429 (3.48), 310 (4.54), 253 (5.01). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (br. s, 2 H, phenyl), 7.23−7.36 (m, 3 H, phenyl), 5.47 [dd, ^3J (5-H/3-H) = 2.8 Hz, ^3J(5-H/4-H) = 14.1 Hz, 1 H, 5-H], 5.11 [d, ^2J(1-H/2-H) = 15.2 Hz, 1 H, 1-H or 2-H], 4.25 [dd, ^3J(4-H/5-H) =

14.1 Hz, ^2J(4-H/3-H) = 19.6 Hz, 1 H, 4-H], 4.19 [d, ^2J(2-H/1-H) = 15.2 Hz, 1 H, 2-H or 1-H], 3.59 [dd, ^3J(3-H/5-H) = 2.8 Hz, ^2J(3-H/4-H) = 19.6 Hz, 1 H, 3-H]. − ^{13}C-NMR ($CDCl_3$): δ = 156.09, 155.54, 153.57, 150.98, 147.77, 147.72, 146.77, 146.69, 146.59, 146.56, 146.54, 146.41, 146.40, 146.35, 146.27, 145.83, 145.78, 145.61, 145.60, 145.58, 145.57, 145.56, 145.54, 145.49, 145.48, 144.77, 144.68, 144.63, 144.61, 144.50, 144.44, 143.15, 143.14, 142.80, 142.72, 142.70, 142.68, 142.21, 142.21, 142.18, 142.17, 141.94, 141.93, 141.94, 141.88, 141.77, 141.51, 141.45, 140.55, 140.41, 138.86, 138.34, 137.44, 137.43, 136.22, 135.41, 134.76, 134.27 (58 sp^2 C_{60} carbon atoms), 208.18 (C=O), 68.87, 63.31 (2 sp^3 C_{60} carbon atoms), 52.62, 50.29, 44.94 (2 CH_2 and 1 CH). − $C_{70}H_{10}O$: calcd. 866.0732; found 866.0648 (HR-PIEI-MS). − MS (PI-FDMS); *m/z* (%): 866(7) [M$^+$], 720 (100) [C_{60}^+].

4-Anthryl-2-trimethylsiloxy-1,3-butadiene (**TB2**): To a suspension of 69.0 mg (0.51 mmol) of vacuum-dried $ZnCl_2$ in 3.38 g (33.6 mmol, 4.65 ml) of NEt_3 a solution of 4-anthryl-3-buten-2-one[36] in 140 ml of dry toluene and a solution of 3.32 g (30.5 mmol, 3.86 ml) of Me_3SiCl in 30 ml of dry toluene was added simultaneously within 20 min. After stirring for 30 min at room temp., the reaction mixture was heated to 60°C for 17 h, to 90°C for 72 h and stirred again at room temp. for 50 h. After filtration and washing the residue with CH_2Cl_2, the solvent was removed. After washing with water and extraction of the aqueous phase with 75 ml of toluene, the organic phase was dried with Na_2SO_4. By column chromatography on silica gel with CH_2Cl_2 the blue fluorescent product was isolated as an orange, unstable oil (800 mg, 17%) which could be stored under nitrogen for a few hours without significant decomposition. − IR (KBr): ν = 3083 cm^{-1}, 3055, 3031, 2962, 2925 (C−H), 1594, 1496, 1457, 1348, 1316, 1255, 1022, 849, 786, 732, 694. − ^{1}H NMR ($CDCl_3$): δ = 8.38 (s, 1 H, anthracene 10-H), 8.27−8.31 (m, 2 H, anthracene H), 7.98−8.03 (m, 2 H, anthracene H), 7.65 [dd, ^3J(3-H/4-H) = 15.9 Hz, ^4J(3-H/1-H, or 3-H/2-H) = 0.6 Hz, 1 H, 3-H], 7.43−7.54 (m, 4 H, anthracene H), 6.47 [d, ^3J(4-H/3-H) = 15.9 Hz, 1 H, 4-H], 4.58 [dd, ^3J(1-H/3-H or 2-H/3-H) = 0.6 Hz, ^2J(1-H/2-H) = 0.8 Hz, 1-H or 2-H], 4.53−4.59 (m, 1 H, 2-H or 1-H), 0.43 (s, 9 H, $OSiMe_3$).

1,2-(6-Anthryl-4-oxocyclohexano)buckminsterfullerene (**BK2**): 406 mg (0.57 mmol) of C_{60} and 400 mg (1.26 mmol) of butadiene **TB2** were dissolved in 300 ml of dry toluene and refluxed for 38 h. While still hot, the reaction mixture was added to 200 ml of H_2O, 10 ml of CF_3COOH, 100 ml of THF and stirred for 1 h. After washing with 0.6 l of a satured solution of $NaHCO_3$ in H_2O, the organic phase was dried with Na_2SO_4 and the solvent was removed. After column chromatography with toluene on silica gel, the product was obtained as a brownish solid, which was further purified by ultrasonic treatment in methanol (8.3 mg, 2%). − M. p. > 360°C. − IR (KBr): ν = 3051 cm^{-1}, 2923, 2853 (C−H), 1726 (C=O), 1623, 1528, 1429, 1408, 1262, 1229, 1187, 1159, 1099, 1021, 951, 888, 839, 801, 765, 728, 672, 613, 572, 526. − UV (chloroform): λ_{max} (lg ε) = 701 nm (2.68), 689 (2.66), 629 (sh, 2.77), 478 (sh, 3.42), 429 (3.64), 397 (4.10), 374 (4.23), 357 (sh, 4.30), 310 (4.56), 252 (5.18). − ^{1}H NMR ($CDCl_3/CS_{2\,=\,1}$:2): δ = 9.00−9.02 (m, 1 H, anthracene H), 8.47−8.52 (m, 1 H, anthracene H), 8.42 (s, 1 H, anthracene 10-H), 7.96−7.99 (m, 1 H, anthracene H), 7.91−7.95 (m, 1 H, anthracene H), 7.65−7.69 (m, 1 H, anthracene H), 7.44−7.48 (m, 1 H, anthracene H), 7.31−7.36 (m, 2 H, anthracene H), 7.21 (ddd, ^3J = 13.9 Hz, ^3J = 2.6 Hz, ^5J = 0.8 Hz, 1 H, 5-H), 5.35 (d, ^3J = 16.0 Hz, 1 H, 1-H), 5.07 (dd, ^3J = 13.9 Hz, ^3J = 18.9 Hz, 1 H, 4-H), 4.33 (d, ^3J = 16.0 Hz, 1 H, 2-H), 3.69 (dd, ^3J = 18.9 Hz, ^3J = 2.6 Hz, 1 H, 3-H). − $C_{78}H_{14}O$: calcd. 966.1045; found 966.1026 (HR-NI-DCIMS). - MS (PI-FDMS); *m/z* (%) = 966 (100) [M$^+$], 720 (76) [C_{60}^+].

1,2-[6-(4-Anthrylphenyl)-4-oxocyclohexano]buckminsterfullerene (**BK3**): 0.94 g (2.93 mmol) **TB3** in 100 ml of dry toluene and 1.72 g (15.8 mmol) of Me_3SiCl were added to a suspension of 37 mg (0.27 mmol) of $ZnCl_2$ in 2.0 ml of NEt_3 under N_2. After stirring for 2 d at 110°C, 156 mg (0.22 mmol) of C_{60} fullerene was added. The reaction mixture was heated under reflux for two more days. Afterwards, the content of the flask was poured into a mixture of 350 ml of THF, 150 ml of CH_3OH, 1 ml of CF_3COOH, 1.00 g of KF, and stirred for 6 h. The mixture was then washed with 1 l of water and the combined organic phases were dried with Na_2SO_4. After removal of the solvent, the residue was purified by twofold chromatography on silica gel (toluene). The yield was 21 mg (10%). − M.p. > 360°C.− IR (KBr): ν = 3047 cm^{-1}, 2923, 1726, 1433, 1408, 1188, 1097, 885, 734, 527. − UV (CH_2Cl_2): λ_{max} (lg ε) = 431 nm (3.61), 387 (4.29), 366 (4.43), 345 (4.52), 313 (4.66).− ^{1}H NMR (CD_2Cl_2/CS_2): δ = 8.33 (s, 1 H, anthracene 10-H) 7.89 (^3J = 7.8 Hz, 2 H, 3-H or 4-H), 7.70−7.00 (m 10 H, phenylanthracene H), 5.60 (dd, ^3J = 2.8 Hz, ^3J = 14.1 Hz, 1 H, 5-H), 5.11 (d, ^2J = 15.2 Hz, 1 H, 1-H), 4.25 (dd, ^2J = 19.3 Hz, ^3J = 14.1 Hz, 1 H, 4-H), 4.15 (d, ^2J = 15.2 Hz, 1 H, 2-H), 3.69 (dd, ^2J = 19.3 Hz, ^3J = 2.8 Hz, 1 H, 3-H). − $C_{84}H_{18}O$: calcd. 1042.1357; found 1042.1339 (HR-NIDCI-MS). − MS (FI/FDMS); *m/z* (%): 1042 (100) [M$^+$], 720 (4) [C_{60}^+].

Buckminsterfullerene Ester (**BE1**): 55 mg (69 mmol) of 1,2-(4-hydroxycyclohexano)buckminsterfullerene[15], 30 mg (104 mmol) of 1-pyrenebutanoic acid[37], and 34 mg (276 mmol) of DMAP were dissolved in 70 ml of dry chloroform, cooled to 0°C and treated with 22 mg (104 mmol) of DCC. After stirring for 40 min, the ice bath was removed and the solution was stirred for another 6 h at room temp. The reaction mixture was separated by column chromatography on silica gel. The brown main fraction was eluated with chloroform. After evaporation of the solvent an additional careful column chromatography on silica gel with toluene as eluent was undertaken. The solid obtained was suspended in methanol by ultrasonic treatment. After filtration, washing with methanol and drying, 30.0 mg of brownish-black fine crystals (yield: 41%) were obtained. − M. p. > 360°C. − IR (KBr): ν = 3039 cm^{-1}, 2931, 2861 (C−H), 1730 (C=O), 1460, 1431, 1243, 1213, 1184, 1161, 1141, 1065, 1030, 1002, 844, 762, 726, 527. − UV (chloroform): λ_{max} (lg ε) = 700 nm (2.49), 431 (3.49), 409(3.57), 341 (4.64), 325(4.66), 313 (4.58), 273 (sh, 4.90), 264 (4.97), 253 (4.99). − ^{1}H NMR ($CDCl_3/CS_2$ = 1:2): δ = 8.27 (d, *J* = 9.2 Hz, 1 H, pyrene), 8.03−8.09 (m, 4 H, pyrene), 7.95 (s, 2 H, pyrene), 7.92 (pt, *J* = 7.7 Hz, 1 H, pyrene), 7.83 (d, *J* = 7.7 Hz, 1 H, pyrene), 6.01−6.08 (m, 1 H, R−OC*H*R_2), 3.57−3.66 (m, 3 H, cyclohexyl), 3.43 (t, ^3J = 7.6 Hz, 2 H, −CO−C*H*$_2$−CH_2−CH_2−R), 3.25−3.40 (m, 2 H, cyclohexyl), 2.64−2.73 (m, 1 H, cyclohexyl), 2.59 (t, ^3J = 7.2 Hz, 2 H, −CO−CH_2−CH_2−C*H*$_2$−R), 2.21−2.31 (m, 2 H, −CO−CH_2−C*H*$_2$−CH_2−R). − ^{13}C NMR ($CDCl_3/CS_2$ = 1:2): δ = 172.08 (*C*=O), 156.74, 155.89, 155.74, 155.74, 147.50, 147.47, 146.29, 146.28, 146.21, 146.08, 146.06, 146.06, 146.05, 146.04, 145.64, 145.48, 145.36, 145.31, 145.29, 145.28, 145.27, 145.25, 145.24, 145.22, 145.20, 145.13, 145.06, 144.82, 144.50, 144.49, 144.45, 144.38,143.03, 142.90, 142.41, 142.40, 142.36, 142.35, 141.87, 141.87, 141.82, 141.76, 141.72, 141.53, 141.46, 141.43, 141.41, 141.41, 140.15, 140.15, 140.12, 139.96, 135.23, 135.23, 135.14, 135.12, 134.80, 128.64 (58 sp^2 carbon atoms of the fullerene core), 135.34, 131.27, 130.72, 129.90, 128.11, 127.46, 127.46, 127.26, 126.78, 125.85, 125.21, 124.98, 124.86, 124.79, 123.15,123.15 (pyrene[37]), 69.54 (*C*−OR), 63.33, 61.50 (2 sp^3 carbon atoms of the fullerene core), 40.47 (O−CO−C*H*$_2$), 34.94, 34.24, 32.94, 29.53, 27.04 (5 C*H*$_2$). − $C_{84}H_{22}O_2$: calcd. 1062.1620;

found 1062.1595 (HR-PIEI-MS). − MS (PI / FD-MS); *m*/*z* (%): 1062 (100) [M^+], 1063 (93) [$M^+ + 1$], 1064 (40) [$M^+ + 2$].

C_{70} Fullerene Ketone (**FK**): Under nitrogen, 103 mg (123 mmol) of C_{70} was dissolved in 100 ml of dry toluene and while refluxing, a solution of 21 mg (147 mmol) of 2-trimethylsilyloxy-1,3-butadiene in 80 ml of dry toluene was added dropwise within 2 h. After complete addition, the reaction mixture was refluxed for 25 h and stirred at room temp. for another 50 h. While still hot, the reaction mixture was added to 100 ml of THF, 50 ml of H_2O, and 5 ml of CF_3COOH and stirred at room temp. for 2 h. After washing with 1.0 l of H_2O and a saturated solution of $NaHCO_3$ in H_2O, the organic phase was dried with Na_2SO_4 and the solvent was removed. The product was isolated by column chromatography on silica gel with toluene. Additional purification by ultrasonic treatment in methanol afforded black microcrystals (36 mg, 32%). − M. p. > 360°C. − IR (KBr): ν = 2920 cm^{-1}, 2850 (C−H), 1722 (C=O), 1558, 1427, 1416, 1396, 1319, 1128, 795, 725, 670, 533. − UV (chloroform): λ_{max} (lg ε) = 667 nm(3.18), 536 (2.94), 453 (4.24), 393 (4.35), 344 (sh, 4.34). − ^1H NMR [$CDCl_3/CS_2$ (1:2), 193 K]: δ = 4.12 (d, ^2J = 14.6 Hz, 1 H, 1-H), 3.83 (d, ^2J = 14.6 Hz, 1 H, 2-H), 3.31−3.41 (m, 1 H, 4-H), 3.03−3.23 (m, 2 H, 5-H and 6-H), 2.74−2.84 (m, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 160.21, 154.35, 151.63, 151.62, 151.43, 151.41, 151.11, 150.73, 150.72, 150.10, 149.98, 149.62, 149.53, 149.40, 149.10, 149.05, 148.88, 147.47, 147.09, 147.07, 147.04, 147.02, 146.37, 146.32, 145.95, 143.23, 143.16, 143.08, 143.08, 140.13, 133.97, 133.94, 131.53, 131.39, 131.34 (35 signals for the sp^2 C_{70} carbon atoms), 56.43, 54.91 (2 sp^3 C_{70} carbon atoms), 51.57, 39.24, 33.90 (3 *C*H_2). − $C_{74}H_6O$: calcd. 910.0418; found 910.0421 (HR-PIEI-MS) − MS (PI-DCI-MS, isobutane); *m*/*z* (%): 911 (100) [$M^+ + H$], 841 (95) [$C_{70}^+ + H$].

C_{70} Fullerene Alcohol (**FA**): To a solution of 136 mg (149 mmol) of C_{70} ketone (**FK**) in 120 ml of dry toluene, 370 ml of diisobutylaluminium hydride (20% solution in *n*-hexane, 370 mmol) was added within 1 min under nitrogen. After stirring the solution for 1 h at room temp., the reaction mixture was washed with 400 ml of a saturated solution of NH_4Cl in H_2O, the aqueous phase was extracted with 200 ml of toluene, the organic phase was dried with Na_2SO_4 and the solvent was removed. Purification by column chromatography on silica gel with toluene and ultrasonic treatment in methanol afforded 91 mg of black microcrystals (67%). − M. p. > 360°C. − IR (KBr): ν = 3432 cm^{-1}, 2926, 2860 (C−H), 1633, 1562, 1425, 1127, 1067, 1023, 987, 793, 725, 693, 670, 636, 569, 531. − UV (chloroform): λ_{max} (lg ε) = 677 nm (sh, 3.17), 535 (sh, 3.96), 451 (4.23), 395 (4.35), 342 (sh, 4.33), 234 (5.10). − ^1H NMR [$CDCl_3/CS_2$ (1:2)]: δ = 4.81−4.90 (m, 1 H, 3-H), 3.21 (dd, ^2J = 13.6 Hz, ^3J = 5.3 Hz, 1 H, 2-H), 3.06 (dd, ^2J = 13.6 Hz, ^3J = 9.0 Hz, 1 H, 1-H), 2.69−2.88 (m, 2 H, cyclohexyl H), 2.36−2.43 (m, 1 H, cyclohexyl H), 2.14−2.22 (m, 1 H, cyclohexyl H), 1.93 (d, *J* = 3.8 Hz, 1 H, OH). − $C_{74}H_8O$: calcd. 912.0575; found 912.0605 (HR-PIEI-MS). − MS (PIEI-MS); *m*/*z* (%): 912 (20) [M^+], 840 (100) [C_{70}^+].

C_{70} Fullerene Ester (**FE1**): 55 mg (61 mmol) of C_{70} alcohol (**FA**), 52 mg (182 mmol) of 1-pyrenebutanoic acid[38], and 37 mg (303 mmol) of DMAP were dissolved in 90 ml of dry $CHCl_3$, cooled to 0°C, and 41 mg (200 mmol) of DCC was added. After 30 min at 0°C, stirring at room temp. for 150 min was performed. The reaction mixture was separated by column chromatography on silica gel. The brown main fraction was eluated with chloroform. After removal of the solvent, another column chromatography was performed. The resulting solid was purified by ultrasonic treatment in methanol. Yield: 49 mg of black microcrystals (69%). − M. p. > 360°C. − IR (KBr): $\tilde{\nu}$ = 3032 cm^{-1}, 2928, 2859 (C−H), 1728 (C=O), 1426, 1179, 1158, 1133, 841, 793, 725, 671, 534. − UV (chloroform): λ_{max} (lg ε) = 676 nm (sh, 3.26), 535 (sh, 4.02), 451 (4.23), 394 (4.41), 342(4.74), 326 (4.69), 311 (4.62), 275 (5.02), 264 (sh, 5.05), 240 (5.27), 234 (5.26). − ^1H NMR ($CDCl_3/CS_2$ = 1:2): δ = 8.29−8.34 (m 1 H, pyrene), 8.05−8.17 (m, 4 H, pyrene), 7.87−8.03 (m, 4 H, pyrene), 5.62−5.70 (m, 1 H, 3-H), 3.47 (t, ^3J = 7.7 Hz, 2 H, $COCH_2CH_2CH_2$), 3.15 (dd, ^3J = 5.2 Hz, ^2J = 13.9 Hz, 1 H, 2-H), 3.04 (dd, ^3J = 7.4 Hz, ^2J = 13.9 Hz, 1 H, 1-H), 2.73−2.87 (m, 1 H, cyclohexyl), 2.62 (t, ^3J = 7.6 Hz, 2 H, $COCH_2CH_2CH_2$), 2.48−2.69 (m, 1 H, cyclohexyl H), 2.38−2.46 (m, 1 H, cyclohexyl H), 2.25−2.38 (m, 2 H, $COCH2CH_2CH2$), 2.11−2.21 (m, 1 H, cyclohexyl H). − ^{13}C NMR [$CDCl_3/CS_2$ (1:2)]: δ = 172.43 (*C*=O), 160.49, 160.41, 154.69, 54.30, 151.52, 151.34, 151.29, 151.29, 151.14, 150.91, 150.56, 150.54, 150.49, 150.46, 149.94, 149.82, 149.78, 149.46, 149.44, 149.42, 149.38, 149.36, 149.32, 148.93, 148.91, 148.91, 148.90, 148.90, 148.77, 148.75, 148.23, 147.36, 147.32, 147.26, 146.96, 146.92, 146.85, 146.83, 146.49, 146.30, 146.24, 146.08, 145.74, 145.55, 143.06, 142.93, 142.93, 142.88, 142.80, 142.74, 142.66, 142.51, 140.07, 139.80, 139.78, 139.58, 136.68, 136.56, 133.85, 133.82, 133.80, 133.53, 131.35, 131.29, 131.21, 131.18, 131.11, 130.91 (68 sp^2 C_{70} carbon atoms), 135.45, 131.44, 130.87, 130.06, 128.82, 127.62, 127.56, 127.42, 126.84, 125.94, 125.24, 125.07, 124.97, 124.89, 123.20, 123.20 (pyrene[37]), 68.27 (*C*−OR), 56.68, 53.21 (2 sp^3 C_{70} carbon atoms), 39.79 (CO*C*H_2), 34.53, 33.04, 31.12, 28.77, 27.28 (5 *C*H_2). − MS (PIEI-MS); *m*/*z* (%): 1184 (58) [M^+], 840 (100) [C_{70}^+].

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