Chem. Rev. **1998,** *98,* 2527–2547

C_{60}-Based Electroactive Organofullerenes

Nazario Martín,* Luis Sánchez, Beatriz Illescas, and Ignacio Pérez

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain

Received November 4, 1997 (Revised Manuscript Received July 8, 1998)

Contents

1. Introduction 2527
2. [60]Fullerene–Electron Donor Systems 2527
    - 2.1. Intermolecular C_{60}/Donor CT Complexes 2527
    - 2.2. Photoinduced Electron Transfer (PET) from Donor Polymers to C_{60} 2529
    - 2.3. Covalently Linked C_{60}–Donor Dyads 2530
        - 2.3.1. Dyads Prepared by 1,3-Dipolar Cycloadditions 2530
        - 2.3.2. Dyads Prepared by Diels–Alder Cycloadditions 2532
        - 2.3.3. Dyads Prepared by Bingel's Reaction 2533
        - 2.3.4. Photoinduced Electron Transfer (PET) in Dyads 2534
3. [60]Fullerene–Electron Acceptor Systems 2538
    - 3.1. Covalently Linked C_{60}–*p*-Benzoquinonoid Systems 2539
    - 3.2. Spiroannelated Methanofullerenes as Electron Acceptors 2542
    - 3.3. Other Electron Acceptor Organofullerenes 2543
4. Summary and Perspectives 2544
5. Acknowledgments 2545
6. References 2545

1. Introduction

[60]Fullerene[1,2] is a redox-active chromophore which, according to theoretical calculations, exhibits a LUMO (t_{1u}) comparatively low in energy and is triply degenerate. Consequently, C_{60} behaves like an electronegative molecule which reversibly accepts up to six electrons in solution.[3] The cyclic voltammetry and the electron affinity measured for [60]fullerene clearly confirm that it is a moderate electron acceptor comparable to other organic molecules such as benzo- and naphthoquinones.[4,5] This electron-accepting ability of C_{60} to form stable multianions[6] is in sharp contrast with the ability to generate the very unstable cationic species.[7] Fullerenes, and in particular the readily available C_{60}, present a wide range of chemical and physical properties that make them promising chromophores in photoinduced redox processes.

One of the most remarkable properties of [60]fullerene in electron-transfer processes is that it efficiently gives rise to a rapid photoinduced charge separation and a further slow charge recombination in the dark.[8] These unique photophysical properties are attributed to a combination of the symmetry of the C_{60} π-system and the pyramidal nature of the fullerene constituent carbon atoms,[9] and are currently being studied in the search of artificial photosynthetic systems with efficient and long-lived charge separation.

In this paper, we will focus our attention on the synthesis and properties of [60]fullerene derivatives bearing electron donor (D) or electron acceptor (A) units covalently attached to the C_{60} core.

The design of novel organofullerenes containing electron donor moieties constitutes a promising field due to the interesting optical and electronic properties they can display. D–A dyads are the basis for molecular electronic devices,[10–14] for the preparation of systems exhibiting nonlinear optical properties[15–17] and, as stated above, for the design of artificial photosynthetic systems.[18–20] On the other hand, much less is known on modified fullerenes bearing an electron-poor fragment linked to the C_{60} cage. These double electron acceptor systems could be attractive for the preparation of photovoltaic cells by blending C_{60} with appropriate semiconducting electron donor polymers, or used as precursors for the formation of triads of multichromophoric systems with a gradient of redox centers ($D-A_1-A_2$) with spacially well-defined structures.[21] The synthesis of these triads would involve the regioselective addition of a donor unit to the previously formed C_{60}–acceptor dyad.[22]

2. [60]Fullerene–Electron Donor Systems

2.1. Intermolecular C_{60}/Donor CT Complexes

The discovery of superconductivity in the alkali metal intercalated fullerides[23] led to the exploration of C_{60} charge-transfer complexes (CTCs) with organic donors as countercations in the search of a metallic state or superconducting properties. However, reaction of C_{60} with a wide variety of electron-donor molecules such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)[24a] (**1**), the dimer of BEDT-TTF[24b] (**2**), ferrocene[25] (**3**), or hexamethylenetetratellurafulvalene[26] leads to insulating neutral CT complexes in which C_{60} cocrystallizes with the donor molecule. Other C_{60}-based intermolecular CT complexes with different TTF-type donor molecules bearing S, Se, Te, or N atoms have also been recently prepared.[27] Complex **2** showed, however, an absorption band at 750 nm in the solid-state assigned to a charge transfer. C_{60} cocrystallizes with ferrocene to form C_{60}(ferrocene)$_2$ in which the fullerene molecule is not reduced by the donor unit. However, a two-dimen-

10.1021/cr9701039 CCC: \$30.00

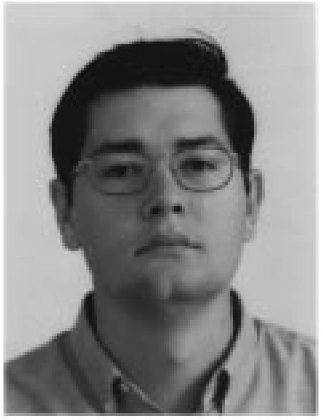
Nazario Martín was born in 1956 in Madrid. He studied chemistry at the Universidad Complutense de Madrid (UCM), where he obtained his Doctorate on the synthesis of 4*H*-pyrans at the Department of Organic Chemistry under Professor C. Seoane in 1984. After spending a year working on X-ray contrast agents in a pharmaceutical company, he worked as postdoctoral fellow (1987–1988) at the Institut für Organische Chemie der Universität Tübingen in Germany under Professor M. Hanack on electrically conducting organic materials. In 1994, he spent three months as a visiting Professor at the Institute for Polymers and Organic Solids (IPOS) at the University of California, Santa Barbara (UCSB) working with Professor F. Wudl on modified fullerenes. Since 1989, he has been Associate Professor of Organic Chemistry at the University Complutense (UCM). His research interests range over electroactive molecules with emphasis on the electrical and optical properties, the chemistry of fullerenes and, in particular, the design and synthesis of electroactive organofullerenes. He is also active in the asymmetric synthesis of heterocyclic systems.

Luis Sánchez was born in Toledo, Spain, in 1970. He studied Chemistry at the Universidad de Castilla-La Mancha (UCLM). He obtained his Ph.D. working on TTF and C_{60} electroactive derivatives at the Universidad Complutense de Madrid (UCM) under Professors N. Martín and C. Seoane in 1997. Since 1998, he has been teaching Assistant at the Department of Organic Chemistry (UCM) where he is currently working in the synthesis and study of the properties of D-σ-A and D-π-A systems based on C_{60} and TTF.

sional crystal structure made by two-dimensional layers of C_{60} molecules sandwiched by layers of ferrocene molecules is formed as a result of weak intermolecular CT interactions (Figure 2). Complexation with strong electron donors such as $Fe(C_5H_5)(C_6Me_6)$,[28] cobaltocene[29] or tetrakis(dimethylamino)ethylene (TDAE)[30a] formed fully ionic CT complexes being electrically insulating, although the TDAE complex showed interesting ferromagnetic properties.[30b]

Only recently, the crystalline 1:1 salt decamethylnickelocenium buckminsterfulleride formed by combination of decamethylnickelocene, $Ni(C_5Me_5)_2$, with C_{60} in CS_2 yielded a good conductor[31] (**4**) with $\sigma_{rt} \sim 0.01$ S cm^{-1}. Decamethylnickelocene selectively reduces C_{60} to its monoanion to form a highly ordered 1:1 salt. The packing diagram (Figure 2) shows that the C_{60}^- anions and Ni cations alternate along the (1,0,1) direction. The close interaction of the methyl group C−H bonds of the cations with the hexagonal rings of the C_{60}^- anions seems to be responsible for

Beatriz Illescas was born in Madrid, Spain, in 1969. She studied Chemistry at the Universidad Complutense de Madrid (UCM). She obtained her Ph.D. working on C_{60} electroactive derivatives at the UCM under Professors N. Martín and C. Seoane in 1998. Since then she has been a postdoctoral fellow in the laboratories of Professor Martín and Seoane where she is currently working on C_{60} derivatives with biological properties.



Ignacio Pérez was born in Madrid, Spain, in 1969. He studied Chemistry at the Universidad Autónoma de Madrid (UAM). He has been working toward his Ph.D. on TTF derivatives at the Universidad Complutense de Madrid (UCM) under Professors N. Martín and C. Seoane since 1996. Since 1997 he has been enjoying a grant at the Centro de Estudios de Carreteras (CEC) of Centro de Estudios y Experimentación de Obras Públicas (CEDEX).

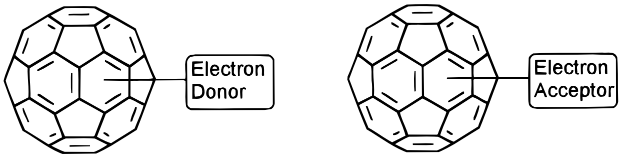
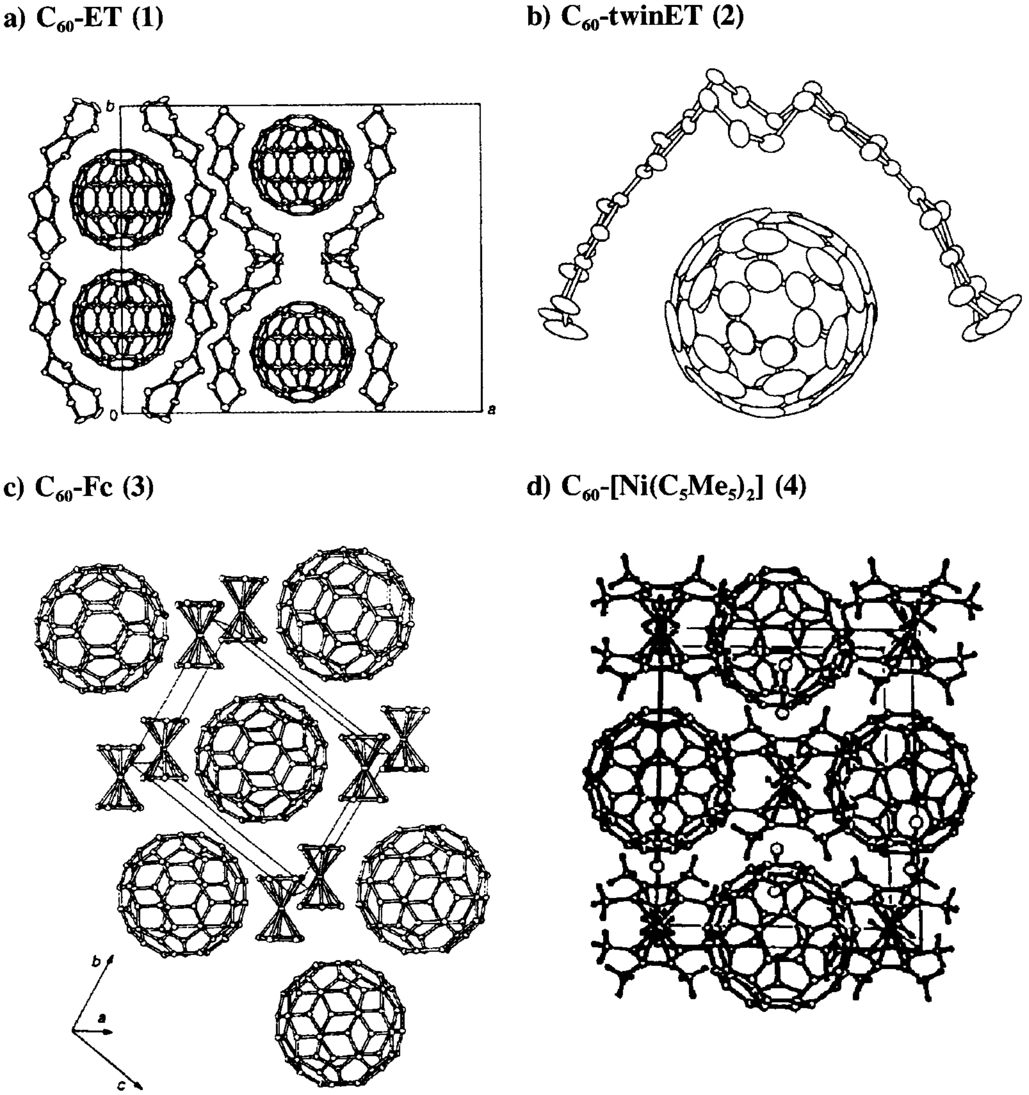


Figure 1. C_{60}−donor and C_{60}−acceptor dyads as general representative examples of electroactive organofullerenes. Bichromophoric systems with electron donors covalently linked to C_{60} efficiently undergo photoinduced charge separation. In dyads bearing electron acceptors it is possible to address the attachment of the first electron in the reduction process either to the C_{60} cage or to the organic addend.


a) C_{60}-ET (1)

b) C_{60}-twinET (2)

c) C_{60}-Fc (3)

d) C_{60}-[Ni(C_5Me_5)$_2$] (4)

Figure 2. Some representative examples (**1**−**4**) of crystal structure and packing arrangements of intermolecular C_{60}-based CT complexes. C_{60} fits in the cavity formed by the donor molecules in **1** and **2**. Ferrocene does not reduce C_{60} in **3** meanwhile decamethylnickelocene and C_{60} form a 1:1salt in **4**.

this first example of a nondisordered monoanionic C_{60} structure in which the C_{60}^- anion presents a slight distortion from icosahedral symmetry.[31]

2.2. Photoinduced Electron Transfer (PET) from Donor Polymers to C_{60}

Photoinduced electron transfer from conducting polymers derived from polyphenylene vinylene (PPV) or oligothiophene to C_{60} have been reported by Sariciftci et al., in a series of papers.[32] The photoluminiscence in the conducting polymer is quenched by the presence of C_{60} molecules. These data imply that the charge transfer from the excited state occurs on a picosecond time scale. These polymer−C_{60} systems have been used to prepare improved polymer photovoltaic cells with higher efficiency,[32d] being one of the most outstanding applications of buckminsterfullerenes. Energy conversion efficiencies of photovoltaic cells prepared from pure conjugated polymers are too low to be used in applications. High-efficiency photovoltaic conversion was discovered in composites of conducting polymers as donors and [60]fullerene and its derivatives as acceptors.[32a] This efficient charge separation results from photoinduced electron transfer which occurs in a subpicosecond time scale. It is worth mentioning that efficient charge separation occurs only at the D−A interface, and photoexcitations that occur far from this D−A junction recombine before diffusing to the heterojunction.[32d] Therefore, interpenetrating phase-separated D−A network composites (Figure 3) are considered as the appropriate photovoltaic materials.[33]

Composite films of poly[2-methoxy-5-[(2′-ethylhexyl)-oxy]-1,4-phenylene vinylene] (MEH−PPV) and C_{60} present efficiencies that are better by more than 2 orders of magnitude than those achieved with devices from pure MEH−PPV.[32] However, this highly efficient photoinduced charge separation does not always result in efficient photocurrent generation in photodiodes. Formation of interpenetrating phases of polymer/C_{60} are, sometimes, obtained only by using high volume fractions of C_{60} (polymer/C_{60}; 1:1). To increase the interaction of the donor polymer with C_{60}, Roman and Inganäs have recently reported

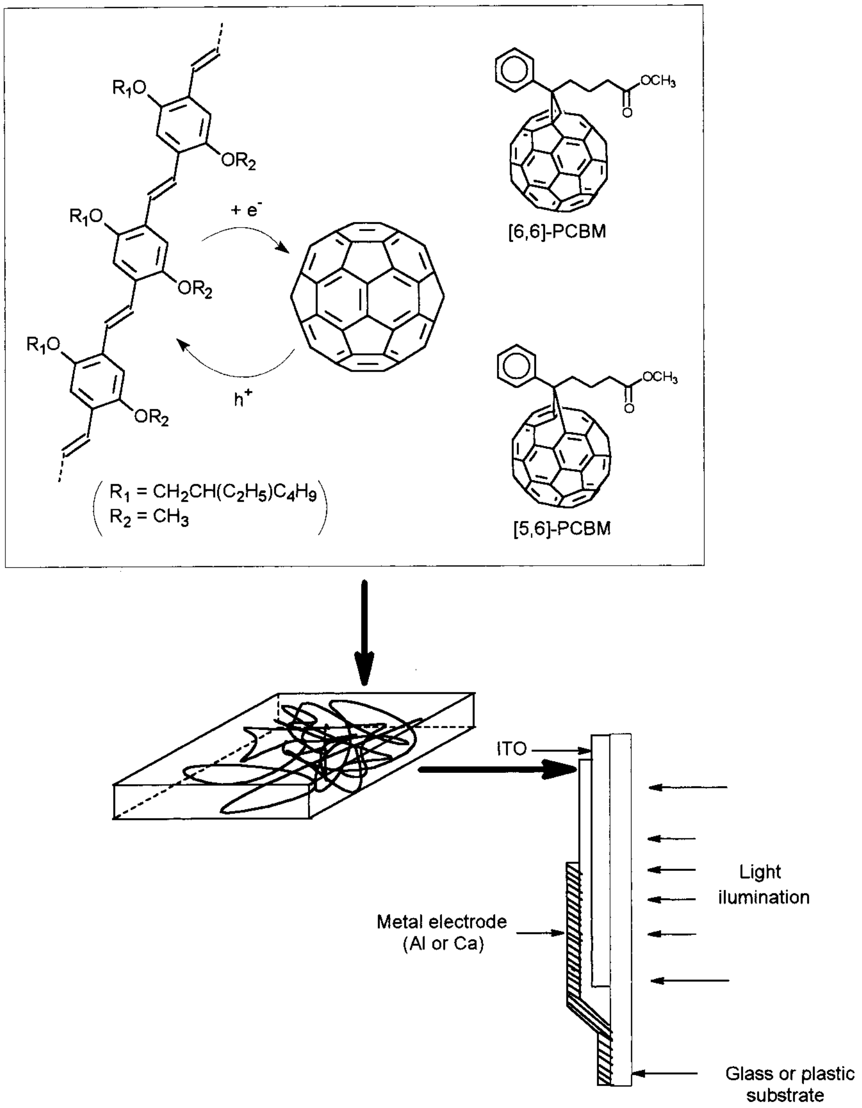


Figure 3. Photoinduced charge-transfer process in semiconducting polymer (MEH−PPV)C_{60} blends. In the film, the polymer and C_{60} species phase separate into a bicontinuous network (bulk heterojunction material). A photovoltaic cell is made with the bulk heterojunction material. (Reprinted with permission from ref 32d. Copyright 1995 American Association for the Advancement of Science.)

polythiophene derivatives, poly[3-(2′-methoxy-5′-octylphenyl)thiophene] (POMeOPT) and poly[3-(4-octylphenyl)-2,2′-bithiophene] (PTOPT), blended with C_{60} to make highly efficient photovoltaic devices.[34] The importance of the morphology of the films on the photovoltaic properties of the devices was determined from the electrical, optical, and morphological properties of the blend.

Thus, although the device efficiencies are not yet optimized, donor polymer/C_{60} systems are promising candidates to prepare polymer photovoltaic cells with enhanced efficiencies through a network of donor−acceptor heterojunctions.

2.3. Covalently Linked C_{60}–Donor Dyads

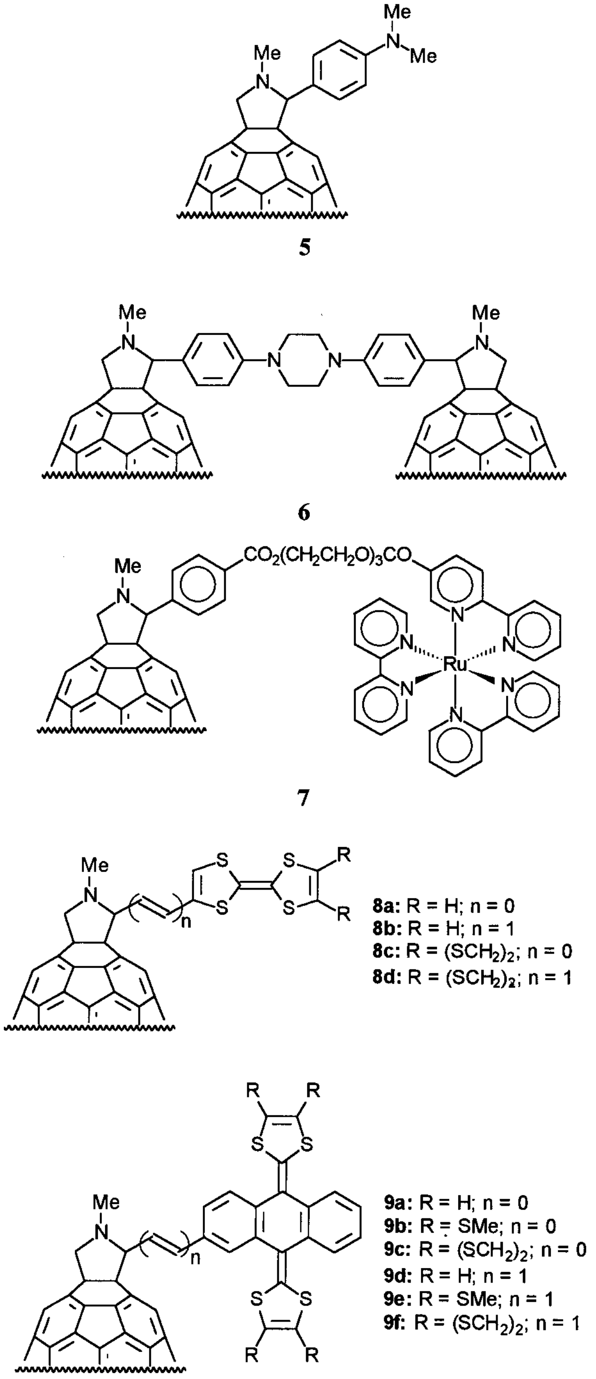
The design of dyads bearing covalently linked strong electron donors in close proximity to the C_{60} surface is a valuable approach to artificial photosynthesis and novel molecular electronic devices.[35] Therefore, a wide variety of C_{60}−donor dyads in which C_{60} and the donor unit are covalently attached were recently synthesized in the search of electron-transfer properties. In this review we will summarize some of the most outstanding compounds prepared for that purpose. These dyads have been grouped according to the different synthetic approaches followed for their preparation. Since in principle all dyads are photochemically active, we will separately discuss those examples in which the photophysical studies have been reported.

2.3.1. Dyads Prepared by 1,3-Dipolar Cycloadditions

Among the suitable procedures for the functionalization of C_{60}, Diels−Alder and 1,3-dipolar cycloadditions to [60]fullerene play a prominent role.[36] Most of the C_{60}−donor dyads reported in the literature were prepared by following both synthetic approaches (see Charts 1−5).

Thus, compounds **5**−**9** were prepared by following Prato's approach[37] from C_{60}, sarcosine (*N*-methylglicine) and the respective formyl-substituted donor molecule (Chart 1). A wide variety of molecules with

Chart 1. Some Representative Examples of C_{60}−Donor Dyads Prepared by 1,3-Dipolar Cycloadditions (5 and 7−9) and a C_{60}−Donor Dimer (6)



different donor fragments such as dimethylaniline (**5**),[38] ruthenium(II)−tris(bipyridine) complexes (**7**),[39] tetrathiafulvalene (TTF) (**8**)[40,41] or, more recently, the highly conjugated π-electron donors derived of TTF with *p*-quinodimethane structure (**9**)[42] are some examples of this type of C_{60} dyads. Recently, we have reported the first example of a C_{60}-based A−D−D−A system (**6**).[43] The cyclic voltammetry (CV) of the dimeric adduct **6** in *o*-dichlorobenzene, using a glassy carbon as electrode, shows four quasireversible reduction waves (−0.67, −1.07, −1.54, −1.98 V vs SCE), similar to that found for the parent C_{60} (−0.65, −1.06, −1.52, and −1.79 V). The reduction potentials of **6** appear at more negative potentials than the parent C_{60} as it is observed for most 1,2-dihydrofullerenes which undergo up to four reversible one-electron reduction waves at potentials slighly more negative (ca. 0.1 V) than those observed for C_{60}.[44] The presence of an irreversible oxidation wave at +0.57 V vs SCE corresponds to the *N*,*N*-dialkylaniline donor fragment (Figure 4). These CV data are similar to those obtained for the related monomeric compound (**5**) which shows four reduction waves (−0.71, −1.09, −1.69, and −2.04 V) and one irreversible oxidation wave (+0.44 V) under the same experimental conditions. These values are in full agreement with those previously reported for **5** by Williams et al.,[38] in toluene/acetonitrile (3:1) (−0.76, −1.24, and −1.79 V).

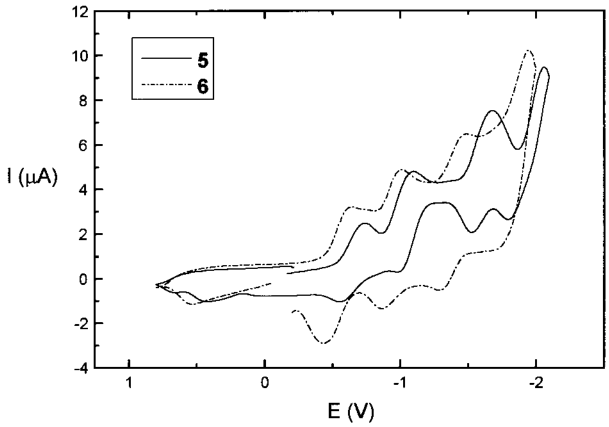


Figure 4. Cyclic voltammogram of monomer **5** and its dumbbell-type dimer (**6**) in *o*-dichlorobenzene (SCE vs Pt) using GCE as working electrode at 200 mV/s

The CV data reported on C_{60}-based dumbbell-shape molecules are scarce and, in this case, reveal that **6** behaves as two independent monomers, similar to that found for **5**. Compound **6** could be envisaged as a prototype to determine by photophysical studies whether intramolecular energy-transfer and electron-transfer processes take place in this dumbbell-type A−D-D−A molecule (see Table 1).

Although these C_{60}-based dyads (**5**−**9**) did not show an intramolecular charge transfer in the ground state, a photoinduced intramolecular electron-transfer process that causes quenching of the fluorescence of the adduct was observed in compound **5**.[38] From the quenching of the photoluminiscence a rate constant of $6.4 \times 10^{6}\ s^{-1}$ was estimated for the photoinduced electron transfer in acetonitrile solutions of organofullerene **7** at 296 K.[39b] On the other hand, preliminary magnetic susceptibility measurements carried out on compounds **9** clearly indicate a paramagnetic behavior in the solid state, showing magnetic moments of $\mu = 1.3{-}2.2$ at 290 K and obeying the Curie−Weiss law in the range of temperatures measured.[42] The structure of compound **9a** was optimized at the semiempirical PM3 level and revealed that the geometry of the donor fragment is severely distorted from planarity due to the strong steric interactions between the sulfur atoms of the 1,3-dithiole rings and the CH units in adjacent *peri* positions. To avoid these interactions, the donor moiety adopts a butterfly-type structure with the

Table 1. Redox Potentials of C_{60}−Donor Dyads

compd	conditions[a]	E^1_{ox}	E^2_{ox}	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^5_{red}	E^6_{red}	ref
C_{60}	A	–	–	−0.65	−1.06	−1.52	−1.79	–	–	
	B	–	–	−0.60	−1.00	−1.52	−2.04	–	–	
	C	–	–	−0.86	−1.38	−1.97	–	–	–	
	D	–	–	−0.72	−1.12	−1.56	−2.19	–	–	
	E	–	–	−0.98	−1.36	−1.83	–	–	–	
	H	–	–	−0.94	−1.33	−1.83	−2.28	−2.74	–	
5	A	0.44	–	−0.71	−1.09	−1.67	−2.04	–	–	43
6	A	0.57	–	−0.67	−1.07	−1.54	−1.98	–	–	43
8a	B	0.41	0.76	−0.67	−1.04	−1.53	−2.05	–	–	41
8b	B	0.43	0.76	−0.67	−1.08	−1.58	−2.19	–	–	41
8c	B	0.50	0.78	−0.71	−1.05	−1.56	−2.10	–	–	41
8d	B	0.54	0.78	−0.71	−1.19	−1.61	−2.20	–	–	41
9a	B	0.46	–	−0.66	−1.01	−1.48	−1.67	−1.96	–	42
9b	B	0.60	–	−0.67	−1.10	−1.67	−2.20	–	–	42
9c	B	0.50	–	−0.64	−0.99	−1.67	−1.95	–	–	42
9d	B	0.50	–	−0.65	−1.05	−1.62	−1.90	–	–	42
9e	B	0.71	–	−0.70	−1.10	−1.70	−2.06	–	–	42
9f	B	0.61	–	−0.66	−1.07	−1.64	−1.93	–	–	42
11a	C	–	–	−1.04	−1.62	−2.26	–	–	–	49
11b	C	–	–	−1.10	−1.69	−2.50	–	–	–	49
11c	C	–	–	−1.08	−1.72	−2.36	–	–	–	49
12a	D	0.60	1.04	−0.76	−1.15	−1.65	−1.92	–	–	46
12b[b]	E	0.18	0.65	−1.08	−1.46	−1.97	–	–	–	47a
13	F	–	–	−0.41	−0.81	−0.90	−1.26	−1.53	–	48
16	G	0.98	–	−0.53	−0.64	−0.94	−1.04	−1.41	−1.66	56
20a[b]	H	0.05	–	−1.08	−1.47	−2.03	−2.44	−3.14	–	40
20c[b]	H	0.00	–	−0.99	−1.40	−1.91	−2.32	−3.00	–	40
20d[b]	H	0.00	–	−1.00	−1.39	−1.97	−2.37	−3.05	–	40

[a] A: ODCB; SCE vs Pt; $Bu_4N^+ClO_4^-$; 200 mV/s. B: Toluene/MeCN 4:1; SCE vs Pt; $Bu_4N^+ClO_4^-$; 200 mV/s. C: THF; Ag/Ag^+ vs Pt; Fc/Fc^+. D: ODCB; SCE vs Pt; $Bu_4N^+PF_6^-$; 100 mV/s. E: CH_2Cl_2; Fc/Fc^+ vs Pt; $Bu_4N^+PF_6^-$. F: Toluene/DMF 3:1; SCE vs Pt; $Bu_4N^+BF_4^-$; 200 mV/s. G: CH_2Cl_2; Ag/Ag^+ vs Pt; Fc/Fc^+; $Bu_4N^+ClO_4^-$; 100 mV/s. H: Toluene/MeCN 3:1; Fc/Fc^+ vs Pt; $Bu_4N^+PF_6^-$; 100 mV/s. [b] Half-wave redox potentials ($E^{1/2}$).

central quinonoid ring in a boat conformation. Two isomers, depending upon the orientation of the two dithiole rings (up and down), are possible (Figure 5). Theoretical calculations predict that conformation **A** with the dithiole rings pointing upward is 1.45 kcal/mol more stable than **B**.

The geometry of the donor fragment produces a cavity with a distance between the outer carbons of the 1,3-dithiole rings of 8.8 Å. This geometrical feature could lead to an arrangement in the solid state in which a part of the fullerene surface is recognized by a neighboring π-extended donor moiety of a different molecule, giving rise to charge transfer and/or van der Waals interactions, thus supporting the found paramagnetic behavior. Similar findings have been observed by X-ray analysis by Kräutler et al. for anthracene 6,6-monoadducts[22j,k] and previuosly for intermolecular CT complexes with TTF dimers.[24b]

Compounds **8** bearing the strong donor TTF molecule covalently linked to the C_{60} cage are very attractive systems for the preparation of CT complexes by reaction with a strong acceptor molecule since, in principle, it should combine the unique properties of C_{60} with those conducting intermolecular CT complexes.[41] Thus, compounds **8a** (R = H, n = 0) and **8b** (R = H, n = 1) formed a black solid when mixed with the strong acceptor tetrafluorotetracyano-p-quinodimethane ($TCNQF_4$, $E^{1/2}_{red}$ = 0.62 V in CH_2Cl_2) which showed the presence of characteristic CT bands in the visible region of the electronic spectrum, showing a D:A stoichiometry of 1:1. These are the first examples of CT complexes in which one of the partners is covalently attached to the C_{60} core.[45] Conductivity measurements on a powdered sample showed the material to be a semiconductor ($\sigma_{rt} = 10^{-7}$ S cm^{-1}). Apparently, the lowering of the conductivity in comparison with the C_{60}-free CT complex (TTF-$TCNQF_4$, $\sigma = 10^{-4}$ S cm^{-1}) should be attributed to the distortion that the C_{60} ball causes in the crystal lattice. Nevertheless, these types of complexes should be more thoroughly studied due to the multiproperties they could exhibit.

2.3.2. Dyads Prepared by Diels–Alder Cycloadditions

Other C_{60}-based dyads have also been prepared by Diels−Alder reaction of the appropriate diene with C_{60}. As representative examples, compounds bearing a dimethylaniline unit (**10**),[9,21] differently substituted TTF (**12**)[46,47] or a nickel phthalocyanine (**13**)[48] are shown in Chart 2.

Compound **10** is a typical example of the well-known bichromophoric "ball-and-chain" systems studied by Paddon-Row and Rubin in which the electron and energy transfer between the donor and acceptor fragments, connected by a norbornylogous bridge, takes place via a through-bond coupling mechanism.[49,50] A wide variety of these "ball-and-chain" systems have recently been prepared[49] by Diels−Alder reaction of C_{60} with bridge 1,3-dienes endowed with different electroactive units (**11a**−**k**) (see Chart 2). Interestingly, the large distance between the donor and acceptor moieties in these compounds should prevent fast electron back-transfer, which is an important problem found in systems designed for the photochemical decomposition of water.[51]

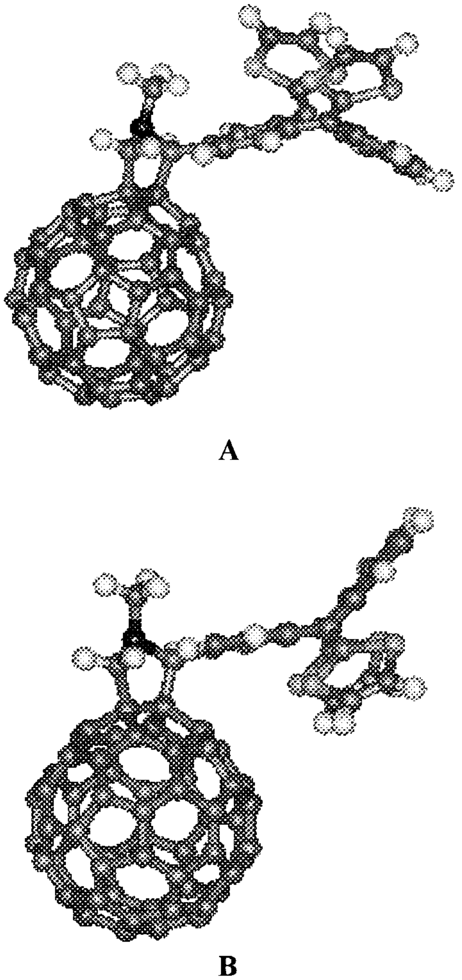


Figure 5. Minimum energy conformations (A and B) calculated (PM3) for the donor-σ-acceptor **9a**.

Compounds of type **10** are not rigid molecules due to the boat conformations that the cyclohexene ring fused to the C_{60} cage is able to adopt. Thus, compound **10** presents an extended and a boat conformation with different spatial interchromophore separation as it is shown in Figure 6.

Theoretical calculations reveal that the energy difference between both conformations is small, being only 0.1 kcal/mol for compound **10**.[49] The X-ray crystal structure of the related molecule prepared from **11a** and C_{60}, bearing a *p*-dimethoxybenzene donor moiety shows that in the solid state, this compound adopts the extended conformation.[52]

Preliminary photophysical studies carried out by Verhoeven and Williams on compound **10** by flash photolysis in benzonitrile reveal a rapid and efficient intramolecular electron transfer from the dimethylaniline donor to the C_{60} acceptor to form a charge-separated state with a rate constant of ca. 5.5×10^9 s^{-1}. Interestingly, a lifetime of 250 ns was determined for the charge-separated state which is quite long compared with other bichromophoric related systems.[53]

Although the green fullerene **13** did not exhibit a charge-transfer from the phthalocyanine to the fullerene at ambient conditions, reduction of the fullerene moiety resulted in having a significant influence on the optical properties of the phthalocyanine (see Table 1).[48] Finally the C_{60}−TTF dyads **12** as well as compounds **8** and **9** represent an interesting class of organofullerenes for which the study of their photophysical properties is currently under study in different laboratories. Preliminary photophysical studies carried out on dyad **12** reveal that the lifetime of the excited triplet state (75−79 μs) and the energy gap between the frontier orbitals is highly dependent on the donor ability of the TTF addend. Both radical−cations and radical−anions of **12** have been fully characterized by EPR measurements.[47b]

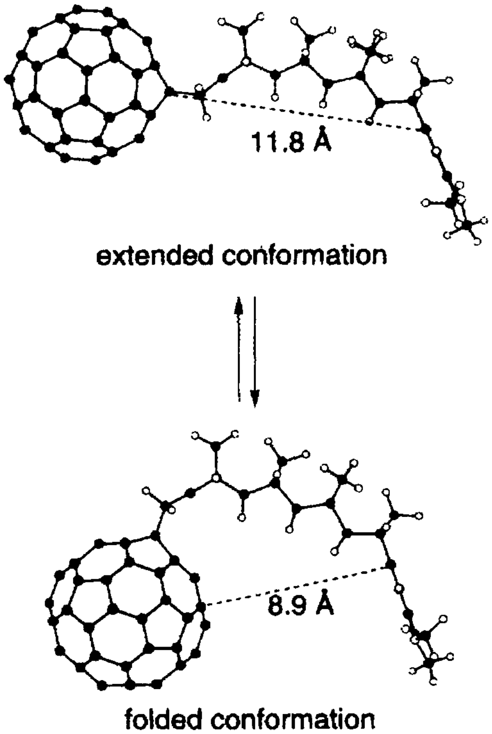
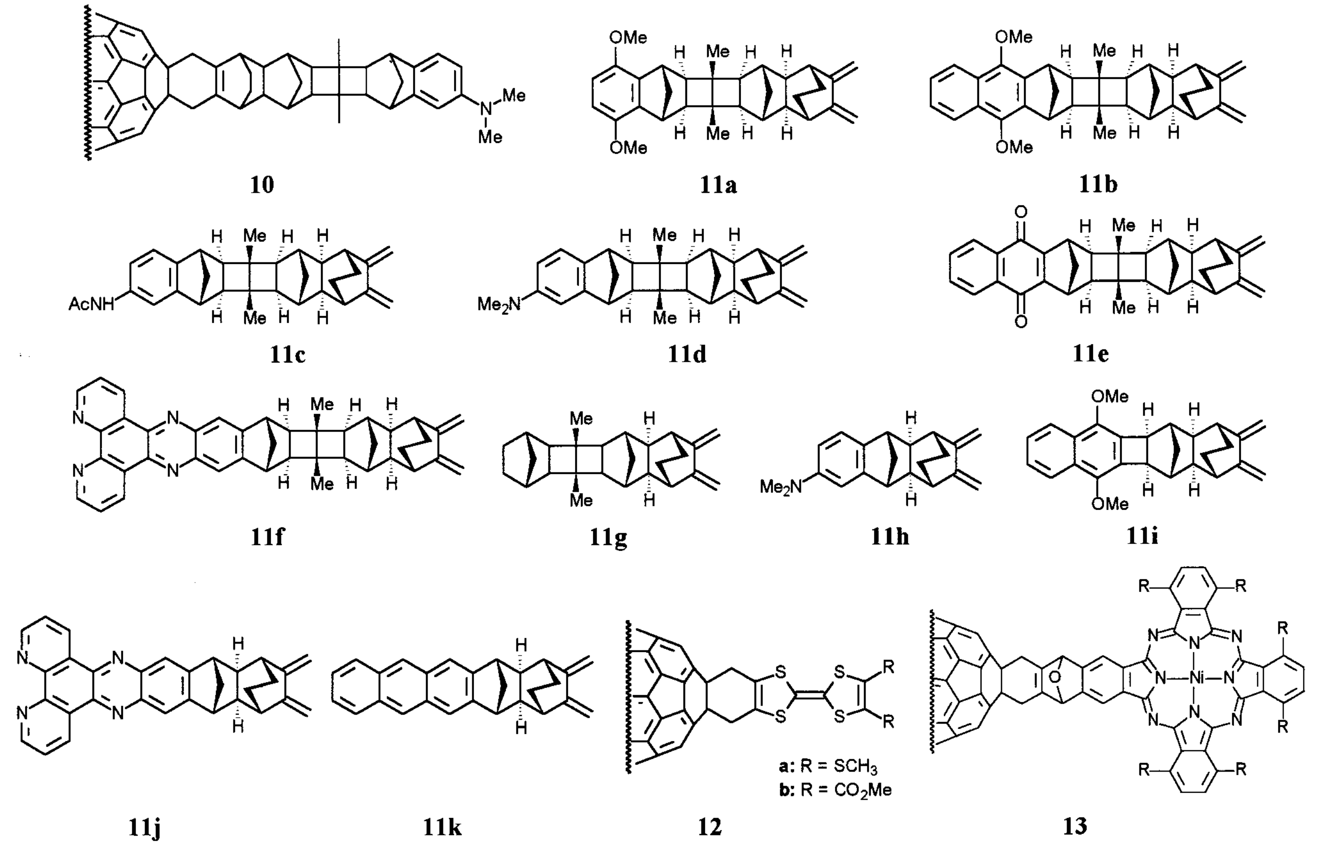


Figure 6. Optimized geometries (AM1) calculated for the dimethylaniline-C_{60} system **10**, showing the different distances between both chromophores in the extended and folded conformations. (Reprinted from ref 49. Copyright 1996 American Chemical Society.)

2.3.3. Dyads Prepared by Bingel's Reaction

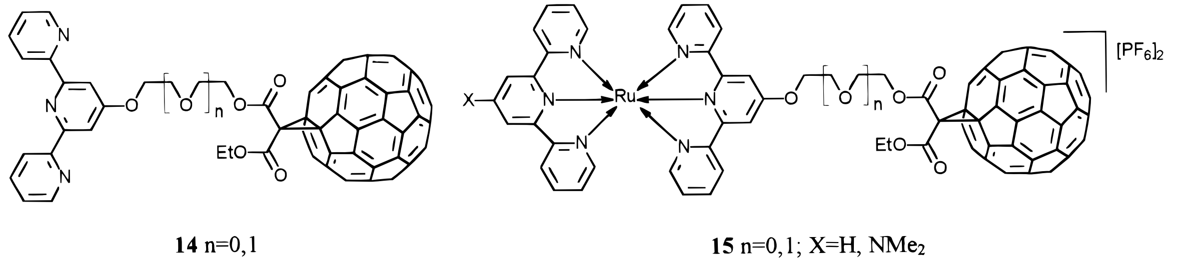
Bingel's reaction[54] has also been used for the preparation of dyads and triads in which the pendant fullerene acts as an electron acceptor. Thus, a new series of ligands in which C_{60} is covalently attached to 2,2′:6′,2″-terpyridines (tpy) (**14**) were prepared by Constable and Diederich[55] which were in turn used as precursors for the synthesis of ruthenium(II) dyad and triad systems (**15**) (Chart 3). Complexes **15** show a CT absorption band at 480 nm in their electronic spectra as well as the $Ru^{II}-Ru^{III}$ process at around +0.800 V (vs Fc-Fc^+) and the fullerene reduction waves in their cyclic voltammograms. Introduction of the electron-releasing dimethylamino substituent to form triad **15** ($X = NMe_2$) shifts the $Ru^{II}-Ru^{III}$ redox process to +0.500 V and, however, no significant effect was observed on the reduction potentials of the [60]fullerene moiety. Although no charge transfer occurs in compound **15** from the amine to the fullerene fragment in the ground state, these complexes are attractive systems for the investigation

Chart 2. Some Representative Diels−Alder Cycloadducts of Type C_{60}−Donor Dyads (10−13)[a]



[a] A wide variety of bichromophoric “ball-and-chain” systems based on C_{60} (**10** and **11**) have been prepared for the study of intramolecular electron- and energy-transfer processes.

Chart 3. Some Representative Methanofullerenes of Type C_{60}−Donor Dyads (14) and Triads (15) Prepared by Using Bingel’s Reaction



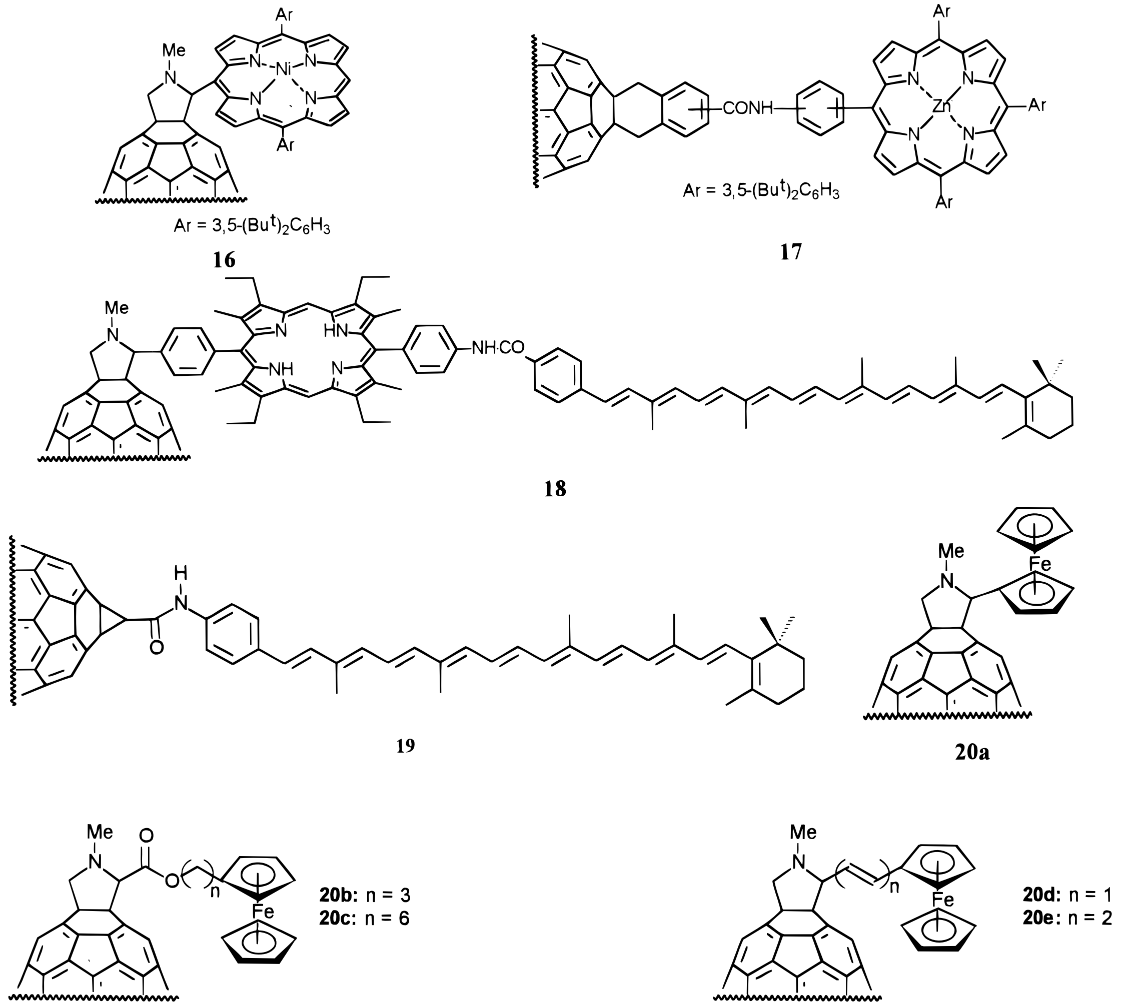
of further photochemical and photophysical properties.

2.3.4. Photoinduced Electron Transfer (PET) in Dyads

Chart 4 shows some selected examples of C_{60}−donor dyads in which the C_{60} moiety is linked to different porphyrins (**16**−**18**), carotenoid (**19**), or ferrocene (**20**) through a pyrrolydine ring or other more complex spacers. Several papers have been recently published dealing with the synthesis and photophysical properties of C_{60}-linked porphyrins since Gust et al. in 1994 reported the first of this type of dyads.[8] C_{60}−porphyrin dyads exhibit long-lived charge-transfer states which have been successfully used in the generation of photocurrent, thus proving the interest of these systems as photoactive materials. The state of the art on these attractive C_{60}−porphyrin dyads has been recently collected in an excellent review by Imahori and Sakata[56] to which the reader is referred. Very recently, a molecular triad (**18**) consisting on a diarylporphyrin covalently attached to a carotenoid polyene and a fullerene has been prepared and studied using time-resolved spectroscopic methods.[57] Interestingly, a long-lived charge-separated state generated by photoinduced electron transfer and the formation of a triplet state by charge recombination was observed in this triad.

Carotenoid pigments are present in photosynthetic organisms participating with chlorophylls in energy- and electron-transfer processes. As they can act as electron donor molecules, the first carotenoid containing dyad (**19**) in which carotenoid polyenes are linked to C_{60} has also been reported.[58] In dyad **19**, the lowest excited singlet state of the fullerene is strongly quenched by electron transfer from the carotenoid moiety to generate the charge-separated species $Car^{\bullet+}$−$C_{60}{}^{\bullet-}$ which has a rise time in CS_2

Chart 4. Representative Examples of Porphyrin-Containing (16 and 17) and Carotenoid-Containing (19) Dyads and a Triad (18) and Ferrocene-Containing Dyads with Different Spacers (20a–20e), Showing Energy and/or Photoinduced Electron Transfer



solution of 0.8 ps and decays by charge recombination in 534 ps.

An interesting and systematic steady-state fluorescence and time-resolved flash photolytic study of a series of ferrocene containing C_{60}-based dyads has been recently reported by Guldi *et al.*[59] An intramolecular quenching of the fullerene excited singlet state was observed in systems **20a**–**e** (Chart 4). Picosecond-resolved photolysis of dyads **20a**–**e** in toluene led to the initial formation of the excited singlet state (absorption at 886 nm), which for dyads **20b** and **20c** is rapidly quenched ($\tau_{1/2} = 100$ and 200 ps, respectively) and transforms into a broadly absorptive species. No absorption features corresponding to the excited triplet state (around 705 nm) were observed for these compounds. A photoinduced electron transfer occurs to yield $C_{60}{}^{\bullet -}-Fc^{\bullet +}$ via reductive quenching (Figure 7). The charge-separated state was characterized spectroscopically by nanosecond-resolved photolysis (absorption maximum at 400 nm). However, the characteristic absorption band of C_{60} radical anions around 1080 nm was not observed due to the short half-lifes [$\tau_{1/2} = 0.62$ μs (**20b**) and $\tau_{1/2} = 1.06$ μs (**20c**)] for these transient radical anions. The charge-separated state was stabilized in benzonitrile [$\tau_{1/2} = 1.8$ μs (**20b**) and $\tau_{1/2} = 2.5$ μs (**20c**)] and the absorption band at 1055 nm observed.[59]

In these dyads, and depending upon the flexible or rigid nature of the spacer connecting C_{60} and

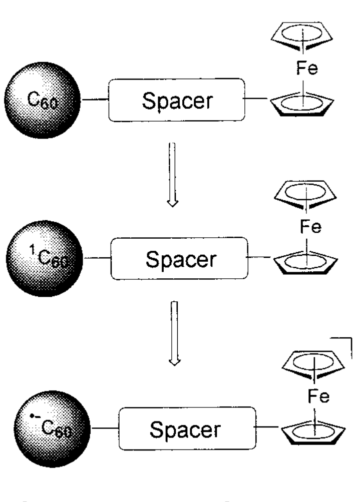
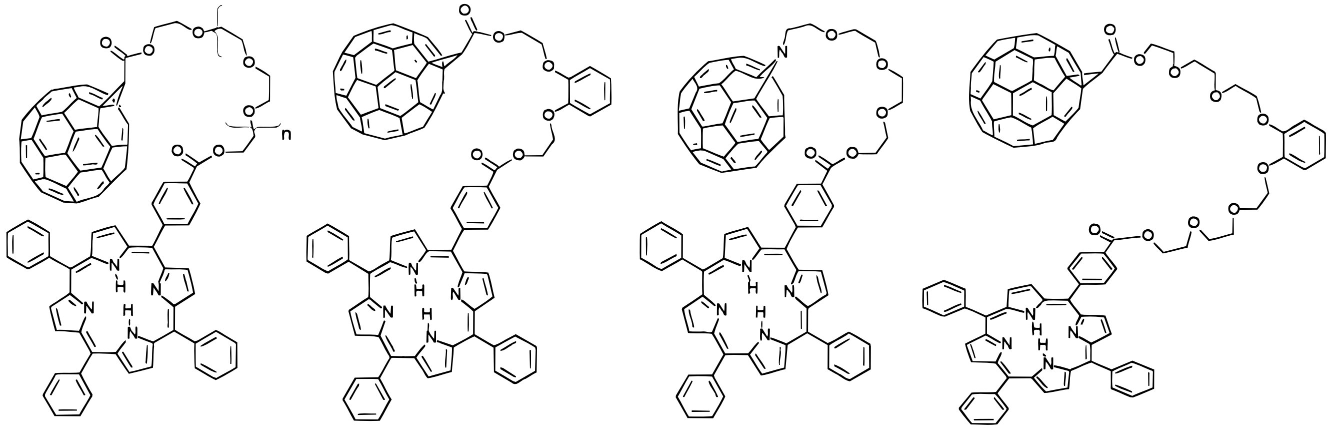


Figure 7. Photoexcitation and generation of a charge-separated state in C_{60}–spacer–ferrocene dyads (**20a**–**e**). The presence of a saturated hydrocarbon spacer leads to long-lived charge-separated states.

Chart 5. C_{60}–Porphyrin Dyads Bearing Conformationally Flexible Spacers for Complexation with Metal Cations[a]



21a: n=1

21b: n=2

22

23

24

[a] Both porphyrin (donor) and C_{60} (acceptor) moieties are brought closer together in the complexed state. In contrast to **21**–**23**, dyad **24** does not undergo comformational reorganization in the presence of metal cations.

ferrocene moieties, two different quenching mechanisms by through-bond electron transfer or by formation of a transient intramolecular exciplex were suggested. In this study it was concluded that the presence of a saturated hydrocarbon spacer results in a higher stabilization leading to long-lived charge-separated states in the time range of microseconds.[59]

An efficient and versatile synthesis which provides an access to different structures has been used for the preparation of the novel dyads **21a,b** and **22**, as well as for the first aza-linked porphyrin–C_{60} dyad (**23**) (Chart 5). The nature of the spacer has been skillfully exploited in the construction of structurally flexible porphyrin–C_{60} dyads in which intramolecular interactions are enhanced as a result of complexation with metal cations.[60] Interestingly, electronic interactions were observed in the ground state, despite the nonrigid skeleton of the spacer. These interactions were observed in the electronic spectra of dyads **21a,b** and **22** and their metalated derivatives which show bathochromic shifts of 6–10 nm relative to model methyl ester substituted porphyrin. Shifts of only 2–4 nm were observed for dyad **23**. The crown-ether-like structure of the chain linking the porphyrin moiety to the C_{60} cage allows complexation with cations, thus appearing a dynamic equilibrium between complexed and uncomplexed states. According to theoretical and experimental data, both donor (porphyrin) and acceptor (C_{60}) moieties are brought closer together in the complexed state, thus increasing the intramolecular interactions. An efficient quenching of the porphyrin S_1 excited state by the C_{60} unit was observed in these dyads (**21**–**23**) by fluorescence spectra. By using ultrasensitive Ge-based near-IR detector, quantum efficiencies ϕ_Δ for sensitized formation of $^1O_2$ based on steady-state emission of $^1O_2$ at 1270 nm were measured (0.10–0.21) for dyad **21a**.

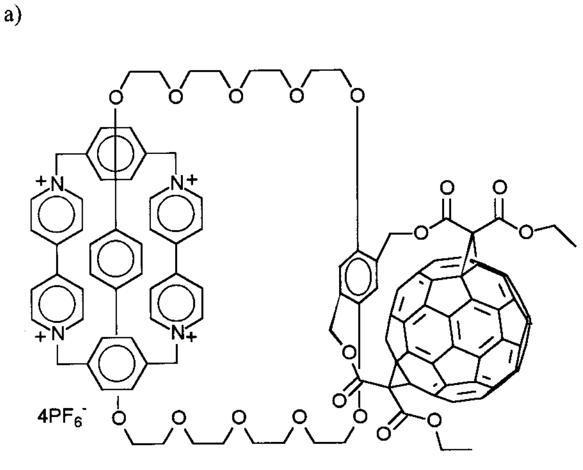
In contrast to the above dyads (**21**–**23**), the recently reported dyad **24** did not undergo conformational reorganization in the presence of different cations (Li^+, Na^+, K^+, t-Bu_4N^+) (no variation of the UV–vis absorption spectra was observed).[61] These findings suggest that the greater conformational flexibility of the polyether spacer, compared with those spacers in dyads **21**–**23**, inhibit the expected crown ether-like complexation with metal cations. It is interesting to note that the measured steady-state quantum yield for triplet-sensitized formation of $^1O_2$ from **24** ($\phi_\Delta = 0.40 \pm 0.04$) resulted to be the highest value observed for a porphyrin–C_{60} dyad. Although the reason for this high value is not explained, these results should aid in the design of novel organofullerenes with long-lived triplet states able to undergo energy-transfer processes.

The above approach represents an alternative procedure to the use of other systems such as rotaxanes[62] and catenanes[63] or to the formation of complexes from calixarenes[64] in the search for C_{60}-based electronic interactions.

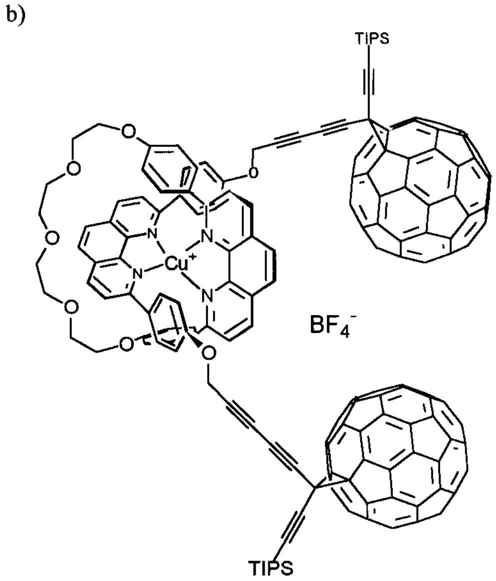
The first example of a C_{60}-containing catenane has been recently reported by Diederich and Stoddard[63] in which the unique shape and electronic properties of C_{60} are combined with noncovalent bonding interactions to self-assemble different interlocked molecules[65] (Chart 6). In addition to the previously observed intramolecular D–A–D–A stacks involving electron-donor hydroquinone rings and electron-deficient bipyridinium units,[66] the hydroquinone unit in compound **25** undergoes additional interactions with the electron-accepting C_{60} moiety. This intramolecular interaction has no precedents in [2]-catenanes, and therefore, these novel compounds are excellent candidates for the study of their electrochemical and photophysical properties.

A copper(I)-complexed rotaxane (**26**) bearing two fullerene stoppers has been prepared by Diederich and Sauvage in an interesting extension of the use of electro- and/or photoactive species in the preparation of multicomponent molecular systems displaying

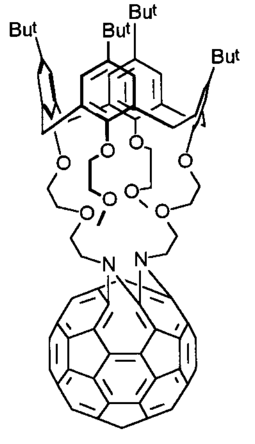
Chart 6. (A) C_{60}-Containing Catenane in Which the Hydroquinone Ring Is Interacting with Both Bipyridinium and C_{60} Moieties and (B) Copper(I)-Complexed Rotaxane with Two C_{60} Stoppers[a]



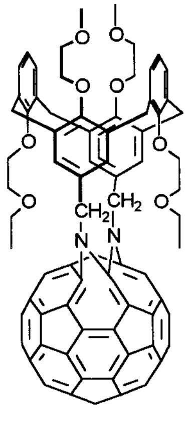
25



26



27a



27b

[a] The fullerene units significantly influence the redox properties of the metal center.

electronic and photochemical properties[62] (Chart 6). Rotaxane **26** was synthesized by oxidative coupling reaction of terminal alkynes[67,68] using in situ preparation of the Hay catalyst [CuCl-TMEDA-O_2] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Electrochemical studies carried out on rotaxane **26** by cyclic voltammetry clearly indicate a strong effect of the fullerene moiety, leading to a significant anodic shift of the $Cu^{I/II}$ redox potential (+0.865 V vs SCE in CH_2Cl_2) as compared to other related complexes ($\Delta E° \approx 0.2$ V). In contrast, the metal center does not seem to change the redox properties of the fullerene units which show the first reduction potential at around −0.6 V.

Luminiscence measurements show that emission from the metal-to-ligand charge-transfer triplet state of the copper(I) complex **26** is quenched by the two C_{60} units acting as stoppers.

“Fullerenocalixarenes” in which [60]fullerene is covalently attached through two ionophoric chains to a cone-calix[4]arene (**27a**) or to a 1,3-alternate calix[4]arene (**27b**) have been recently synthesized, showing that the absorption spectra of these “fullerenocalixarenes” are affected by addition of metal cations (Li^+, Na^+, and Ag^+). Although it is not yet clear whether this influence is due to the direct metal−C_{60} surface interaction or due to the indirect inductive effect through the metal−N interaction (Chart 6), this effect represents a new approach to change the electronic state of C_{60} by added metal cations. These novel exohedral metallofullerenes bearing an ionophoric site to trap metal cations located near the [60]fullerene surface are considered a potential alternate approach to the control of fullerene functions.[64c]

Calixarenes have been used for the separation of C_{60} and C_{70} by formation of a clathrate from C_{60} and calix[8]arenes.[64a,b] As a consequence of the smooth and dense surface of C_{60}, it has been bound by an accumulation of weak van der Waals interactions, even in organic solvents, to different calixarenes. The X-ray structure of C_{60} and calix[5]arene in the crystal and in solution has been recently reported.[64e] Interestingly, the guest molecule (C_{60}) is encapsulated

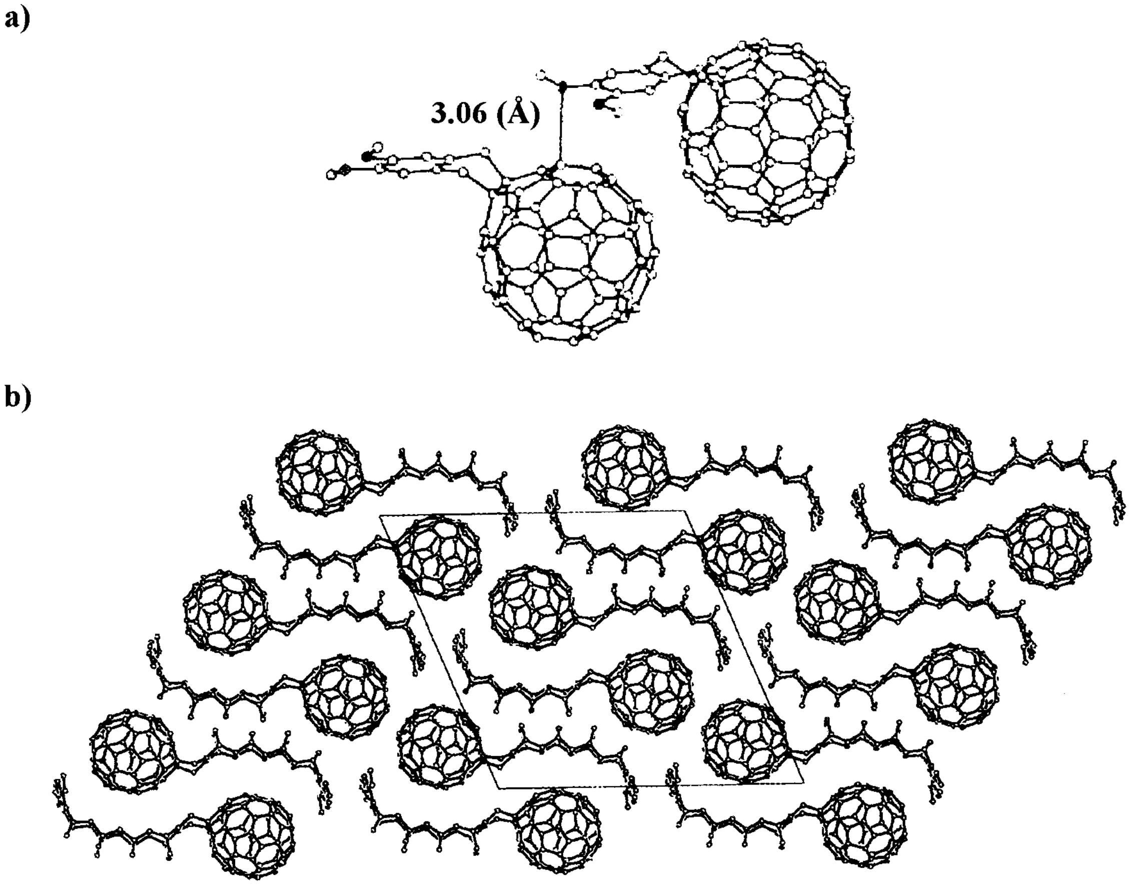


Figure 8. Crystal packing of Diels−Alder cycloadducts showing (a) close intermolecular contacts between C_{60} as acceptor and (b) the respective (dimethoxibenzene) donor moieties. (a: Reprinted with permission from ref 69. Copyright 1993, VCH. b: Reprinted from ref 49. Copyright 1996 American Chemical Society.)

within a cavity of the two host molecules in the solid state.

Finally, it is worth mentioning that some of the prepared C_{60}-based D−A systems, as intended intramolecular complexes, showed interesting intermolecular interactions in the solid state determined by X-ray analysis (Figure 8). Thus, cycloadduct formed by Diels−Alder reaction of C_{60} and 4,5-dimethoxy-*o*-quinodimethane (Figure 8a) presented a close contact of one of the methoxy groups with a neighboring C_{60} [3.06(1) Å], thus forming a chain of interacting fullerene cages.[69,70] This interaction is a specific solid-state effect since the electronic spectra in solution did not reveal any charge-transfer band. Similarly, the first rigid ball-and-chain D−A system prepared from C_{60} and the bridge diene **11a** also showed a beautiful and interesting crystal packing structure in which the dimethoxybenzene group is interacting with a neighboring C_{60} moiety in the solid state[49,52] (Figure 8b). In this case, the rigid norbornylogous bridge has a regular curvature which is an important feature in the ability of this compound to form dimeric pairs in the crystal packing. This self-complementarity into head-to-tail pairs may be originated from the combination of crystal-packing forces and electrostatic or π-stacking interactions between the dimethoxybenzene donor units and the C_{60} moiety. In this regard, it is known that formation of intermolecular CT complexes can be favored in the solid state since, in addition to the striking influence of the solvent on the redox potentials, formation of CT complexes is a reversible process. Thus, as a previously reported representative example, the complex C_{60}−TDAE [TDAE, tetrakis(dimethylamino)ethylene] reverts to the neutral molecules TDAE and C_{60} in toluene solution.[30]

3. [60]Fullerene−Electron Acceptor Systems

In comparison with the above C_{60}−donor dyads, organofullerenes in which the C_{60} cage is covalently attached to an electron-poor organic addend[71] have been scarcely studied. The design and synthesis of novel organofullerenes exhibiting better reduction potentials than the parent C_{60} is still a demanding goal for the development of specific optical and electronic applications. Therefore, the synthesis of compounds of type C_{60}−electron acceptor (Figure 9) is of interest for the preparation of intermolecular CT complexes with strong electron donor molecules[72] or, for instance, for the development of photovoltaic cells by blending the appropriate semiconducting polymer with these fuctionalized C_{60} derivatives.[32] In addition, it should be possible to address the attachment of the first electron in the reduction process either to the C_{60} cage or to the organic addend by choosing the appropriate electron acceptor organic addend. We will present some examples from recent literature in which the reduction ability of the

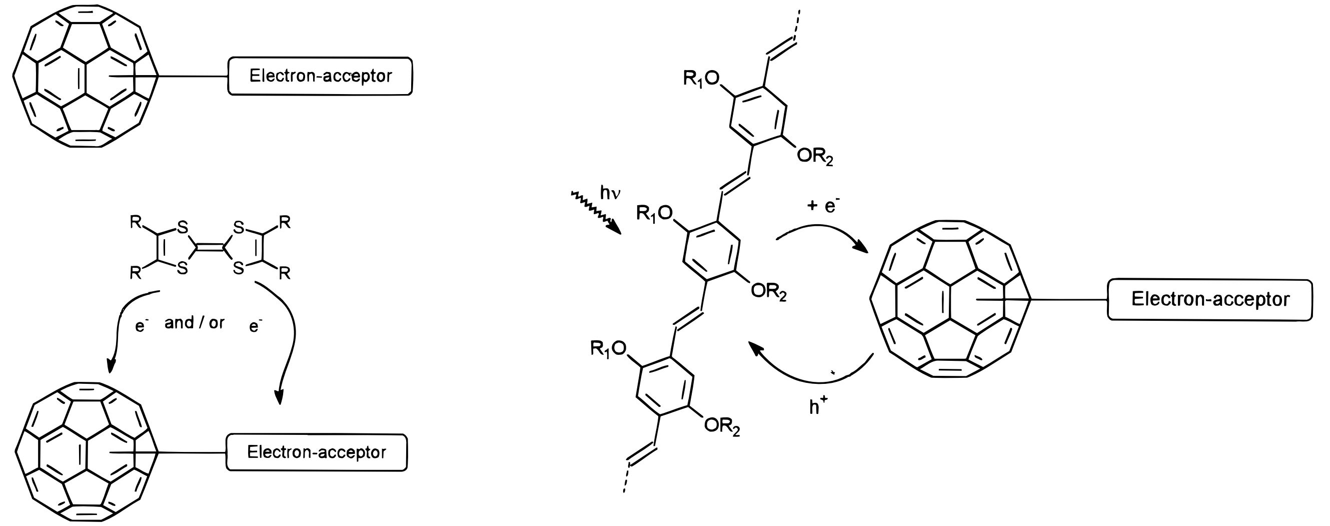


Figure 9. [60]Fullerene−electron acceptor systems and some potential applications as precursors for CT complexes and for the fabrication of devices such as photovoltaic cells. The presence of the organic addend linked to the C_{60} can increase the solubility for blending with molecular or polymeric materials in addition to improve the electron-accepting ability of the system.

Table 2. Reduction Potentials of C_{60}−Acceptor Dyads

compd	conditions[a]	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^5_{red}	E^6_{red}	ref
C_{60}	A	−0.60	−1.00	−1.52	−2.04	–	–	
	B	−1123	−1455	−1913	−2383	–	–	
	C	−1056	−1451	−1906	−2384	–	–	
32a	A	−0.51	−0.68	−1.17	−1.74	–	–	75
32b	A	−0.63	−0.77	−1.11	−1.32	−1.76	−1.94	75
32c	A	−0.21	−0.64	−1.07	−1.68	–	–	75
33	A	−0.40	−0.64	−0.91	−1.07	−1.67	−1.95	88
34	A	−0.70	−1.06	−1.27	−1.70	−2.17	–	88
35	A	−0.64	−0.95	−1.05	−1.40	−1.68	–	88
36	A	−0.38	−0.65	−1.06	−1.67	–	–	89
37	A	−0.32	−0.64	−0.98	−1.07	−1.78	–	89
38	B	−1081	−1559	–	–	–	–	94
39	B	−1042	−1197	−1602	−2016	–	–	94
40	B	−1097	−1620	−2037	–	–	–	94
41	B	−1215	−1525	−1670	−2090	–	–	94
42	B	−1133	−1383	−1537	−1943	–	–	94
43	B	−1142	−1321	−1444	−1536	−1953	–	94
44a	C	−1058	−1438	−1925	−2380	–	–	100
44b	C	−1073	−1458	−1943	−2410	–	–	100
44c	C	−1090	−1495	−1986	−2484	–	–	100
45	C	−935	−1330	−1800	−2225	–	–	100

[a] A: Toluene/MeCN 5:1; SCE vs Pt; $Bu_4ClO_4^-$; 200 mV/s. B: ODCB; Ag/Ag^+ vs Pt; Fc/Fc^+; $Bu_4N^+BF_4^-$; 100 mV/s. C: DMF/toluene 2:3; Ag/Ag^+ vs Pt; Fc/Fc^+; $Bu_4N^+BF_4^-$; 2 mV/s.

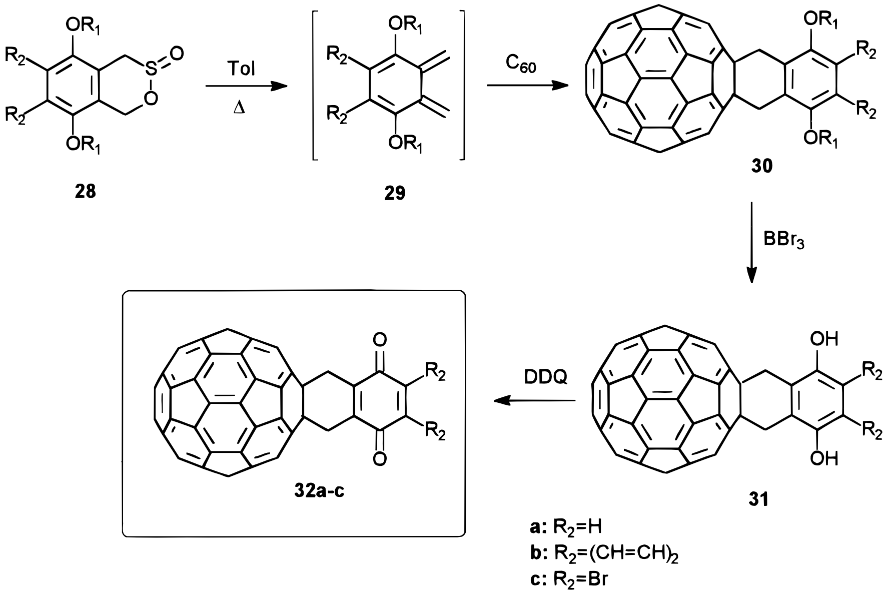
prepared organofullerene is improved in comparison with the parent [60]fullerene (see Table 2).

3.1. Covalently Linked C_{60}–*p*-Benzoquinonoid Systems

A structurally simple type of electron acceptor organofullerenes is [60]fullerene-*p*-benzoquinone systems (**32**) which have been prepared from substituted *o*-quinodimethanes by reaction with C_{60}. Recently, Iyoda et al.[73] have reported the synthesis and characterization, including X-ray analysis of the parent molecule **32a** and generation of mono- and dianion species, of benzoquinone-containing cycloadducts by generating the precursor *o*-quinodimethanes from benzocyclobutenes and using high temperatures. We have also prepared these differently substituted electron acceptor organofullerenes (**32**) under very mild conditions[74,75] by generation of the *o*-quinodimethane intermediates (**29**) from “sultines” (**28**) by using the commercially available rongalite.[76] In contrast to other reported procedures, generation of *o*-quinodimethanes[77] from 4,5-benzo-3,6-dihydro-1,2-oxathiin-2-oxide (sultine) takes place smoothly at around 80 °C by extrusion of sulfur dioxide without production of any organic or inorganic byproducts (Scheme 1).

The prepared cycloadducts **30** can be easily transformed into the corresponding *p*-benzoquinone-containing cycloadducts **32**, by removing the alkyl groups and further oxidation in high yields.[73,75] These compounds (**32**) show a dynamic process due to the boat-to-boat interconversion of the cyclohexene ring, as it has been previously observed for other related 1,2-dihydrofullerenes.[36b,70,78,79] The activation

Scheme 1



free energy for the boat-to-boat inversion for compounds **32** has been determined by DNMR experiments, resulting a value ($\Delta G^\ddagger \approx 11.0-11.5$ kcal mol^{-1}) very low in comparison with other carbocyclic[36b,79−81] or heterocyclic[82] related analogues. These $\Delta G^\ddagger$ values are also low compared with other fullerene adducts. Thus, the boat barriers in higher fullerenes Diels−Alder adducts were determined by Diederich et al.[78] with values ranging between 14.7 and 15.3 ± 0.1 kcal/mol.

An electronic repulsion between the fullerene π-electron and the quinone addend (acceptor−acceptor interaction) has been claimed as responsible for the low activation energy of these systems.[73] Theoretical calculations reveal that the most remarkable geometrical difference between cycloadducts bearing a *p*-benzoquinone moiety and a benzene ring comes from the fused double bond which, according to the X-ray data, is 0.06−0.08 Å shorter for the quinone double bond. The shortening of this bond widens the bond angles of the cyclohexene ring which results in a slightly smaller folding of the cyclohexene ring.[75]

To support this idea, the boat-to-boat inversion barrier through the structure resulting from the planarization of the cyclohexene ring was calculated, thus identifying the C_{2v} structure as a true transition state. The calculated energy differences between C_s and C_{2v} structures is 13.9 kcal mol^{-1}, which is in good agreement with the NMR measurements. In fact, a direct correlation has been found between the length of the C_{60}-fused cyclohexene double bond and the energy barrier.[75]

Cycloadducts **32** show three or four reduction waves at potential values similar to those of C_{60}, which should be attributed to the C_{60} moiety.[73,75] These reduction waves, as expected, are shifted to more negative values in comparison to the parent C_{60}, due to the saturation of a double bond.[44,83,84] In addition, another reduction wave appears at potential values very close to the first reduction potential of the C_{60} moiety. As it is shown in Table 2, substitution on the *p*-benzoquinone moiety has a striking influence on the redox behavior. The CV values were rationalized on the basis of DFT-B3P86/3-21G calculations. Figure 10 sketches the energetic ordering and orbital assignment of the frontier orbitals of the prepared cycloadducts **32**.[75]

According to this diagram, the attachment of the first electron in the reduction process takes place in the *p*-benzoquinone moiety in compound **32a** (R_2 = H). The energy difference between the LUMOs of the C_{60} and the quinone fragment increases when two bromine atoms are linked to the *p*-benzoquinone fragment in **32c** due to the stabilization of the LUMO of this moiety. The effect is much more pronounced for the not yet synthesized molecules in which the carbonyl groups of **32a** are substituted by $C(CN)_2$ groups, or the bromine atoms of **32c** are replaced by cyano groups.

In contrast, the presence of a benzene ring fused to the quinone moiety in **32b** produces a destabilization of the LUMO of the organic addend which now lies above those of the C_{60} core. This destabilization of the LUMO of benzoquinone in passing to naphthoquinone has been previously shown to be due to the antibonding interaction of the fused benzene ring with the quinone.[85]

These electron acceptor systems are very attractive for further applications since, depending upon the nature of the substituents on the *p*-benzoquinone ring, it allows the first electron in the reduction process to be addressed, either to the C_{60} cage or to the organic addend by controlling the relative energy of the LUMO of the organic addend with respect to the LUMO of the C_{60} moiety.[75]

Although the reduction of C_{60} with alkali metals has been widely investigated, much less is known on the alkali metal reduction of fullerene derivatives bearing organic substituents. Reduction of **32a** was carried out with potassium or sodium in THF and the EPR spectra of the dianion **32a**•2K$^+$ (Figure 11) appears as a broad signal at the center and a fine structure, due to triplet species ($g = 2.002$, $D = 45.8$ G) at 77 K.[73b] An unresolved structure is observed

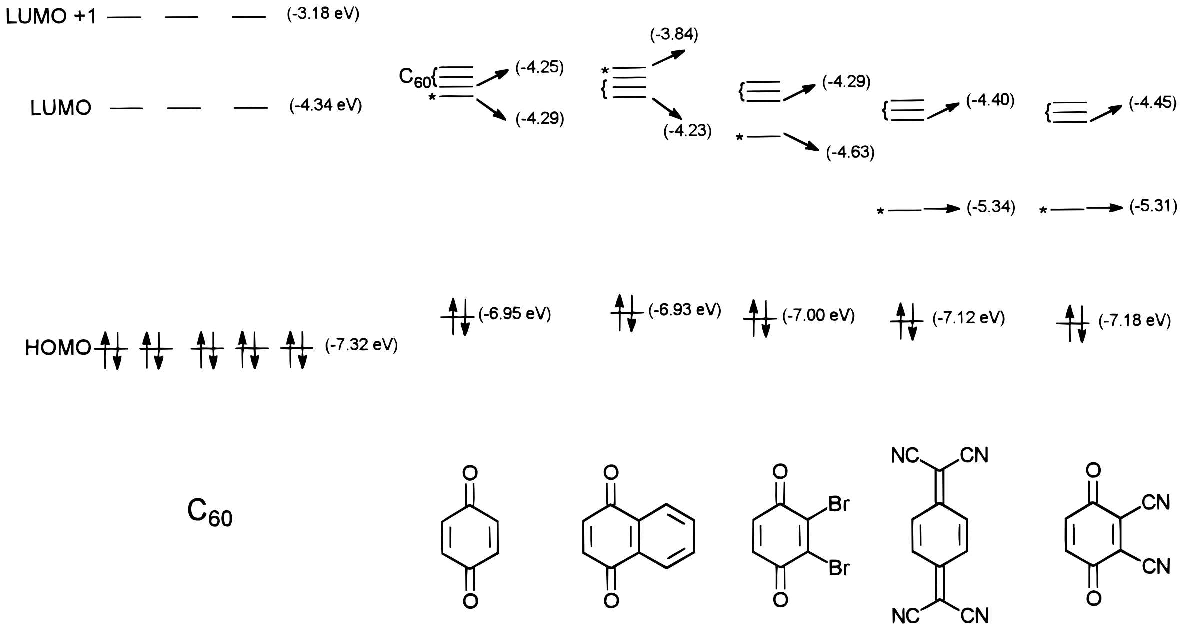


Figure 10. Molecular orbital distribution (B3P86/3-21G) calculated for C_{60} and compounds **32**, showing the chemical structure of the *p*-benzoquinone-type addend. The energy of the orbitals (in electron volts) are given within parentheses. The three LUMOs of C_{60} are enclosed by a brace; the LUMO localized on the *p*-benzoquinone moiety is denoted by an asterisk.

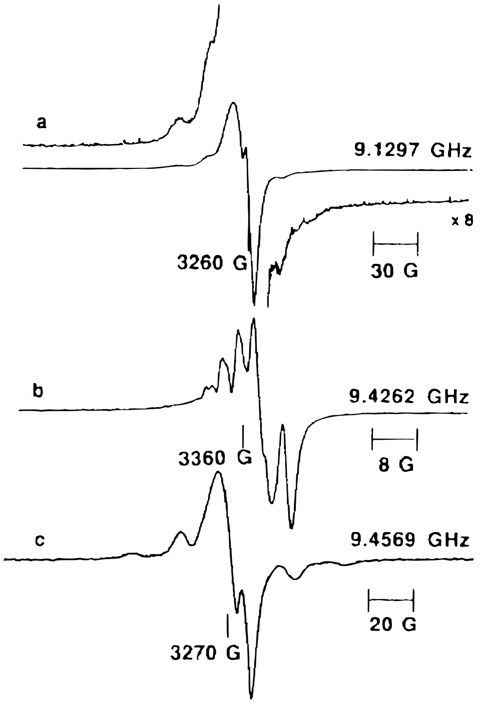


Figure 11. (a) EPR spectra of **32a**·$2K^+$ at 77 K, (b) recorded at 293 K, and (c) **32a**·$2Na^+$ at 77K. (Reprinted with permission from ref 73b. Copyright 1996 Elsevier.)

at 293 K which gradually changes to a more simple one composed of a semiquinone radical anion [$g = 2.005$, $a_H = 2.1$ G (6H)] and a fullerene radical anion ($g = 2.000$) which has been accounted for by the disappearance of the dianion.[73b] The distance between two spins estimated from D value by the point dipole approximation was 8.5 Å, thus showing a marked dipole–dipole interaction between the C_{60} moiety and its substituent at the ground state.

Other functionalized C_{60}-based anthraquinone derivatives were prepared by Diels–Alder reaction of the *o*-quinodimethane, generated “in situ” by iodide-induced 1,4-elimination of 1,4-dihydroxy-2,3-bis(bromomethyl)anthraquinone, with C_{60}.[86] Unfortunately, no CV data was reported for this cycloadduct which readily undergoes deprotonation to give the corresponding dianion on the organic addend.

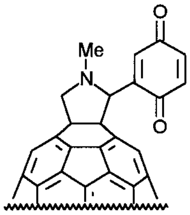
[60]Fullerene-based electron acceptors have also been prepared by following Prato’s procedure.[37] Some electron acceptor fulleropyrrolidines prepared by this procedure are collected in Chart 7. Thus, simultaneously to Iyoda et al.,[87] who has recently reported the synthesis and properties of **33**, we have prepared organofullerenes in which the C_{60} cage is covalently attached to *p*-benzoquinone[87,88] (**33**), naphthoquinone[88] (**34**), and anthraquinone[42] (**35**) (see Table 2).

The interesting redox properties of these novel modified fullerenes (Chart 7) could also be understood in terms of the LUMOs energies as described above for the related systems **32**.

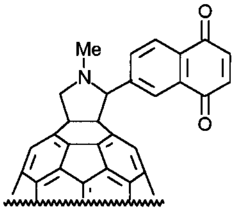
By following the same synthetic procedure, we have recently reported the first C_{60}-based electron acceptors with tetracyano-*p*-quinodimethane (TCNQ) (**36**) and dicyano-*p*-quinonediimine (DCNQI) (**37**) derivatives.[89] The CV of these compounds (**36** and **37**) show, in addition to the reduction waves corresponding to the reduction steps of the fullerene moiety, the presence of the reduction wave of the organic addends which appear as a reversible two-electron reduction wave for the TCNQ derivative ($E^1_{red} = -0.38$ V) (**36**) and two one-electron reduction waves for the DCNQI derivative in **37** ($E^1_{red} = -0.32$ V; $E^2_{red} = -0.98$ V).

The first reduction potentials for these fulleropyrrolidines is remarkably shifted to less negative values related to the parent C_{60} ($E^1_{red} = -0.60$ V vs SCE in toluene/acetonitrile 5:1). Therefore, these electron acceptors **36** and **37** are interesting precur-

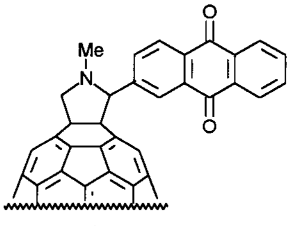
Chart 7. Representative Examples of C_{60}−Acceptors Prepared by 1,3-Dipolar Cycloadditions[a]



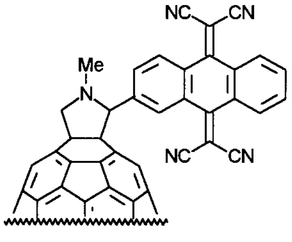
$E^{1}_{\rm red}$ = -0.40 V
33



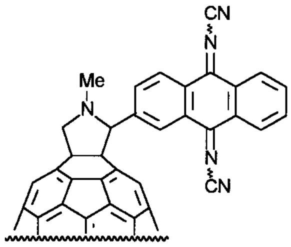
$E^{1}_{\rm red}$ = -0.27 V (2 e^-)
34



$E^{1}_{\rm red}$ = -0.95 V
35



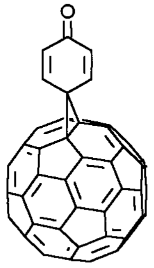
$E^{1}_{\rm red}$ = -0.38 V (2 e^-)
36



$E^{1}_{\rm red}$ = -0.32 V
37

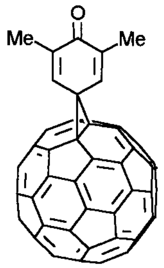
[a] The attachment of the first electron in the reduction process takes place in the organic addend in cycloadducts **33**, **34**, **36**, and **37**, and in the C_{60} unit in **35**. ($E^{1}_{\rm red}$ C_{60} = − 0.60 V vs SCE). Molecules **36** and **37** are the first examples in which the C_{60} unit is covalently attached to TCNQ and DCNQI derivatives.

Chart 8. Quinone-Type Spiroannelated Methanofullerenes Prepared from Diazo Compounds Showing "Periconjugative Effect" (38−40)[a]



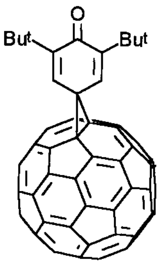
$E^{1}_{\rm red}$ = -1.081 V

38



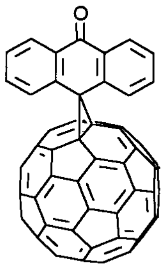
$E^{1}_{\rm red}$ = -1.042 V

39



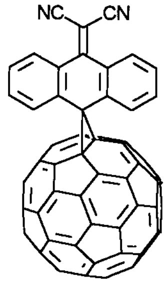
$E^{1}_{\rm red}$ = -1.097 V

40



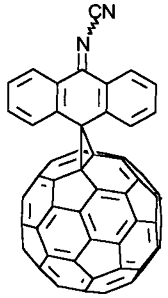
$E^{1}_{\rm red}$ = -1.215 V

41



$E^{1}_{\rm red}$ = -1.133 V

42



$E^{1}_{\rm red}$ = -1.142 V

43

$E^{1}_{\rm red}$ = -1.123 V

C_{60}

[a] The highly distorted structure of the organic addend in **41**−**43** prevents this electronic effect.

sors for the preparation of CT complexes by reaction with strong electron donor molecules.[90]

3.2. Spiroannelated Methanofullerenes as Electron Acceptors

A different approach for the preparation of electron acceptor organofullerenes is based on the periconjugative effect.[91,92] Thus, quinone-type methanofullerene acceptors (**38**−**43**) were prepared by reaction of substituted 1,4-diazoxides with C_{60}[93,94] (Chart 8).

All methanofullerenes prepared (**38**−**43**) were the thermodynamically more stable [6,6] isomer with typical peaks at ca. 430 and 700 nm in the electronic spectra. In principle, the intramolecular electronic interaction (periconjugation) between the p_z−π orbitals of the olefinic carbons of the quinone moiety and the adjacent carbon atoms of C_{60}, separated by a spiro carbon atom, results in more extended conjugated molecules showing good acceptor properties. In agreement with these predictions, the CV data of methanofullerenes **38**−**40** showed a more negative first reduction potential than the parent C_{60} (−1123 mV vs Fc/Fc$^+$) under the same experimental conditions (Chart 8),[93] thus being stronger acceptors than C_{60}.

In contrast, **41** bearing two benzene rings fused to the quinone moiety showed a more negative first reduction potential. This fact has been accounted for by the steric hindrance between the "peri" hydrogens and the surface of the ball, leading to a significant deviation from the orthogonality and hence to the loss of periconjugation.

The structural and electronic properties of these spiroannelated methanofullerenes have been characterized by both experimental techniques and quantum-chemical calculations.[94] For compounds **38**−**40** the periconjugative interactions transmit the inductive effect of the addend and produce a small stabilization of the orbitals of C_{60}, resulting in a less negative first reduction potentials compared to C_{60}. Theoretical calculations indicate that the attachment of the first electron causes the homolytic cleavage of one of the bonds connecting the addend to C_{60} (Figure 12). The resulting open cyclopropane structure is stabilized by the aromaticity of the phenoxyl radical structure presented by the addend. This ring opening has been supported by EPR measurements and explains the irreversible electrochemical behavior of these compounds.[94]

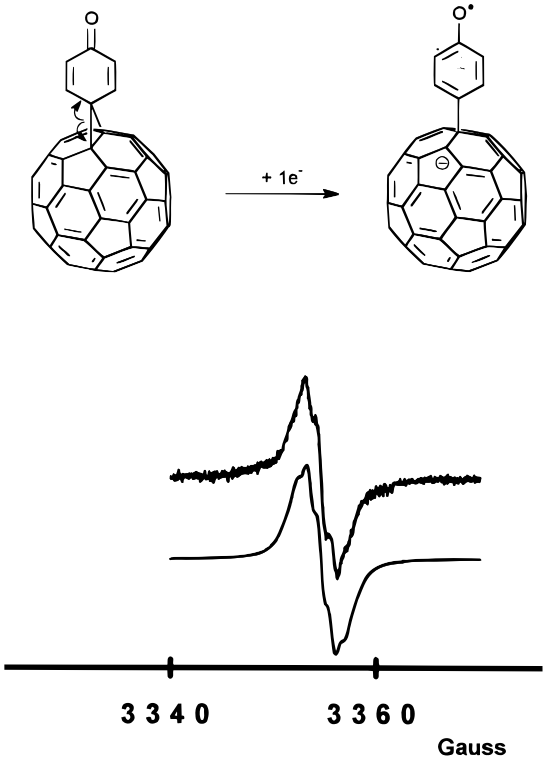


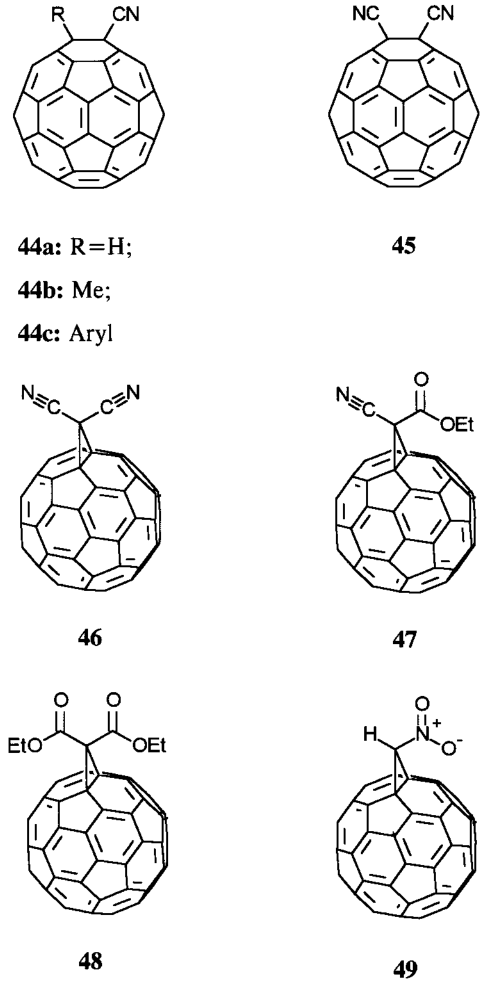
Figure 12. The reduction process in methanofullerene **38** occurs with homolytic cleavage of the cyclopropane ring leading to the formation of a phenoxyl radical whose experimental (up) and calculated (down) EPR spectra (depicted in the figure) explain the electrochemical behavior observed.

Compound **39** was chemically reduced with decamethylnickelocene, $Ni(C_5Me_5)_2$, in benzonitrile to form, selectively, the radical anion of C_{60}.[95] A transient EPR structurated signal (Figure 12) appears at $g = 2.0030$, which is very similar to those reported for substituted 2,6-dimethylphenoxyl radicals and much larger than that of the radical anion of C_{60} ($g = 1.9999$).[96] Simulation of the hyperfine structure was achieved by coupling of the unpaired electron with six equivalent hydrogen atoms of the two methyl groups ($a = 1.0$ G).[94]

Spiroannelated mathanofullerene **41** resulted in being an attractive precursor for the preparation of TCNQ- and DCNQI-type methanofullerenes by reaction of **41** with Lehnert's reagent (malononitrile, $TiCl_4$, pyridine)[97] and bis(trimethylsilyl)carbodiimide (BTC) and $TiCl_4$ by following Hünig's procedure,[98] respectively. Thus, methanofullerenes **42** and **43** were synthesized and the CV data revealed a better acceptor ability than the quinone-type precursor **41** and very close to that of the parent C_{60}.[94,99] Attempts to prepare TCNQ and DCNQI derivatives from quinone-type methanofullerenes **38**−**40** were unsuccessful.

The interest of these methanofullerenes has already been outlined in the Introduction to this section and as novel electron acceptors they are attractive for the development of electronic and optical applications.

Chart 9. Cyanodihydrofullerenes (44) Are Interesting Intermediates Which Allow a "Fine-Tune" of the Electron-Accepting Ability by Selection of the Appropiate Electrophile[a]



[a] Cyano-containing dihydrofullerenes (**44** and **45**) and methanofullerenes bearing strong electron-withdrawing substituents (**46** and **47**) on C_{61} exhibit better acceptor abilities than the parent C_{60}.

3.3. Other Electron Acceptor Organofullerenes

Cyanodihydrofullerenes (**44**) and dicyanodihydrofullerene (**45**) were recently reported by Wudl et al.[100,101] by controlled addition of cyanide anion and quenching of the corresponding intermediate $C_{60}(CN)^-$ with different electrophiles (Chart 9).

Although saturation of a double bond of the C_{60} cage in 1,2-dihydrofullerenes (58 π electrons) is known to cause a negative shift of about 100−150 mV relative to C_{60} for the first three reduction waves,[44,83,84] the presence of the strong electron-withdrawing cyano groups onto the C_{60} skeleton compensates this negative shift. Thus, the CV data show that **44** (R = H) has the same reduction potential values than those of C_{60}. Compound **45**, bearing two cyano groups exhibits a first half-wave reduction potential (−0.935 V) which is exceptionally shifted 120 mV to more positive values than the parent C_{60} (−1.056 V vs Fc/Fc^+ in *o*-dichlorobenzene) (see Table 2).

The X-ray data of compound **45** are shown in Figure 13 and reveal that the molecules are located

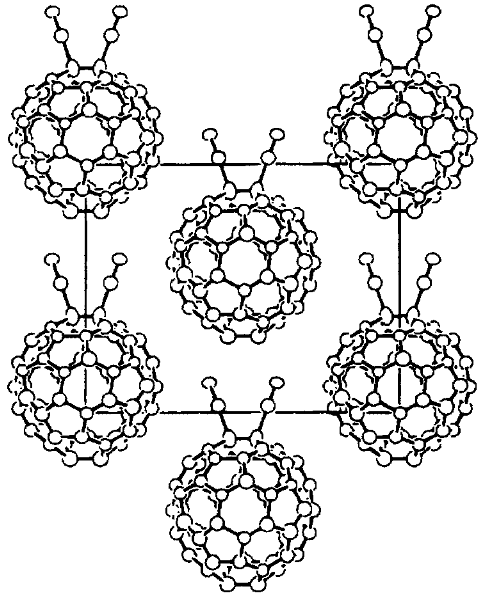


Figure 13. Crystal packing of dicyanodihydrofullerene (**45**) down the crystallographic *c* axis showing that all the molecules are oriented in the same direction. (Reprinted from ref 100. Copyright 1995 American Chemical Society.)

on the 2-fold symmetry axes and oriented in the same direction. Consequently, large second harmonic nonlinear optical properties (NLO) could be expected for this solid. Unfortunately, compound **45** is a highly colored solid which drastically decreases its application for optical devices. However, other properties such as piezoelectricity or pyroelectricity are under investigation.[100,101]

Methanofullerenes endowed with electron-withdrawing substituents on the methano bridge have been synthesized by Wudl et al.[101] and the CV data reveal that depending upon the substituents, stronger acceptors than the parent C_{60} can be achieved. Compound **46** bearing two cyano groups was obtained from C_{60} and dicyanodiazomethane by photolysis or thermolysis (above the decomposition temperature). Methanofullerenes **47** and **49** were prepared by following the same procedure previously reported for **48**.[54] The CV of methanofullerene **46** showed at least nine reduction waves. The first reduction wave changed from irreversible at room temperature to quasireversible at −72 °C, suggesting a possible cyclopropane ring opening upon reduction. Interestingly, the first peak reduction potential of **46** occurs at −967 mV vs Fc/Fc^+, 156 mV more positive than C_{60}, being the most electronegative methanofullerene prepared so far. In comparison, the values found for **47** (−1113 mV), diester **48** (−1164 mV) and nitromethanofullerene **49** (−1163 mV) indicate the remarkable substituent effect on the acceptor ability in these methanofullerenes. In fact, a plot of the first reduction potentials of differently substituted methanofullerenes versus the sum of σ_m of the substituents on C_{61} (inductive effect) (Figure 14), afforded a good linear correlation with two different slopes. The fact that compounds **46** and **47** bearing cyano groups do not fit in the general behavior shown by the remaining substituents, has been accounted for by the orbital interactions (periconjugation) between the cyano groups and the C_{60} cage or, another possible explanation could involve cyclopropane conjugation.[101]

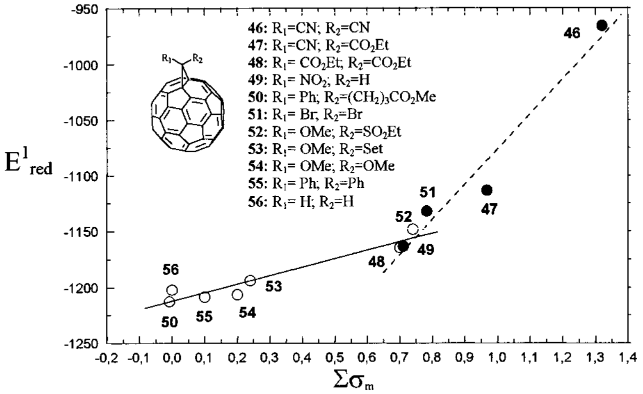


Figure 14. First peak reduction potential vs the sum of σ_m values for different substituents at the methylene bridge. The presence of cyano groups in **46** and **47** significantly deviate from the remaining compounds (**48**−**56**). (Reprinted with permission from ref 101. Copyright 1996 Elsevier.)

4. Summary and Perspectives

Although the chemistry of fullerenes is currently under a very active investigation, the basic chemical reactivity for fullerene C_{60} is already well-stablished and a wide variety of organofullerenes have been reported along the last recent years. These well-known synthetic methodologies[102] pave the way for the preparation of novel compounds of interest in the search of new materials exhibiting nonconventional properties. Thus, in this article we have centered our interest on those organofullerenes in which the good electron acceptor C_{60} is linked to a redox active organic addend. These C_{60}−donor and C_{60}−acceptor systems were synthesized by known synthetic methods, being cycloadditions the most successful and widely used reactions.

No doubt, C_{60}-based dyads in which fullerene C_{60} is covalently attached to an electron donor unit are very attractive systems for the study of electron transfer (ET) processes. In this regard, a wide variety of different bridges connecting the C_{60} cage to the donor fragment can be imagined and, in fact, the length, chemical constitution or the presence of rigid or saturated hydrocarbon bridges is known to play an important role on the electronic coupling between the donor and acceptor chromophores.[50] These systems can mimic the photosynthetic processes and, consequently, construction of photovoltaic cells is being pursued as a realistic application of such dyads.

Highly efficient photovoltaic devices are under investigation using conducting polymers blended with fullerene and modified fullerenes exhibiting improved photovoltaic charge separation. Photovoltaic devices with power conversion efficiencies of around 1% have already been reported.[103] This novel field represents one of the most exciting issues on fullerenes research although many questions related to systematic optimization such as band gaps of the semiconducting polymers and other related topics such as organofullerenes displaying better solubilities and donor−acceptor heterojunctions are not still satisfactorily answered.

Porphyrin−C_{60} dyads have also shown interesting properties for application in photodynamic therapy since they efficiently generate singlet oxygen which has been applied for DNA cleavage.[104] For biological purposes and, in particular for photodynamic therapy, it is critical a high molar absorptivity of the sensitizer in the region of 500−700 nm, in addition to a high solubility in polar solvents.[105] [60]Fullerene hardly satisfies both requirements since it absorbs very weakly in the visible region and is insoluble in polar solvents. Therefore, the presence of porphyrin units or other donor fragments covalently attached to the C_{60} core increases the solubility and acts as an antenna to captivate light at appropriate wavelengths.

In this regard, more work is needed in order to design novel dyads bearing different linkers between the donor and C_{60} moieties which can efficiently form excited $^3C_{60}$.

Although a first example of CT complexes formed from C_{60}−TTF derivatives and strong acceptors such as $TCNQF_4$ have been reported, the presence of the C_{60} moiety in the crystal packing and its effect on the electrical properties is still an unanswered question which deserves a more in-depth study of C_{60}-based salts and CT complexes. In this regard, the presence of the three-dimensional C_{60} cage in the crystal packing could have striking effects on the control of molecular stacking as well as on the intermolecular interactions which could increase the dimensionality resulting in a stabilization of the metallic state.

C_{60}-based electron acceptors are much less known despite the interest they have as giant sponges for the electronic capture. In fact, the presence of an electron acceptor organic addend linked to the C_{60} cage can, in addition to improve the electron acceptor properties of the resulting organofullerene, increase the solubility for blending with other organic molecular or polymeric materials, thus improving its properties for the construction of electronic devices. Finally, the presence of stronger electron acceptors in close proximity to the ball could lead, by reaction with electron donor molecules, to novel C_{60}-based CT complexes thus combining the expected electrically conducting behavior with the unique properties of fullerenes in novel multiproperty materials.[106]

C_{60} crystals irradiated by light in oxygen show weak ferromagnetic properties.[107] Recently, C_{60}-(TDAE)[30] was found to be a ferromagnet below 16 K, although the mechanism for this magnetic behavior is not well understood at present. In this regard, only a few examples of these covalently attached (C_{60}−D or −A) systems have been examined in the search of magnetic properties despite the interest that these systems may display as promising organic ferromagnets. Therefore, this topic represents a future major challenge for the scientists engaged in chemical and physical sciences.

Electroactive organofullerenes thus represent an important class of compounds which are able to display a wide variety of nonconventional properties and could satisfy some of the demanding technological applications for the still young fullerenes.

5. Acknowledgments

We thank Professor Fred Wudl for introducing us to the round world of fullerenes and to Professor Michael Hanack in the field of electroactive molecules. Special thanks to Professor Carlos Seoane for his continuous support along these fruitful years. We are also indebted to the people who collaborated in part of our research on fullerenes: Professors E. Ortí, P. M. Viruela, and R. Viruela (University of Valencia), Professors F. Langa and A. de la Hoz (Universiy of Castilla La Mancha), Professors C. Rovira and J. Veciana (ICMB, Barcelona), and Professors J. Garín and J. Orduna (University of Zaragoza). We also acknowledge financial support from DGICYT of Spain (Grant PB95-0428-CO2).

6. References

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

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulus, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) (a) Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388; (b) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050; (c) Haufler, R. E.; Conceiçao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 1050.

(4) Saito, G.; Teramoto, T.; Otsuka, A.; Sugita, Y.; Ban, T.; Kusunoki, K. *Synth. Met.* **1994**, *64*, 359.

(5) Wang, L. S.; Conceiçao, J.; Jin, C.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *182*, 5.

(6) (a) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978; (b) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781.

(7) (a) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169; (b) Foote, C. S. *Top. Curr. Chem* **1994**, *169*, 347; (c) Lem, G.; Schuster, D. I.; Courtney, S. H.; Lu, Q.; Wilson, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 554; (d) Siedschlag, C.; Luftmann, H.; Wolff, C.; Mattay, J. *Tetrahedron* **1997**, *53*, 3587. The synthesis of fullerene cations requires new strong oxidants having weakly nucleophilic and nonoxidable anions. Recently, the salt $[C_{60}^+][CB_{11}H_6Cl_6^-]$ has been prepared in the solid state using a new brominated *N*-phenylcarbazole cation reagent as the oxidant. Bolskar, R. D.; Fackler, N. L. P.; Mathur, R. S.; Reed, Ch. A. Communication presented at the 193rd meeting of the Electrochemical Society. San Diego, May 3−8, 1998.

(8) Liddell, P. A.; Sunida, J. P.; McPherson, A. N.; Noss, L.; Seely, G. R.; Clark, K. N.; Moore, A. L.; Moore, T. A.; Gust, D. *Photochem. Photobiol.* **1994**, *60*, 537.

(9) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055.

(10) *Molecular Electronic-Science and Technologie*; Aviram, A., Ed.; Engineering Fundation: New York, **1989**.

(11) Aviram, A.; Ratner, M. *Chem. Phys. Lett.* **1974**, *29*, 277.

(12) (a) Metzger, R. M.; Panetta, C. *New J. Chem.* **1991**, *15*, 209; (b) Metzger, R. M.; Chen, B.; Höpfner, U.; Lakshmikantham, M. V.; Vuillaume, D.; Kawai, T.; Wu, X.; Tachibana, H.; Hughes, T. V.; Sakurai, H.; Baldwin, J. W.; Hosch, C.; Cava, M. P.; Brehmer, L.; Ashwell, G. J. *J. Am. Chem. Soc.* **1997**, *119*, 10455. (c) Scheib, S.; Cava, M. P.; Baldwin, J. W.; Metzger, R. M. *J. Org. Chem.* **1998**, *63*, 1198. (d) Gónzalez, M.; Illescas, B.; Martín, N.; Segura, J. L.; Seoane, C.; Hanack, M. *Tetrahedron* **1998**, *54*, 2853. (e) Segura, J. L.; Martín, N.; Seoane, C.; Hanack, M. *Tetrahedron Lett.* **1996**, *37*, 2503.

(13) Launay, J. P. Molecular Electronics. In *Granular Nanoelectronics*; Ferry, D. K., Ed.; New York, **1995**.

(14) *Introduction to Molecular Electronics;* Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press, New York, **1995**.

(15) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley, New York, **1991**.

(16) Nalwa, M. S. *Adv. Mater.* **1993**, *5*, 341.

(17) Long, N. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21.

(18) *Photoinduced Electron Transfer*, Fox, M. A., Chanon, M., Eds.; Elsevier, Amsterdam, **1988**.

(19) Kurreck, H.; Huber, M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849.

(20) Staab, H. A.; Feurer, A.; Hauck, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2428.

(21) (a) Roest, M. R.; Verhoeven, J. W.; Schuddeboon, W.; Warman, J. M.; Lawson, J. M.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1996**, *118*, 1762; (b) Lawson, J. M.; Craig, D. C.; Oliver, A. M.; Paddon-Row, M. N. *Tetrahedron* **1995**, *51*, 3841.

(22) Multichromophoric multiple addends were readily added in the "tether-directed remote functionalization". See: (a) Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339; (b) Isaacs, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1466; (c) Cardullo, F.; Isaacs, L.; Diederich, F.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Chem. Commun.* **1996**, 797; (d) Nierengarten, J.-F.; Gramlich, V.; Cardullo, F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2101; (e) Seiler, P.; Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1996**, *79*, 1047; (f) Isaacs, L.; Diederich, F.; Haldimann, R. F. *Helv. Chim. Acta* **1997**, *80*, 317; (g) Nierengarten, J.-F.; Habicher, T.; Kessinger, R.; Cardullo, F.; Diederich, F.; Gramlich, V.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 2238; (h) Taki, M.; Sugita, S.; Nakamura, Y.; Kasashima, E.; Yashima, E.; Okamoto, Y.; Nishimura, J. *J. Am. Chem. Soc.* **1997**, *119*, 926. For a recent example on the synthesis and characterization of several regioisomeric bis- and tris-adducts of [60]fullerene, see: (i) Djojo, F.; Herzog, A.; Lamparth, I.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1996**, *2*, 1537. For the preparation of symmetric multiadducts by using an "orthogonal transposition", see: (j) Kräutler, B.; Müller, T.; Maynollo, J.; Gruber, K.; Kratky, C.; Ochsenbein, P.; Schwarzenbach, D.; Bürgi, H.-B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1204; (k) Schwenninger, R.; Müller, T.; Kräutler, B. *J. Am. Chem. Soc.* **1997**, *119*, 9317.

(23) (a) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600; (b) Rosseinsky, M. J.; Ramirez, A. P.; Glarum, S. H.; Murphy, D. W.; Haddon, R. C.; Hebard, A. F.; Palstra, T. T. M.; Kortan, A. R.; Zahurak, S. M.; Makhija, A. V. *Phys. Rev. Lett.* **1991**, *66*, 2830; (c) Keltly, S. P.; Chen, C.-C.; Lieber, C. M. *Nature* **1991**, *352*, 223; (d) Chen, C.-C.; Lieber, C. M. *Science* **1993**, *259*, 655; (e) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154; (f) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127; (g) Murphy, D. W.; Rosseinsky, M. J.; Fleming, R. M.; Tycko, R.; Ramirez, A. P.; Haddon, R. C.; Siegrist, T.; Dabbagh, G.; Tully, J. C.; Walstedt, R. E. *J. Phys. Chem. Solids* **1992**, *53*, 1321.

(24) (a) Izuoka, A.; Tachikawa, T.; Sugawara, T.; Suzuki, Y.; Konno, M.; Saito, Y., Shinohara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1472. (b) Izuoka, A.; Tachikawa, T.; Sugawara, T.; Saito, Y., Shinohara, H. *Chem. Lett.* **1992**, 1049.

(25) Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1764.

(26) Pradeep, T.; Singh, K. K.; Shina, A. P. B.; Morris, D. E. *J. Chem. Soc., Chem. Commun.* **1992**, 1747.

(27) (a) Llacay, J.; Tarrés, J.; Veciana, J.; Rovira, C. *Synth. Met.* **1995**, *70*, 1453. (b) Zhang, B.; Li, Y.; Zhu, D. *Synth. Met.* **1995**, *70*, 1483. (c) Li, Y.; Gao, Y.; Wu, Z.; Bai, Y.; Mo, Y.; Zhang, B.; Han, H.; Zhu, D. *Synth. Met.* **1995**, *70*, 1459. (d) Wang, P.; Lee, W.-J.; Shcherbakova, I.; Cava, M. P.; Metzger, R. M. *Synth. Met.* **1995**, *70*, 1457. (e) Metzger, R. M.; Wang, P.; Wu, X.-L.; Tormos, G. V.; Lorcy, D.; Shcherbakova, I.; Lakshmikantham, M. V.; Cava, M. P. *Synth. Met.* **1995**, *70*, 1435.

(28) Bossard, C.; Rigaut, S.; Astruc, D.; Delville, M.-H.; Félix, G.; Février-Bouvier, A.; Amiell, J.; Flandrois, S.; Delhaès, P. *J. Chem. Soc., Chem. Commun.* **1993**, 333.

(29) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212.

(30) (a) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, P.-M.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301; (b) Stephens, P. W.; Cox, D.; Lauher, J. W.; Milahy, L.; Wiley, J. B.; Allemand, P. M.; Hirsch, A.; Holczer, K.; Li, Q.; Thompson, J. D.; Wudl, F. *Nature* **1992**, *355*, 331.

(31) Wan, W.Ch.; Liu, X.; Sweeney, G. M.; Broderick, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 9580.

(32) (a) Saricifti, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474; (b) Janssen, R. A. J.; Christians, M. P. T.; Pakbaz, K.; Moses, D.; Hummelen, J. C.; Saricifti, N. S. *J. Chem. Phys.* **1994**, *102*, 2628; (c) Janssen, R. A. J.; Hummelen, J. C.; Lee, K.; Pakbaz, K.; Saricifti, N. S.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1995**, *103*, 788; (d) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789; (e) Kraabel, B.; Hummelen, J. C.; Vacar, D.; Moses, D.; Saricifti, N. S.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1996**, *104*, 4267.

(33) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510.

(34) Roman, L. S.; Anderson, M. R.; Yohannes, T.; Inganäs, O. *Adv. Mater.* **1997**, *9*, 1164.

(35) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.

(36) (a) For a recent review on addition reactions of Buckminsterfullerene-C_{60}, see: Hirsch, A. *Synthesis* **1995**, 895. Diels–Alder reactions were systematically introduced into fullerene chemistry by Rubin and Müllen. See: (b) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344; (c) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78; (d) Gügel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 559. For recent examples of 1,3-dipolar cycloadditions to C_{60}, see: (e) *Tetrahedron* **1996**, *52*, 4925–5262 (special issue on "Fullerene Chemistry", Smith, A. B., III, Ed.

(37) Maggini, M.; Scorrano, G.;, Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

(38) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.

(39) (a) Maggini, M.; Donó, A.; Scorrano, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1995**, 845; (b) Saricifti, N. S.; Wudl, F.; Heeger, A. J.; Maggini, M.; Scorrano, G.; Prato, M.; Bourassa, J.; Ford, P. C. *Chem. Phys. Lett.* **1995**, *247*, 510.

(40) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandoná, G.; Farnia, G. *Tetrahedron* **1996**, *52*, 5221.

(41) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1996**, *37*, 5979.

(42) Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. *J. Org. Chem.* **1997**, *62*, 5690; Herranz, M. A.; Martín, N.; Sánchez, L.; Seoane, C. *Fullerene Sci. Technol.* in press.

(43) de Lucas, A. I.; Martín, N.; Sánchez, L.; Seoane, C. *Tetrahedron Lett.* **1996**, *37*, 9391.

(44) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Isaacs, L.; Anderson, H. L.; Faust, R.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 1334 and references therein.

(45) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Phys. Chem. Solids* **1997**, *58*, 1713.

(46) Boullé, C.; Rabreau, J. M.; Hudhomme, P.; Cariou, M.; Jubault, M.; Gorgues, A.; Orduna, J.; Garín, J. *Tetrahedron Lett.* **1997**, *38*, 3909.

(47) (a) Llacay, J.; Mas, M.; Molins, E.; Veciana, J.; Powell, D.; Rovira, C. *Chem. Commun.* **1997**, 659; (b) Llacay, J.; Veciana, J.; Vidal-Gancedo, J.; Bourdelande, J. L.; Gónzalez-Moreno, R.; Rovira, C. *J. Org. Chem.* **1998**, *63*, 5201.

(48) Linssen, T. G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 103.

(49) Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row, M. N.; Rubin, Y. *J. Org. Chem.* **1996**, *61*, 5032.

(50) Paddon-Row, M. N.; Shephard, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 5355.

(51) (a) Igarashi, M.; Fukuda, M.; Taki, M.; Tago, T.; Minowa, T.; Okada, Y.; Nishimura, J. *Fullerene Sci. Technol.* **1995**, *3*, 37; (b) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081.

(52) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919.

(53) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958.

(54) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.

(55) Armspach, D.; Constable, E. C.; Diederich, F.; Housecroft, C. E.; Nierengarten, J.-F. *Chem. Commun.* **1996**, 2009.

(56) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537.

(57) Liddell, P. A.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400.

(58) Imahori, H.; Cardoso, S.; Dereck, T.; Lin, S.; Noss, L.; Seely, G. R.; Sereno, L.; De Silber, J. C.; Moore, T. A.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **1995**, *62*, 1009.

(59) Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974.

(60) Baran, P. S.; Monaco, R. R.; Khan, A. U.; Schuster, D. I.; Wilson, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 8363.

(61) Safonov, I. G.; Baran, P. S.; Schuster, D. I. *Tetrahedron Lett.* **1997**, *38*, 8133.

(62) Diederich, F.; Dietrich-Buchecker, C.; Nierengarten, J.-F.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 781.

(63) Ashton, P. R.; Diederich, F.; Gómez-López, M.; Nierengarten, J.-F., Preece, J. A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1448.

(64) (a) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699; (b) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229; (c) Kawaguchi, M.; Ikeda, A.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 179; (d) Ikeda, A.; Yoshimura, M.; Shinkai, S. *Tetrahedron Lett.* **1997**, *38*, 2107; (e) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259; (f) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 997; (g) Atwood, J. L.; Barbour, L. J.; Raston, C. L.; Sudria, I. B. N. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 981.

For a recent review on calixarene−fullerene systems, see: Shinkai, S.; Ikeda, A. *Gazz. Chim. Ital.* **1997**, *127*, 657. For a recent review on fullerene inclusion complexes see: Boulas, P. L.; Gómez-Kaifer, M.; Echegoyen, L. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 216.
(65) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.
(66) (a) Amabilino, D. B.; Stoddart, J. F.; Williams, D. J. *Chem. Mater.* **1994**, *6*, 1159; (b) Ashton, P. R.; Claessens, C. G.; Hayes, W.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1862.
(67) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1366.
(68) Timmerman, P.; Witxhel, L. E.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1996**, *79*, 6.
(69) Belik, P.; Gügel, A.; Kraus, A.; Spickermann, J.; Enkelmann, V.; Frank, G.; Müllen, K. *Adv. Mater.* **1993**, *5*, 854.
(70) Diederich, F.; Jonas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thilgen, C. *Helv. Chim. Acta* **1993**, *76*, 2445.
(71) For recent reviews on organic electron-acceptor molecules see: Martín, N.; Seoane, C. In *Handbook of Organic Conductive Molecules and Polymers* Nalwa, H. S., Ed.; John Wiley & Sons Ltd: New York, 1997; Vol. 1, Chapter 1. Martín, N.; Segura, S.; Seoane, C. *J. Mater. Chem.* **1997**, *7*, 1661.
(72) For recent reviews on TTF derivatives, see: Garín, J. *Adv. Heterocycl. Chem.* **1995**, *62*, 249. Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481.
(73) Iyoda, M.; Sultana, F.; Sasaki, S.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1929; (b) Iyoda, M.; Sasaki, S.; Sultana, F.; Yoshida, M.; Kuwatani, Y.; Nagase, S. *Tetrahedron Lett.* **1996**, *37*, 7987.
(74) Illescas, B. M.; Martín, N.; Seoane, C.; de la Cruz, P.; Langa, F.; Wudl, F. *Tetrahedron Lett.* **1995**, *36*, 8307.
(75) Illescas, B. M.; Martín, N.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela R.; de la Hoz, A. *J. Org. Chem.* **1997**, *62*, 7585.
(76) Hoey, M. D.; Dittmer, D. C. *J. Org. Chem.* **1991**, *56*, 1947.
(77) For a review on *o*-quinodimethanes, see: Martín, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237.
(78) Coalescence, temperatures, and energy barriers were also determined for the cyclohexene-ring inversion in two isomeric C_{70} derivatives. Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, H. *Helv. Chim. Acta* **1994**, *77*, 1689.
(79) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235.
(80) Tago, T.; Minowa, T.; Okada, Y.; Nishimura, J. *Tetrahedron Lett.* **1993**, *34*, 8461.
(81) Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351.
(82) Fernández-Paniagua, U. M.; Illescas, B.; Martín, N.; Seoane, C.; de la Cruz, P.; de la Hoz, A.; Langa, F. *J. Org. Chem.* **1997**, *62*, 3705.
(83) For a recent review on the electrochemistry of fullerenes, see: Chlistunoff, J.; Cliffel, D.; Bard, A. J. In *Handbook of Organic Conductive Molecules and Polymers* Nalwa, H. S., Ed.; John Wiley & Sons Ltd.: New York, 1997; Vol. 1, Chapter 7.
(84) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.
(85) Illescas, B.; Martín, N.; Segura, J. L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1995**, *60*, 5643.
(86) Bidell, W.; Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1641.
(87) Iyoda, M.; Sultana, F.; Kato, A.; Yoshida, M.; Kuwatani, Y.; Komatsu, M.; Nagase, S. *Chem. Lett.* **1997**, 63.
(88) Illescas, B.; Martín, N.; Seoane, C. Unpublished results.
(89) Illescas, B.; Martín, N.; Seoane, C. *Tetrahedron Lett.* **1997**, *38*, 2015.
(90) Mukai, T.; Suzuki, T.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 243.
(91) Wudl, F.; Suzuki, T.; Prato, M. *Synth. Met.* **1993**, *59*, 297.
(92) Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q. C.; Maggini, M.; Martín, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591.
(93) Ohno, T.; Martín, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306.
(94) Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 9871.
(95) Wan, W. C.; Liu, X.; Sweeney, M.; Broderick, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 9580.
(96) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465.
(97) Lehnert, W.; *Tetrahedron Lett.* **1970**, *11*, 4723. Lehnert, W. *Synthesis* **1974**, 667.
(98) Aümuller, A.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 447. Hünig, S.; Erk, P. *Adv. Mater.* **1991**, *3*, 225. See also: Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. *J. Org. Chem.* **1997**, *62*, 870.
(99) Martín, N.; Knight, B.; Wudl, F. *Synth. Met.* **1997**, *86*, 2771.
(100) Keshavarz-K., M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.
(101) Keshavarz-K., M.; Knight, B.; Haddon, R. C.; Wudl, F. *Tetrahedron* **1996**, *52*, 5149.
(102) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
(103) Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585.
(104) For a recent review on biological applications of fullerenes, see: Jensen, A. W.; Wilson, S. R.; Schuster, D. L. *Bioorg. Med. Chem.* **1996**, *4*, 767.
(105) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19.
(106) For a recent review on the applications of C_{60} for materials science, see: Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097.
(107) Murakami, Y.; Suematsu, H. *Pure & Appl. Chem.* **1996**, *68*, 1463.

CR9701039