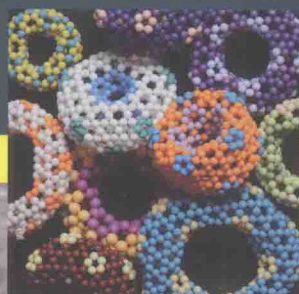
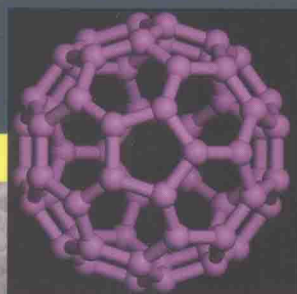


CHEMICAL MODIFICATION of FULLERENES

富勒烯的化学修饰

韩爱鸿 著



科学出版社

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北 京

内 容 简 介

本书介绍了富勒烯家族成员的物理及化学性质;结合作者的研究成果,重点介绍了高级富勒烯(C_{76} , C_{78} , C_{84})及其异构体的分离、纯化、结构表征方法,以及同一种高级富勒烯异构体之间化学反应性的差异。此外,还介绍了三种不同结构富勒烯(C_{76} , C_{78} , C_{84})衍生物的制备方法、光电特性及其在光伏领域的应用前景。

本书可供高等院校化学专业高年级本科生和研究生阅读,也可供光伏太阳能领域的研究人员参考。

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Preface

In the past decades, great changes have taken place for the family of carbon, its isotopes increase from diamonds, graphites to carbon nanotubes, Buchyballs and grapheme. Since the isolation of C_{60} in preparatively useful quantities, much attention has been devoted to chemical derivatization of this new allotropic form of carbon, which continuously yields fascinating results. Exohedrally derivatized fullerenes have been extensively developed to explore their potential usefulness as novel materials, for example, the fullerene derivative acceptors are the key photovoltaic materials for high performance polymer solar cells (PSCs). Most of the studies have been focused on C_{60} and C_{70} . The research of the chemical reactivity of higher fullerenes, however, is very limited. Isolation of single species of higher fullerenes is proved to be difficult due to not only their structural similarity, but also their low abundance in the soot, which requires time-consuming intensive HPLC separation. Recently, isolation and structure determination of higher fullerenes as D_2 - C_{76} , C_{78} and C_{84} allowed investigation into the chemical reactivity of the higher fullerenes. Although the studies concerning the reactivity of higher fullerenes are still limited, those results reveal the unique properties of higher fullerenes differing significantly from the known chemistry of C_{60} and C_{70} .

In the book, the chemical functionalization of higher fullerenes (C_{76} , C_{78} , C_{84}) were introduced. In order to obtain the pure isomers of these higher fullerenes to enable investigating their chemical and physical properties, a special multi-stage HPLC separation was performed and then three isomers of C_{78} , five isomers of C_{84} and pure C_{76} were obtained. These isomers were characterized by the analysis of NMR, UV-VIS, Mass as well as cyclic voltammetry (CV). On the basis of investigation of CV of the higher fullerenes along with the theoretical calculation, the higher fullerenes, for example C_{76} , C_{78} , and C_{84} , have higher HOMO and lower LUMO level

than those of C_{60} . Meanwhile, the results from silylation of C_{60} display that silylated C_{60} has lower oxidation potential than that of C_{60} . So it is expected that the silylation of the higher fullerenes will produce the silylfullerenes with lower oxidation potentials than analogous of C_{60} , which forces author to carry out the researches on the silylation of the higher fullerenes. In the course of studies on chemical functionalization of higher fullerenes with organosilicon compounds, by using the same multi-stage HPLC, pure mono-adducts of C_{76} (D_2), C_{78} (C_{2v}) and C_{84} (D_2 and D_{2d}) were isolated, then their structures were confirmed by their spectral data, for example, NMR (1H , ^{13}C , ^{29}Si , HMQC, HMBC, DEPT), CV, and UV-VIS. The results of redox potentials of the higher silylfullerenes are consistent with previous observation for other silylfullerenes.

Finally, considering the importance of the fullerene acceptors, the synthesis and physicochemical properties of several new fullerene (C_{60}) derivatives acceptors for high performance PSCs are introduced.

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Chapter 1 Introduction

1.1 The Discovery of C_{60}

Carbon has been known as the pure element in the form of diamond and graphite. But in 1985, a stable carbon molecular ion consisting of sixty carbon atoms was observed by H. W. Kroto in the mass spectrum of laser ablate graphite ^[1, 2], and he predicted that it was the third form of carbon, and named as Buckminsterfullerenes derived from the name of the American engineer and philosopher R. Buckminster Fuller who invented the geodesic dome architecture. The discovery of C_{60} was a milestone in science, and Robert F. Curl, Harold W. Kroto and Richard E. Smally were rewarded with Nobel Prize in 1996. But because of some limitation of technique, there was little progress several years since then. It is until 1990 that a breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and coworkers having been engaged for decades in the study of interstellar dust reported the evidence for the presence of C_{60} in a sample of carbon dust prepared from vaporized graphite and were able to isolate macroscopic quantities of C_{60} and C_{70} ^[3, 4]. Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and fullerenes had been the province of the few select groups. Many groups made their own fullerenes. Physicists, chemists and material sciences thus began an interdisciplinary feeding frenzy that continues to intensify as these articles. The key results have been quickly reported in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air. They are perfectly to a wide range of techniques.

One of the most powerful technique-nuclear magnetic resonance (NMR) has confirmed the single most critical aspect of the soccer-ball structure ^[5, 6]: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability.

Reports of the synthesis of gram quantities of C_{60} and C_{70} have generated a fully of interest in this new class of closed-caged carbon molecules, referred as “fullerenes”. The molecular models of C_{60} and C_{70} are demonstrated in Figure 1.1.

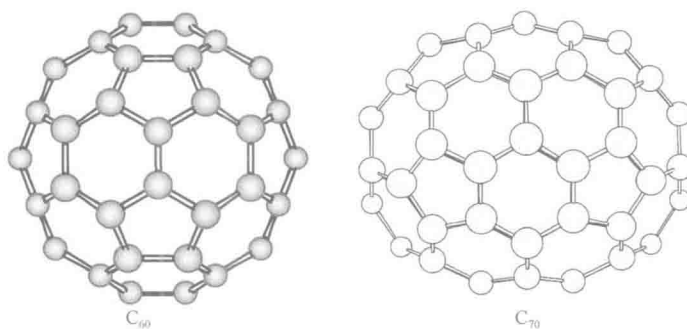


Figure 1.1 The models of C_{60} and C_{70}

1.2 The Property of C_{60}

Shortly after the discovery of the bulk fullerene soot production process in 1990s, the fullerenes, C_{60} as represent, has been attracting wide interest because of its unique structure, photonic, electronic properties. A lot of works on applications of fullerene have been piled up, including their use as superconductivity^[7-10], chemical probe^[11], pharmaceutical chemistry^[12], photoconductivity^[13, 14] etc, and many papers have been described. Investigation of the physical properties of fullerenes has been most intensive, and has resulted in the publication of many thousands of papers. Up to now, the physical and chemical property of C_{60} has been unambiguously displayed.

The electron-accepting ability of C_{60} , the archetypal fullerene, is its most characteristic chemical property. It is a natural consequence of electronic structure and was anticipated in the early molecular orbital calculation^[15], which place a low-lying unoccupied t_{1u} level about 2 eV above the h_u HOMO^[16-18]:



Early in the gas-phase investigations of fullerenes, the electron affinity of C_{60} was measured and found to be high (2.69 eV)^[19-21]. When the macroscopic era of C_{60} chemistry began in 1990, this property was soon found to translate into the solution phase^[22]. In a rather remarkable cyclic voltammogram (see Figure 1.2), the reversible stepwise addition of up to six electrons was soon demonstrated electrochemically^[23, 24].

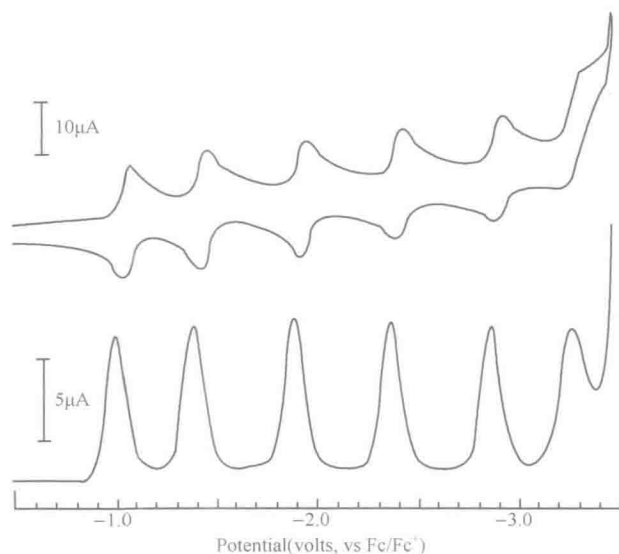


Figure 1.2 Cathodic cyclic and differential plus voltammograms of C_{60} in CH_3CN /toluene at $-10^\circ C$ showing successive reversible reduction to C_{60}^{n-}

However, the best known demonstration of the electronegative nature of C_{60} is the solid-state intercalation of electropositive metals producing a large family of M_xC_{60} salts called fullerides. The most remarkable of these are the superconducting phase, A_3C_{60} (A = alkali metal cation) [7]. The extended properties of these systems have been extensively reviewed elsewhere [25-28].

In the early stage of the macroscopic fullerene era, carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) played a crucial role in establishing the structure and integrity of C_{60} . A single, sharp ^{13}C NMR resonance was observed in solution near 143 ppm [5, 6]. The magnetic equivalence of all sixty carbon atoms, in conjunction with the observation of only four infrared absorption, allowed the confident conclusion that C_{60} had the spherical geometry and icosahedral symmetry originally proposed by Kroto, Heath, O'Brien, Curl, and Smalley [1]. The observation of five lines in the ^{13}C NMR spectrum of C_{70} established its D_{5h} structure [3, 29].

With development of NMR technique, Solid-state ^{13}C NMR spectroscopy quickly became a significant tool for investigating the wide variety of charge states and electronic properties of metal-intercalated C_{60} fullerides [29-32]. The data for C_{60}^{n-} ($n=1-6$) were obtained. Meanwhile, the other spectroscopy of C_{60} , for example, electronic spectroscopy [33, 34], vibrational spectroscopy [35-37], X-ray crystallography [38-40], magnetic susceptibility and spin states [41-43] have been investigated. Up to now, the physical properties of C_{60} have been well known, theory and experiment both explain

the third form of carbon-Buckminsterfullerene.

1.3 The Reactivity of C₆₀

Fullerenes represent an intriguing new class of carbons, which have attracted the attention of chemists interested in exploring the fundamental properties of these novel materials, both as molecular entities and as an anchoring base or building blocks essential to design of specialty chemicals and polymer. The increasing availability of fullerenes with reproducible quantity, and lower cost, has encouraged more research and development effort targeted for potential technological application. In the past decade years, intensive research activities have been focused on understanding the distinguishing physical and chemical properties among C₆₀, C₇₀, and higher fullerenes. The molecular behavior of C₆₀ has been reviewed in the previous section. In the part, the reactivity of C₆₀ will be described following.

The unique structural properties of C₆₀, the most abundant, the least expensive, and therefore the most thoroughly investigated of fullerenes, govern its chemical behavior. The six-membered rings are not classically aromatic in that they contain alternating single and double bonds. The C-C bonds are located exclusively between two six-membered rings (so-called 6,6-bonds, bond length 1.38Å) and are exocyclic with respect to the five-membered rings. Thus, the C-C bonds between five- and six-membered rings, the 5,6-bonds, are essentially single bonds with length 1.45Å. The overall fullerene structures can therefore be viewed as fused 1,3,5-cyclohexatrienes and radialenes. The structures of higher fullerenes are built using increasingly large chains of six-membered rings, while the number of five-membered rings remains constant at twelve.

Second, the bonds at each of the carbons on the fullerene surface deviate substantially from the ideal for sp²-hybridized carbons. The pyramidalization angle defined by Haddon and Raghavachari^[44] is $\theta_p = \theta_{\sigma\pi} - 90^\circ$, and the θ_p of C₆₀ is 11.6°, which is the largest value of any of the fullerenes ($\theta_{\sigma\pi} = 0^\circ$ for graphite). This pyramidalization angle induces strain of 8.5 kcal/mol/per carbon atom, the single largest contribution to total heat of formation of C₆₀ (10.16 kcal/mol/per carbon atom)^[45]. Exohedral additions to the sphere are therefore driven by relief of strain, while endohedral addition cause an increase in strain and are consequently strongly inhibited. For example, even when isolated nitrogen atoms are inserted into C₆₀ using a beam technique, they do not bond to carbon and remain spectroscopically indistinguishable from nitrogen atoms in vacuo^[46]. Similarly, fluorine atoms and methyl radicals within the C₆₀ sphere are predicted to be chemically inert^[47].

Third, theory predicts three low-lying degenerate lowest unoccupied molecular orbital (LUMOs) in C_{60} , which accounts for its exceptionally low reduction potential (-0.99 eV versus SCE) and its ability to reversibly accept up to six electrons electrochemically, up to the hexa-anion^[48, 49]. In contrast, oxidation of C_{60} is relatively difficult (IP $+1.76$ eV)^[48]. Although C_{60} radical cations can be generated by photoinduced electron transfer and by other methods^[50].

Certain general patterns of reactivity emerge from these basic properties of C_{60} , and to lesser extent apply to C_{70} and higher fullerenes:

1. C_{60} behaves essentially as an electron-deficient alkene, not as an aromatic hydrocarbon. Its characteristic reactions involve cycloadditions as well as additions of nucleophiles and free radicals across the bonds between two six-membered rings, that is 6,6-bonds. Hydroborations, hydrometallations, hydrogenations, halogenations, and metal complex formation are also observed^[51].

2. The main deriving force for additions to fullerenes is the relief of strain, leading to change in hybridization at the reacting carbons on the surface of the sphere from sp^2 to sp^3 , which is readily detected by ^{13}C NMR spectrometry. X-ray structures of mono-adducts of C_{60} and C_{70} indicate distortions to relieve strain on the fullerene surface, which have strong implications with respect to subsequent additions^[52]. Since fullerene additions are generally exothermic and exergonic, due to relief of strain, it is often difficult to stop at the mono-adduct stage. Multi-adducts are well known and have very interesting structures and properties. At an advanced stage of the addition sequence, the remaining unreacted six-membered rings become essentially isolated aromatic rings, and consequently addition comes to a stop.

3. The regioselectivity of addition reactions is governed by avoidance of products with a 5,6 double bond, since each such bond carries a price tag of 8.5 kcal/mol. Thus, 1,2-addition occurs to give ring-closed 6,6-adducts, with two sp^3 carbon atoms on the fullerene, and in some case ring-opened 6,5-adduct known as fulleroids, analogous to bridged annulenes, where all fullerene atoms are still sp^2 hybridized. Generally, 6,5-open adducts are thermodynamically more stable than corresponding to 6,5-closed structures (which necessarily contain 5,6 double bonds) but are less stable than the corresponding 6,6-closed adducts^[53]. Isomerization of 6,5-open to 6,6-closed adducts in some cases can be brought about by light or heat^[54].

4. Bis-addition to C_{60} , even when restricted to 6,6-bonds, is a complicated process since there are eight different sites for reaction. The selectivity of the second addition reaction is governed by differences in bond order and LUMO coefficients at each site^[55]. Although the term “regioselectivity” is not the proper term to describe discrimination between the chemically distinct 6,6-bonds on the surface of a C_{60} mono-adduct, this

term is so firmly entrenched in the fullerene literature that it seems futile to suggest abandoning it at this late stage. Problems in the preparation of bis and higher adducts of C_{60} will be difficult. In Akasaka's lab. of Japan, the tetra- and hexa-addition of C_{60} is being researched.

1.4 The Physical and Chemical Properties of Higher Fullerenes

1.4.1 The C_{76}

1.4.1.1 The photophysical properties of C_{76}

When macroscopic quantities of C_{60} and C_{70} were isolated and characterized in pure form, the isolation of higher fullerenes, for example, C_{76} , C_{78} and C_{84} were also reported. Up to now, these physical properties of higher fullerenes have been systematically investigated recent years.

The C_{76} , the third molecular form of fullerenes, was isolated and characterized in 1991^[56]. Its D_2 symmetry has been determined by ^{13}C NMR. The described constitutional isomer of C_{76} was predicted by theoretical calculations to be the only two different form of [76] fullerene obeying the "isolated pentagon rule" (IPR; each pentagon on the fullerene surface is surrounded by five hexagons)^[57]. The one with T_d symmetry has an open shell HOMO, thus it cannot correspond to the experimentally observed molecule. The other, having D_2 symmetry and a pseudo-closed shell, was proposed to be the most likely structure for C_{76} . The NMR spectrum^[56, 58, 59], tight-binding molecular dynamics calculations^[60, 61], and a quantum chemical calculation at the AM1 level^[56], as well as HF SCF in double- ξ basis set^[62] confirmed the chiral D_2 structure of this molecule. The two isomers are referred as ^fA and ^fC , and the chiral structure with D_2 symmetry C_{76} is shown in Figure 1.3.

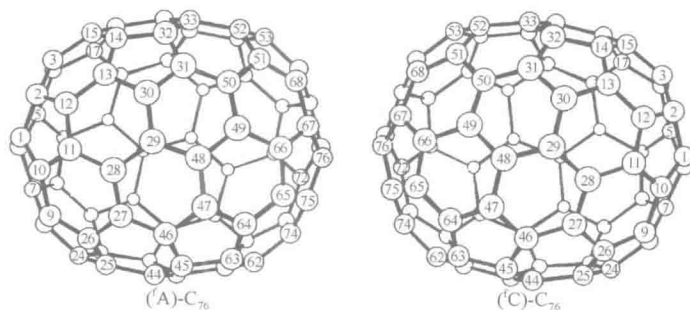
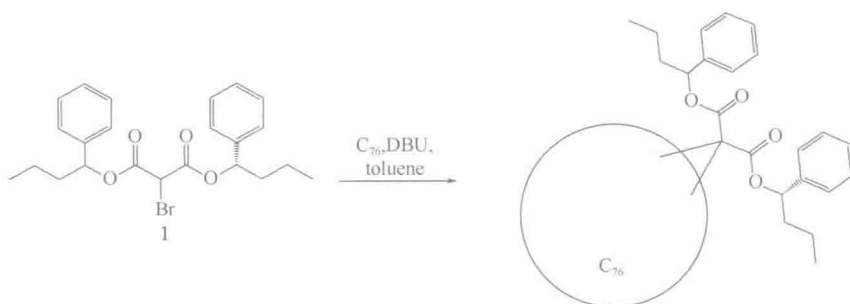


Figure 1.3 Molecular structures and numbering of (^fA)- and (^fC)- D_2 - C_{76}

In 1993, Hawkins and Meyer reported the kinetic resolution of C_{76} enantiomers by asymmetric osmylation on a small scale ^[63], and this method was successfully applied to the resolution of other chiral fullerenes, C_{78} and C_{84} ^[64]. But in 1998, L. Echegoyen and F. Diederich reported the chemical resolution of C_{76} enantiomers through the retro-Bingel reaction using the electrochemical reduction technique ^[65]. They first prepared the isomeric pairs of diastereoisomeric mono-adduct by nucleophilic cyclopropanation of C_{76} using an optically active 2-bromomalonate derivative in the presence of base ^[66] (Scheme 1.1).



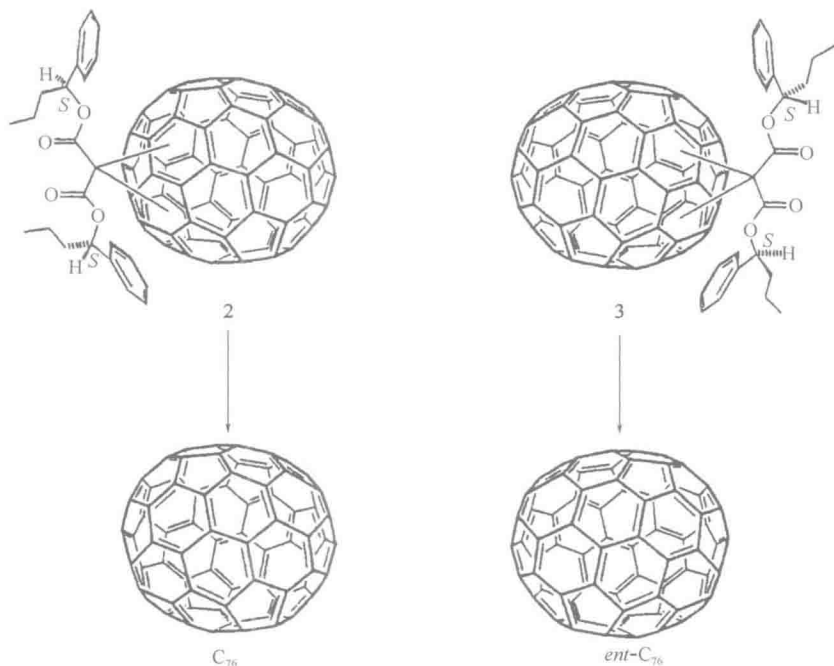
Scheme 1.1 The Bingel reaction

Then one of three pairs of diastereoisomeric mono-adducts was performed the retro-Bingel reaction to remove the di(alkoxycarbonyl) methano bridges by controlled potential electrolysis (CPE). The enantiomerically pure D_2 - C_{76} was prepared (Scheme 1.2). The optically active C_{76} mono-adducts **2** and **3** are associated pairs of diastereoisomers, which were unambiguously determined by CD spectra. However, the location of the malonate adduct was not exactly known although tentative constitutional assignments had been made. The two pure C_{76} monoadducts **2** and **3** were submitted to CPE and subsequent purification by HPLC, the two enantiomers, C_{76} and *ent*- C_{76} were obtained in low yields (about 5-10%) which have not yet been optimized because of the limited availability of the starting materials.

According to their reported results, the enantiomeric purity of their samples was higher than that reported by Hawkins and Meyer by the comparison of the circular dichroism (CD).

With the development of high performance liquid chromatography (HPLC), the number of LC stationary phases for the purpose of isolation has increased tremendously over the past few years. Although chiral fullerene C_{60} and C_{76} derivatives with achiral substituents have been successfully resolved into enantiomers using chiral stationary phase (CSPs) based on a cellulose derivative ^[67], and a tetranitrofluorenylidene derivative ^[68]. It was until 2001 that Y. Okamoto reported the direct resolution of C_{76}

enantiomers by HPLC using an amylose-based chiral stationary phase ^[69]. But the low degree of resolution and very low loading capacity of the column restrict its application.

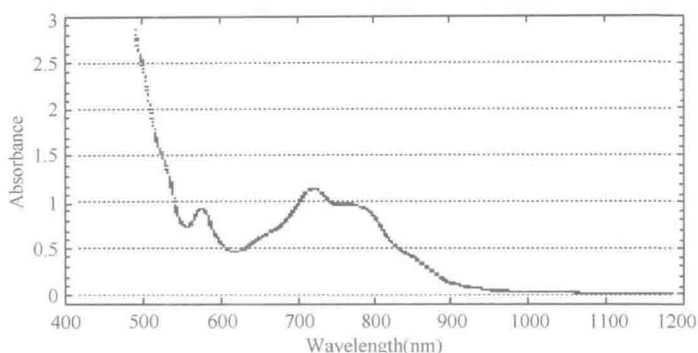


Scheme 1.2 Retro-Bingel reaction 2 and 3 are a pairs of diastereoisomerically pure, optically active C₇₆ mono-adducts

After the successful isolation of C₇₆, its physical properties firstly have been studied. M. Guldi's group has systematically investigated the photophysical properties of fullerenes, they studied the excited state and redox properties of C₇₆ and C₇₈ using laser flash photolysis and pulse radiolysis experiments.

The solubility of C₇₆ in nonpolar solvent makes it possible to employ them in conventional as well as transient absorption measurements. The absorption spectrum of C₇₆ in CS₂ is shown in Figure 1.4.

Like C₆₀ and C₇₀, the C₇₆ absorbs strongly in the UV and visible, but the increase in carbon atom count and change in symmetry alter the nature of electronic and vibrational transitions. The absorption in the visible and ease of inducing reversible reduction make the higher fullerenes potentially useful as photosensitizers and/or building blocks for electron relay systems.

Figure 1.4 UV-VIS spectrum of $C_{76}(D_2)$ in CS_2

In order to probe the excited singlet and triplet state characteristic of C_{76} , the time-resolved absorption spectrum was recorded following picosecond laser excitation (Figure 1.5).

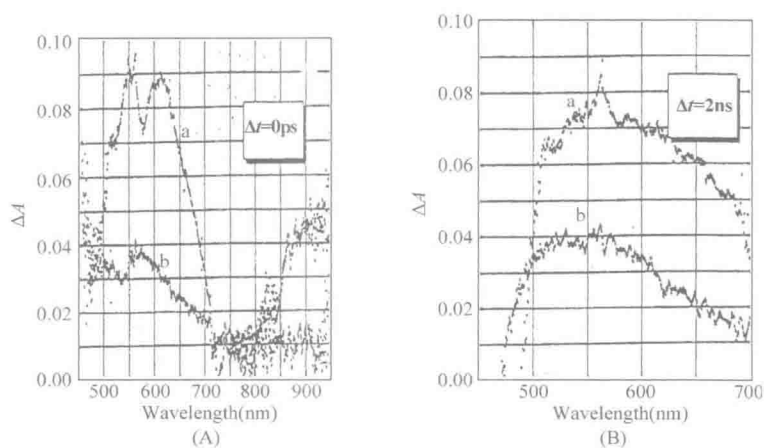


Figure 1.5 Transient absorbance changes observed following picosecond flash photolysis immediately(A) and 2000ps(B) after 355nm laser pulse (pulse width 18ps, 1.6mJ) excitation. The difference absorption spectra were recorded following excitation of (a) C_{76} and (b) C_{78} ($2.0 \times 10^{-5}M$) in deaerated toluene

The triplet quantum yield of C_{76} was measured using triplet-triplet energy transfer method, the results are summarized in Table 1.1.

Table 1.1 Photophysical properties of $C_{76}(D_2)$, $C_{78}(D'_{2v})$

Fullerene	Single-singlet	Triplet-triplet	Triplet quantum	Radical cation
C_{60}	920	400,750	0.93	980
C_{70}	660	435,970	0.90	930

Fullerene	Single-single	Triplet-triplet	Triplet quantum	Continued
				Radical cation
$C_{76}(D_2)$	560,620,900	560-640	0.05	960
$C_{78}(D_{2v})$	890	490	0.12	975
C_{84}		310		920

It is interesting to note that the triplet quantum yield values for these higher fullerenes are significantly smaller than that of C_{60} and C_{70} . A qualitative observation regarding the low triplet quantum yield has also been made earlier for larger fullerenes [70, 71]. These results suggest that a nonradiative decay process is also dominant in the deactivation of the single excited states of higher fullerenes. And the kinetic properties of excited triplet were summarized in Table 1. 1, along with the Figure 1.6.

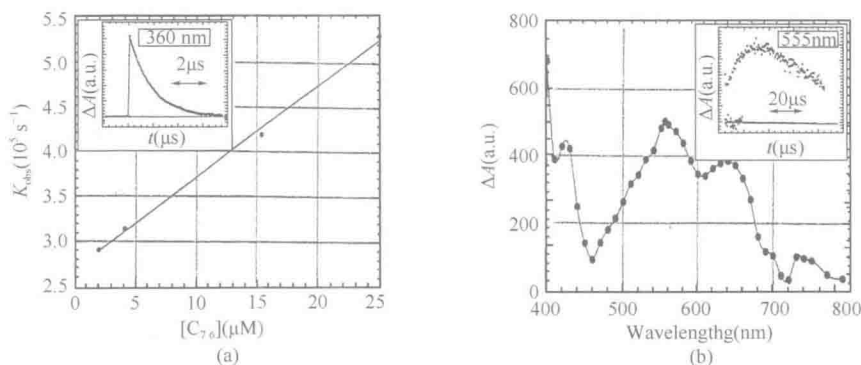
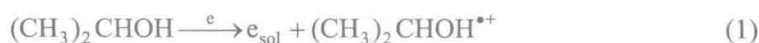


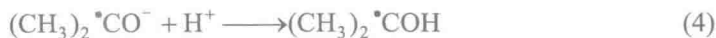
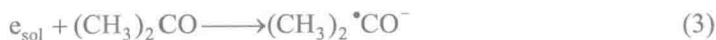
Figure 1.6 (a) Plot of k_{obs} vs initial concentration of C_{76} representing bimolecular triplet-triplet energy transfer between ${}^3\text{BP}^*$ (0.02M) and ground state C_{76} in deoxygenated toluene. The absorption-time profile recorded at 360nm in the presence of $1.55 \times 10^{-3}\text{M}$ C_{76} is shown in the inset. (b) Difference absorption spectra recorded 20μs after the electron pulse in a nitrogen-saturated toluene solution containing 0.02M biphenyl and $4.0 \times 10^{-6}\text{M}$ C_{76} . The absorption-time profile recorded at 555nm shows the formation of ${}^3C_{76}$ and its decay

The quenching rate constant of the energy transfer was determined from the decay kinetics of the transient absorption decay at 360 nm following pulse irradiation. The quenching of the ${}^3\text{BP}^*$ obeys the first-order kinetics. On a time scale of 100 μs, to regenerate the ground state (see inset in Figure 1.6b).

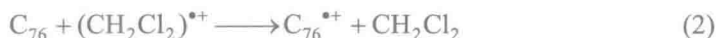
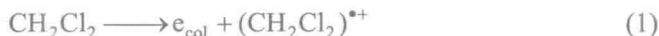
Meanwhile, the radical cation and radical anion of C_{76} also were obtained by the radiolytic reduction and oxidation according to the route **a** and **b**.

Route **a** [72]:





Route **b** [73]:



One-electron reduction of fullerenes was achieved by reaction of these substrates with $(\text{CH}_3)_2^{\bullet}\text{COH}$ radicals generated in a toluene/2-propanol/acetone (8:1:1, v/v) solvent mixture. The reducing species generated in this solvent mixture is that radical formed by hydrogen abstraction from 2-propanol and form electron capture of acetone followed by subsequent protonation to form $(\text{CH}_3)_2^{\bullet}\text{COH}$ radicals.

The strongly reducing $(\text{CH}_3)_2^{\bullet}\text{COH}$ radicals ($E_{1/2} = -1.39$ V vs NHE) are then expected to undergo electron transfer with the C_{76} (route **a**-5). The difference absorption spectra obtained upon electron plus irradiation of C_{76} in a N_2 -saturated, toluene/2-propanol/acetone mixture (8:1:1 v/v) are shown in Figure 1.7 (a, b).

Fullerenes are rather difficult to oxidize and usually undergo irreversible oxidation with few selective oxidizing species. However, one-electron oxidation of fullerenes can be conveniently studied by irradiating a solution of this solute in dichloromethane (CH_2Cl_2). The radical cations $(\text{CH}_2\text{Cl}_2)^{\bullet+}$ generated via ionization of the solvent are strong oxidizing species that remove an electron from fullerene, as shown in route **b**.

