PAPER

NJC
www.rsc.org/njc

Cycloaddition reactions of hydrofullerenes with cyano-substituted alkenes under basic conditions

Yu-Jin Li,[ab] Guan-Wu Wang,*[ab] Jia-Xing Li[b] and You-Cheng Liu[ab]

[a] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: gwang@ustc.edu.cn; Fax: +86-551-360-7864*

***Received** (in Montpellier, France) 25th February 2004, Accepted 1st April 2004*
First published as an Advance Article on the web 16th July 2004

Hydrogenated [60]fullerenes, prepared from [60]fullerene and sodium borohydride, react with alkylidenecyanoacetates [RCH=CCN(CO_2Et): R = C_6H_5 (**2a**), 4-CH_3O–C_6H_4 (**2b**), 4-NO_2–C_6H_4 (**2c**), H (**2d**)] and alkylidenemalononitriles [RCH=C$(CN)_2$: R = C_6H_5 (**2e**), 4-CH_3O–C_6H_4 (**2f**), 4-NO_2–C_6H_4 (**2g**), 4-$(CH_3)_2N$–C_6H_4 (**2h**)] under basic conditions to afford cyclopentenylfullerenes **3**. No multi-cycloaddition products are obtained. Several bases including organic and inorganic bases can be utilized in these reactions. It is proposed that the reactions take place *via* the Michael addition of $C_{60}H^-$, generated *in situ* by deprotonation of dihydrofullerene with a mild base, to the electrophilic carbon-carbon double bond of substrate **2**, followed by intramolecular proton transfer and nucleophilic addition of the resulting fullerene carbanion to the nitrile group, and finally isomerization to the more stable conjugated ester or nitrile **3**.

Introduction

The chemical reactivity of [60]fullerene (C_{60}) resembles that of an electron-deficient alkene.[1] Thus, C_{60} behaves as an electrophilic molecule with highly strained double bonds and can react with nucleophiles, carbenes, radicals to give various functionalized fullerenes.[2] Fullerene anions are of great interest due to their versatile properties such as electron donor, nucleophile, or Brönsted base, as exemplified in a recent review.[3] C_{60} can be readily reduced and can accept as many as six electrons to form $C_{60}{}^{n-}$ (n = 1–6).[4] Fullerene anions reverse the normal reactivity of fullerene to become nucleophiles and hence open up new avenues for fullerene derivatization. Kadish and co-workers were the first to conduct the reaction of $C_{60}{}^{2-}$, generated by controlled-potential bulk electroreduction of C_{60}, with a large excess of methyl iodide and they obtained a mixture of 1,2- and 1,4-isomers of dimethylated [60]fullerene.[5] Later, the reaction of $C_{60}{}^{2-}$ generated by reduction of C_{60} electrochemically[6] or chemically[7] with various alkyl halides was investigated and generally monoalkylated ($C_{60}RH$) and dialkylated ($C_{60}R_2$ and $C_{60}RR'$) fullerene derivatives were obtained.

Fullerenic C–H bonds are quite acidic. The pK_a values of $C_{60}H_2$ are remarkably low (pK_{a1} = 4.7, pK_{a2} = 16[8]), suggesting that $C_{60}H^-$ and $C_{60}{}^{2-}$ should be readily available by deprotonation of $C_{60}H_2$ with appropriate bases.[8,9] Meier and co-workers reported the reaction of $C_{60}{}^{2-}$, formed by deprotonation of $C_{60}H_2$ with tetrabutylammonium hydroxide, with alkylating agents to give mono- or dialkylated products under scrupulous deoxygenation conditions.[10] In the previous reactions of $C_{60}{}^{2-}$, all electrophiles used are alkyl bromides or iodides. In this paper, we wish to report the reaction of a hydrofullerene mixture with alkylidenecyanoacetates (**2a**–**2d**) and alkylidenemalononitriles (**2e**–**2h**) in the presence of a base. These reactions result in the formation of cyclopentenylfullerenes (**3**) and provide powerful ways for the preparation of highly functionalized fullerenes. The reactions are rationalized by a mechanism *via* a Michael addition, followed by an intramolecular proton transfer and nucleophilic addition, and finally isomerization.

Results and discussion

Hydrogenated fullerenes are usually prepared by hydroboration[11] or hydrozirconation[12] followed by hydrolysis, or by reduction with hydrazine,[13] or by reduction with zinc in the presence of water.[14] We wondered whether the reaction of C_{60} with $NaBH_4$ could be used to synthesize dihydrofullerene. When $NaBH_4$ was directly added to the toluene solution of C_{60}, no expected product was obtained. This was probably due to the insolubility of $NaBH_4$ in toluene. However, it was found that $NaBH_4$ dissolved in ethanol could react efficiently with C_{60}. The reaction proceeded at 60 °C for 30 min and gave $C_{60}H_2$ (**1**) in 59% isolated yield (62% yield along with 21% of multi hydro-adducts based on the measurement by high-performance liquid chromatography). The identity of $C_{60}H_2$ was confirmed by the comparison of its ^1H NMR and UV-vis spectra with those reported in the literature.[11a]

Meier and co-workers reported that the treatment of $C_{60}H_2$ and its multi-adducts, formed from the reaction of C_{60} with Zn/H^+, with 2,3-dichloro-5,6-dicyanobenzoquinone resulted in smooth conversion of the reaction mixture back to C_{60}.[15] Meanwhile, Becker *et al.* reported that isolated $C_{60}H_2$ was readily converted back to C_{60} in the presence of oxygen.[16] We found that C_{60} could be regenerated quantitatively under air if triethylamine or pyridine was added to the reaction mixture of C_{60} and $NaBH_4$ containing $C_{60}H_2$ and higher reduced fullerenes. The transformation of the multi hydro-adducts $C_{60}H_n$ ($n \geq 4$) to C_{60} should proceed *via* $C_{60}H_2$.

In view of the strong acidity of the C–H bond of $C_{60}H_2$, $C_{60}H^-$ can be obtained from $C_{60}H_2$ in the presence of a mild base and thus can be utilized as a nucleophile. We therefore investigated the reactions of hydrofullerenes with alkylidenecyanoacetates (**2a**–**2d**) and alkylidenemalononitriles (**2e**–**2h**) in the presence of a base in order to see whether the expected

DOI: 10.1039/b402986k

$C_{60}H^-$ anion could be formed and then undergo Michael addition with cyano-substituted alkenes. Because the separation of $C_{60}H_2$ from C_{60} and multi hydro-adducts was rather difficult on a silica gel column and because multi hydro-adducts of C_{60} could convert to $C_{60}H_2$ in the presence of a base and under air, we employed the reaction mixture of C_{60} and $NaBH_4$ directly instead of isolating $C_{60}H_2$ for practical purposes.

Ethyl benzylidenecyanoacetate (**2a**) was first chosen for our investigation. The ethanol solution of $NaBH_4$ was added to the toluene solution of C_{60} and the reaction mixture was stirred at 60 °C for 30 min, thus leading to a mixture of hydrofullerenes that contained $C_{60}H_2$ as the major product along with multi hydro-adducts as the minor products. The resulting hydrofullerene mixture was treated with 2 equiv of **2a** in the presence of triethylamine and the reaction mixture was maintained at the same temperature for an additional 1 h. This one-pot reaction afforded the cycloaddition product **3a** in 57% yield (84% based on consumed C_{60}; Scheme 1).

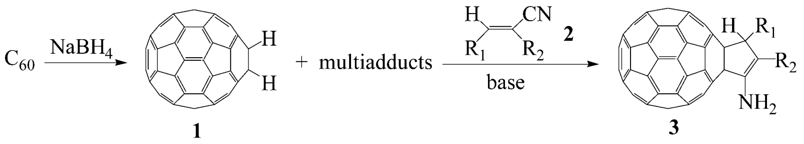
Several organic and inorganic bases were employed in the reaction of **2a** with the hydrofullerene mixture to find the best reaction conditions and the results are summarized in Table 1. It is seen that inorganic bases such as $NaOCH_3$ and K_2CO_3 afforded **3a** in lower yields, probably due to their low solubility in the reaction media. Triethylamine (Et_3N) and pyridine as well as 4-dimethylaminopyridine (DMAP) and piperidine performed better.

This type of cycloaddition reaction of hydrofullerenes could be successfully extended to other alkylidenecyanoacetates and alkylidenemalononitriles in the presence of Et_3N or pyridine; cycloadducts **3** rather than the Michael addition products were obtained (Scheme 1). Et_3N and pyridine were chosen as the base in these reactions because they gave the best results among all investigated bases. The yields along with recovered C_{60} for the reaction of the hydrofullerene mixture with **2b**–**2h** in the presence of Et_3N and pyridine are collected in Table 2. Cycloaddition products **3** were formed in about 90% yields based on consumed C_{60} in most cases.

The structures of products **3a**–**3h** were established by MALDI-TOF MS, ^1H NMR, ^{13}C NMR, FT-IR, and UV-vis spectral data. MALDI-TOF mass spectra of **3a**–**3h** gave correct molecular ions. An absorption peak around 3450 cm^{-1} for the NH_2 group, absorption peaks around 1680 and 1730 cm^{-1} for the conjugated ester group of **3a**–**3d** and peaks at about 1660 and 2200 cm^{-1} for the conjugated cyano group of **3e**–**3h** were observed in the FT-IR spectra. The UV-vis spectra of **3a**–**3h** exhibited the characteristic peak at 429 or 430 nm for the 1,2-adduct of C_{60}. Compounds **3d**–**3h** have poor solubility in CS_2, $CHCl_3$, THF or DMSO. However, they can be readily dissolved in a mixture of CS_2 and THF or CS_2 and DMSO. The ^1H NMR and ^{13}C NMR spectra of **3d**–**3h** were taken in CS_2 with a small amount of DMSO-d_6 added; the others were in a mixture of CS_2 and $CDCl_3$. A broad singlet for the NH_2 group of **3a**–**3c** at 6.7–6.9 ppm and at 7.3–7.4 ppm for **3d**–**3h**, a singlet for the methine group at 5.8–6.2 ppm as well as the signals for the phenyl and ethoxy groups were observed in the ^1H NMR spectra of **3**. It should be noted that in the ^1H NMR spectra of **3a**–**3c**, the two methylene protons in the OCH_2CH_3 group appear as two doublets of quartets in an AB splitting pattern and all phenyl protons are magnetically inequivalent due to the nearby chiral methine group and restricted rotation of the phenyl ring. The observed signals at about 167, 62, and 14 ppm for the ethoxycarbonyl group, at about 96 ppm for the olefinic carbon bearing carbonyl group, at about 60 ppm for the methine group in the ^{13}C NMR spectra of **3a**–**3c**, those at about 116 ppm for the cyano group, at about 72 ppm for the olefinic carbon bearing cyano group, at about 60 ppm for the methine group in the ^{13}C NMR spectra of **3e**–**3h**, and more than 48 partially overlapped peaks for the fullerene skeletons of both **3a**–**3c** and **3e**–**3h** are consistent with molecular structures of **3a**–**3c** and **3e**–**3h** having C_1 symmetry. The ^1H NMR and ^{13}C NMR spectra of **3d** are simpler than those of **3a**–**3c** and **3e**–**3h** due to its higher molecular symmetry. The ^1H NMR spectrum of **3d** displayed a broad singlet at 7.39 ppm for the NH_2 protons, a singlet at 4.50 ppm for the methylene protons of the five-membered ring, and a quartet at 4.31 ppm and a triplet at 1.41 ppm for the ethoxy protons. In the ^{13}C NMR spectra of **3d**, there exist peaks at 165.62, 58.55, and 14.39 ppm for the ethoxycarbonyl group, at 43.91 ppm for the methylene carbon of the five-membered ring, at 88.48 ppm for the olefinic carbon carrying the carbonyl group, and 30 peaks including an overlapping one integrating totally as 59 sp^2-carbons (58 carbons of C_{60} and one olefinic carbon carrying the amino group) in the 156–133 ppm region, and two sp^3-carbons of C_{60} at 75.42 and 64.55 ppm, fully consistent with the C_s symmetry of compound **3d**.

It was observed that deoxygenation was unnecessary for the reactions of hydrofullerenes with **2a**–**2h** in the presence of a base as it had little effect on the yields of the reactions. Therefore, the cycloaddition reactions of hydrofullerenes were conducted under air. Multiple addition has always been a real problem for the preparation of C_{60} monoadducts.[2,17] However, no trace of bisadduct could be isolated from our reaction mixtures, even though 21% of $C_{60}H_4$ and higher reduced fullerenes was present in the hydrofullerene mixture. These $C_{60}H_4$ and higher reduced fullerenes must be transformed into $C_{60}H_2$, which subsequently reacts with **2a**–**2h** in the presence of a base.

Since the reaction of the hydrofullerene mixture with cyano-substituted alkenes does not take place in the absence of a base, the formation of conjugated ester or nitrile **3** is supposed to take place *via* the following sequence of reactions: Michael addition of $C_{60}H^-$ (**4**), generated *in situ* from $C_{60}H_2$ in the presence of a mild base, to ethyl alkylidenecyanoacetates or alkylidenemalononitriles to give intermediate **5**; intramolecular proton transfer within the intermediate carbanion **5** to give fullerene anion **6**; intramolecular addition of the resulting



2a, **3a**: R_1 = Ph $R_2 = CO_2Et$
2b, **3b**: $R_1 = 4\text{-}CH_3OC_6H_4$ $R_2 = CO_2Et$
2c, **3c**: $R_1 = 4\text{-}NO_2C_6H_4$ $R_2 = CO_2Et$
2d, **3d**: R_1 = H $R_2 = CO_2Et$
2e, **3e**: R_1 = Ph R_2 = CN
2f, **3f**: $R_1 = 4\text{-}CH_3OC_6H_4$ R_2 = CN
2g, **3g**: $R_1 = 4\text{-}NO_2C_6H_4$ R_2 = CN
2h, **3h**: $R_1 = 4\text{-}(CH_3)_2NC_6H_4$ R_2 = CN

Scheme 1

Table 1 Yields of **3a** and recovered C_{60} for the reaction of **2a** with hydrofullerenes in the presence of different bases

Base	% Yield	% Recovered C_{60}
Et_3N	57	32
Pyridine	55	38
DMAP	50	43
Piperidine	46	37
$NaOCH_3$	35	60
K_2CO_3	30	64

fullerene carbanion to the cyano group to afford *exo*-cyclic imine **7**; and, finally, isomerization of **7** to the more stable conjugated ester or conjugated nitrile **3**. This sequence is illustrated in Scheme 2.

Cycloaddition products **3** were formed with good selectivity, while neither bisadducts nor Michael addition products were observed. This result indicates that the proton transfer in **5** and the intramolecular nucleophilic addition to the cyano group in **6** are both fast reactions.

Although the hydrofullerene mixture reacted efficiently with ethyl alkylidenecyanoacetates and alkylidenemalononitriles in the presence of a base and under air, it failed to react with MeI, EtI, $PhCH_2Br$ or $BrCH_2CO_2Et$ under the same conditions. The reaction mixture was instead converted back to C_{60} under the reaction conditions. This phenomenon can be rationalized on the assumption that the reaction of $C_{60}H^-$ anion with cyano-substituted alkenes is much faster than the reaction with O_2 and the reaction of $C_{60}H^-$ anion with these alkyl halides is much slower than the reaction with O_2.

In conclusion, we have uncovered a highly effective and practical method for preparing cyclic products of C_{60} by the reaction of C_{60} with $NaBH_4$, followed by the reaction with ethyl alkylidenecyanoacetates or alkylidenemalononitriles in one pot. A reaction mechanism that involves Michael addition, followed by intramolecular proton transfer and subsequent nucleophilic addition, and finally isomerization, has been proposed to rationalize the formation of the cyclic adduct **3**. The cyclic adducts **3** bearing reactive NH_2, C=C, and CN or CO_2Et groups, which are difficult to synthesize by other routes, can be further employed to prepare various functionalized derivatives of C_{60}. Further applications of the hydrofullerene mixture as a reactant, especially as precursor of $C_{60}H^-$ rather than $C_{60}{}^{2-}$, to other fullerene functionlizations are under investigation.

Experiment

General methods

^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, in a mixed solvent of CS_2 and $CDCl_3$ or CS_2 and DMSO-d_6. FT-IR spectra were recorded on a Brucker Vector-22 spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2501PC spectrophotometer. Mass spectra were taken on a BIFLEXIII MALDI-TOF mass spectrometer with 4-hydroxy-α-cyanocinnamic acid as the matrix.

Table 2 Yields of **3b**–**3h** and recovered C_{60} for the reaction of hydrofullerenes with **2b**–**2h** in the presence of Et_3N and pyridine

	Et_3N		Pyridine	
Compound	% Yield	% Recovered C_{60}	% Yield	% Recovered C_{60}
3b	47	49	33	62
3c	54	42	55	40
3d	59	34	58	31
3e	51	43	53	41
3f	51	41	50	41
3g	55	41	60	34
3h	50	45	55	40

C_{60} (> 99.9%) was purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. Ethyl alkylidenecyanoacetates (**2a**–**2d**) and alkylidenemalononitriles (**2e**–**2h**) were prepared according to the reported procedures.[18] All other reagents were commercially available and of R. A. grade.

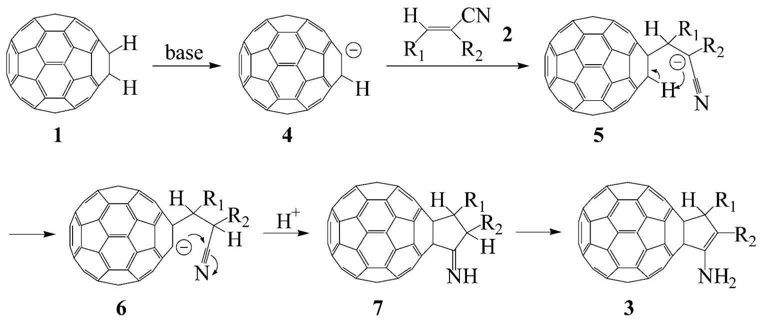
Syntheses

Preparation of hydrofullerene mixture. To a toluene (35 mL) solution of C_{60} (36.0 mg, 0.05 mmol) was added 1 mL of an ethanol solution of $NaBH_4$ (1.0 mg, 0.026 mmol); the reaction mixture was stirred at 60 °C for 30 min. The reaction mixture consisted of 17% C_{60}, 62% $C_{60}H_2$, and 21% multi hydroadducts, as determined by high-performance liquid chromatography on a 4.6 × 250 mm Cosmosil Buckyprep column with the detection wavelength of the diode detector set at 326 nm. Column separation of the reaction mixture on a silica gel column with CS_2 as the eluent afforded pure $C_{60}H_2$[11a] (21.4 mg, 59%) along with recovered C_{60} (7.0 mg, 19%).

Preparation of 3. To the above-prepared hydrofullerene mixture were added ethyl benzylidenecyanoacetate (**2a**; 20.2 mg, 0.1 mmol) and Et_3N (1 mL). The reaction mixture was stirred at 60 °C for an additional 1 h and then evaporated *in vacuo*. The residue was separated on a silica gel column with toluene as the eluent to afford **3a** (26.3 mg, 57%) along with recovered C_{60} (11.5 mg, 32%). The yields of **3a** and recovered C_{60} are listed in Table 1 for the reaction using pyridine, DMAP, piperidine, $NaOCH_3$ or K_2CO_3 as the base. Compounds **3b**–**3h** were prepared by the same procedure as that for compound **3a** with Et_3N or pyridine as the base. The yields of **3b**–**3h** along with recovered C_{60} for the reaction of hydrofullerenes with **2b**–**2h** in the presence of Et_3N and pyridine are collected in Table 2.

3a. ^1H NMR (300 MHz, CS_2–$CDCl_3$) δ 7.79 (d, J = 6.6 Hz, 1H), 7.55 (d, J = 6.6 Hz, 1H), 7.40–7.32 (m, 1H), 7.28–7.20 (m, 1H), 7.20 (tt, J = 6.7, 1.2 Hz, 1H), 6.76 (bs, 2H), 5.98 (s, 1H), 4.18 (dq, J = 10.8, 7.2 Hz, 1H), 4.08 (dq, J = 10.8, 7.2 Hz, 1H), 1.04 (t, J = 7.2 Hz, 3H). ^{13}C NMR [75 MHz, CS_2–$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent] δ 167.31, 157.63, 156.58, 154.33, 150.40, 147.43, 146.38, 146.04, 146.00, 145.84, 145.74, 145.71, 145.69, 145.54, 145.44, 145.39, 145.33, 145.24, 145.22, 145.06, 144.94, 144.60, 144.27, 144.10, 143.19, 143.13, 142.76, 142.65, 142.57, 142.50, 142.28, 142.25, 142.07, 141.99, 141.92, 141.81, 141.78, 141.75, 141.69, 141.61, 140.61, 140.53, 140.33, 139.59, 136.81, 135.99, 135.12, 133.78, 130.50, 128.97, 128.25, 127.27, 96.28, 75.49, 72.43, 61.74, 59.64, 14.28. FT-IR (KBr) ν/cm^{-1}: 3460, 2921, 1732, 1679, 1634, 1548, 1511, 1454, 1287, 1265, 1225, 1134, 1107, 721, 699, 574, 544, 526. UV-vis ($CHCl_3$) λ_{max}/nm: 245, 274, 310, 430, 701. MALDI-TOF MS m/z 923.

3b. ^1H NMR (300 MHz, CS_2–$CDCl_3$) δ 7.75 (d, J = 6.2 Hz, 1H), 7.48 (d, J = 6.2 Hz, 1H), 6.97 (d, J = 6.2 Hz, 1H), 6.79 (d, J = 6.2 Hz, 1H), 6.74 (bs, 2H), 5.97 (s, 1H), 4.22 (dq, J = 10.2, 7.1 Hz, 1H), 4.15 (dq, J = 10.2, 7.1 Hz, 1H), 3.79 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR [75 MHz, CS_2–$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent] δ 167.33, 158.48, 157.30, 156.57, 154.48, 150.44, 150.38, 147.30, 146.25, 146.23, 145.92, 145.90, 145.87, 145.84, 145.80, 145.76, 145.58, 145.55, 145.53, 145.41, 145.36, 145.26, 145.19, 145.09, 145.02, 144.92, 144.80, 144.47, 144.14, 143.96, 143.03, 143.00, 142.61, 142.50, 142.41, 142.39, 142.15, 142.11, 141.93, 141.85, 141.77, 141.75, 141.66, 141.62, 141.56, 141.45, 140.44, 140.37, 140.12, 139.51, 136.71, 135.86, 134.93, 134.88, 133.57, 131.23, 128.19, 114.50, 113.06, 96.43, 75.31, 72.63, 60.89, 59.53, 55.00, 14.18. FT-IR (KBr) ν/cm^{-1}: 3460, 2922, 1734, 1676, 1571, 1520, 1427, 1382,



Scheme 2

1278, 1249, 1108, 1028, 934, 754, 679, 594, 526, 458. UV-vis ($CHCl_3$) λ_{max}/nm: 246, 273, 326, 430, 704. MALDI-TOF MS m/z 953.

3c. ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 8.34 (d, $J = 8.3$ Hz, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 6.90 (bs, 2H), 6.15 (s, 1H), 4.23 (dq, $J = 10.7$, 7.1 Hz, 1H), 4.18 (dq, $J = 10.7$, 7.1 Hz, 1H), 1.12 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR [75 MHz, CS_2–$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent] δ 166.67, 158.36, 155.58, 152.77, 150.58, 149.71, 149.68, 147.39, 147.35, 147.03, 146.29, 145.98, 145.96, 145.88, 145.65, 145.61, 145.51, 145.46, 145.33, 145.29, 145.26, 145.22, 145.19, 145.17, 145.03, 145.01, 144.79, 144.44, 144.35, 144.15, 144.00, 143.12, 143.08, 142.66, 142.62, 142.52, 142.20, 142.11, 142.07, 141.96, 141.82, 141.68, 141.64, 141.58, 141.55, 140.57, 140.47, 140.41, 139.65, 136.25, 135.73, 135.18, 133.85, 130.8, 128.17, 123.94, 123.50, 94.94, 75.37, 71.61, 61.21, 59.76, 14.14. FT-IR (KBr) ν/cm^{-1}: 3464, 2923, 1732, 1681, 1568, 1520, 1428, 1377, 1279, 1216, 1109, 1028, 941, 803, 752, 679, 593, 527, 458. UV-vis ($CHCl_3$) λ_{max}/nm: 246, 273, 307, 429, 698. MALDI-TOF MS m/z 968.

3d. ^{1}H NMR (300 MHz, CS_2–DMSO-d_6) δ 7.39 (bs, 2H), 4.50 (s, 2H), 4.31 (q, $J = 7.0$ Hz, 2H), 1.41 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR [75 MHz, CS_2–DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent] δ 165.62 ($C = O$), 155.86 (2C), 155.54 (1C), 149.08 (2C), 146.61 (2C), 146.33 (2C), 145.37 (2C), 145.11 (2C), 144.99 (3C), 144.92 (2C), 144.83 (2C), 144.69 (2C), 144.30 (2C), 144.26 (2C), 144.18 (2C), 143.65 (2C), 143.57 (1C), 143.30 (2C), 142.16 (2C), 141.72 (2C), 141.62 (2C), 141.44 (2C), 141.23 (2C), 141.14 (2C), 141.03 (2C), 140.91 (2C), 140.47 (2C), 139.49 (2C), 138.96 (2C), 135.03 (2C), 133.17 (2C), 88.48 (1C, C–C=O), 75.42 (1C, sp^3-C of C_{60}), 64.55 (1C, sp^3-C of C_{60}), 58.55 (1C, OCH_2CH$_3$), 43.91 (1C, CH_2), 14.39 (1C, OCH$_2$$CH_3$). FT-IR (KBr) ν/cm^{-1}: 3443, 2921, 1732, 1676, 1630, 1428, 1263, 1109, 1033, 767, 575, 527. UV-vis ($CHCl_3$) λ_{max}/nm: 245, 273, 313, 430, 693. MALDI-TOF MS m/z 847.

3e. ^{1}H NMR (300 MHz, CS_2–DMSO-d_6) δ 7.77 (d, $J = 6.6$ Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 2H), 7.39 (bs, 2H), 7.34 (tt, $J = 7.4$, 1.2 Hz, 1H), 5.92 (s, 1H). ^{13}C NMR [75 MHz, CS_2–DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent] δ 158.51, 155.39, 152.62, 149.63, 149.17, 146.66, 146.41, 146.38, 146.16, 145.46, 145.43, 145.12, 145.07, 145.02, 145.00, 144.92, 144.84, 144.73, 144.70, 144.37, 144.32, 144.29, 144.24, 144.09, 144.05, 143.61, 143.52, 143.36, 143.34, 142.13, 142.08, 141.73, 141.67, 141.61, 141.40, 141.25, 141.22, 141.17, 140.94, 140.88, 140.86, 140.79, 140.69, 140.59, 140.55, 139.44, 139.11, 139.03, 138.71, 138.53, 135.12, 134.98, 134.37, 132.97, 128.23, 127.36, 116.50, 74.13, 72.46, 71.84, 61.15. FT-IR (KBr) ν/cm^{-1}: 3446, 2920, 2200, 1651, 1607, 1454, 1428, 1185, 762, 699, 597, 575, 549, 527. UV-vis ($CHCl_3$) λ_{max}/nm: 246, 275, 312, 429, 695. MALDI-TOF MS m/z 876.

3f. ^{1}H NMR (300 MHz, CS_2–DMSO-d_6) δ 7.67 (d, $J = 7.1$ Hz, 2H), 7.33 (bs, 2H), 6.97 (d, $J = 7.1$ Hz, 2H), 5.88 (s, 1H), 3.85 (s, 3H). ^{13}C NMR [75 MHz, CS_2–DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent] δ 158.37, 158.29, 155.56, 152.94, 149.83, 149.23, 146.84, 146.38, 146.35, 146.29, 145.43, 145.40, 145.22, 145.07, 145.04, 144.97, 144.88, 144.82, 144.69, 144.41, 144.29, 144.26, 144.21, 144.18, 144.07, 144.00, 143.59, 143.53, 143.34, 143.33, 142.09, 142.05, 141.70, 141.65, 141.63, 141.58, 141.42, 141.24, 141.20, 141.15, 140.92, 140.88, 140.85, 140.76, 140.66, 140.55, 140.49, 139.40, 138.93, 138.58, 135.10, 134.96, 134.26, 132.87, 130.94, 116.69, 113.62, 74.04, 72.53, 72.11, 60.43, 54.14. FT-IR (KBr) ν/cm^{-1}: 3445, 2920, 2200, 1654, 1608, 1509, 1425, 1303, 1250, 1172, 1035, 832, 773, 597, 574, 546, 527. UV-vis ($CHCl_3$) λ_{max}/nm: 246, 275, 312, 429, 697. MALDI-TOF MS m/z 905 (M-1$^+$).

3g. ^{1}H NMR (300 MHz, CS_2–DMSO-d_6) δ 8.26 (d, $J = 7.9$ Hz, 2H), 7.98 (d, $J = 7.8$ Hz, 2H), 7.67 (bs, 2H), 6.05 (s, 1H). ^{13}C NMR [75 MHz, CS_2–DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent] δ 159.38, 154.82, 151.58, 149.23, 148.90, 146.90, 146.72, 146.69, 146.47, 146.39, 145.48, 145.20, 145.13, 145.05, 144.96, 144.86, 144.83, 144.77, 144.65, 144.56, 144.37, 144.32, 144.22, 144.11, 143.58, 143.41, 142.16, 142.10, 141.74, 141.67, 141.30, 141.27, 141.21, 140.93, 140.84, 140.78, 140.75, 140.58, 139.45, 138.99, 138.74, 138.67, 134.88, 134.82, 134.62, 133.18, 123.26, 116.33, 74.14, 71.21, 70.90, 60.36. FT-IR (KBr) ν/cm^{-1}: 3444, 2921, 2199, 1654, 1600, 1519, 1424, 1344, 1182, 1045, 858, 702, 598, 575, 527. UV-vis ($CHCl_3$) λ_{max}/nm: 245, 276, 313, 429, 695. MALDI-TOF MS m/z 921.

3h. ^{1}H NMR (300 MHz, CS_2–DMSO-d_6) δ 7.51 (d, $J = 7.2$ Hz, 2H), 7.31 (bs, 2H), 6.70 (d, $J = 7.2$ Hz, 2H), 5.78 (s, 1H), 2.99 (s, 6H). ^{13}C NMR [75 MHz, CS_2–DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent] δ 157.86, 155.79, 153.31, 150.04, 149.32, 148.78, 146.79, 146.33, 146.14, 145.45, 145.40, 145.37, 145.01, 144.93, 144.83, 144.78, 144.69, 144.64, 144.51, 144.28, 144.22, 144.13, 144.04, 143.96, 143.58, 143.54, 143.31, 143.28, 142.04, 142.01, 141.66, 141.59, 141.58, 141.53, 141.46, 141.23, 141.17, 141.15, 141.10, 140.91, 140.90, 140.84, 140.73, 140.62, 140.55, 140.45, 139.35, 138.93, 138.59, 138.50, 135.21, 135.01, 134.15, 132.73, 126.14, 116.67, 111.81, 74.01, 73.24, 72.56, 60.59, 39.41. FT-IR (KBr) ν/cm^{-1}: 3444, 2920, 2197, 1652, 1609, 1519, 1427, 1354, 1226, 1184, 1162, 1061, 945, 816, 781, 706, 596, 575, 545, 526. UV-vis ($CHCl_3$) λ_{max}/nm: 245, 275, 327, 429, 697. MALDI-TOF MS m/z 919.

Acknowledgements

We thank the National Science Fund for Distinguished Young Scholars (21025205), the Fund for Innovative Research Groups of the National Science Foundation of China (20321101), Anhui Provincial Bureau of Personnel Affairs (2001Z019) and Anhui Provincial Natural Science Foundation (00045306) for financial support. We are grateful to Prof. Yun-Dong Wu for his manuscript reading.

References

1 (*a*) M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519; (*b*) R. C. Haddon, *Science*, 1993, **261**, 1545.

2 (*a*) R. Taylor and D. R. M. Walton, *Nature (London)*, 1993, **363**, 685; (*b*) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme Verlag, Stuttgart, 1994; (*c*) A. Hirsch, *Synthesis*, 1995, 895; (*d*) F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317; (*e*) A. Hirsch, *Top. Curr. Chem.*, 1999, **199**, 1.

3 C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.

4 (*a*) D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufler, L. P. F. Chibante and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364; (*b*) F. Zhou, C. Jehoulet and A. J. Bard, *J. Am. Chem. Soc.*, 1992, **114**, 11 004; (*c*) R. Subramanian, P. Boulas, M. N. Vijayashree, F. D'Souza, M. T. Jones and K. M. Kadish, *J. Chem. Soc., Chem. Commun.*, 1994, 1847; (*d*) L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

5 C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505.

6 (*a*) P. L. Boulas, Y. Zuo and L. Echegoyen, *Chem. Commun.*, 1996, 1547; (*b*) K.-M. Mangold, W. Kutner, L. Dunsch and J. Fröhner, *Synth. Met.*, 1996, **77**, 73; (*c*) K. M. Kadish, X. Gao, E. Van Caemelbecke, T. Hirasaka, T. Suenobu and S. Fukuzumi, *J. Phys Chem. A*, 1998, **102**, 3898; (*d*) M. W. J. Beulen and L. Echegoyen, *Chem. Commun.*, 2000, 1065.

7 (*a*) J. Chen, R.-F. Cai, Z.-E. Huang, H.-M. Wu, S.-K. Jiang and Q.-F. Shao, *J. Chem. Soc., Chem. Commun.*, 1995, 1553; (*b*) R. Subramanian, K. M. Kadish, M. N. Vijayashree, X. Gao, M. T. Jones, M. D. Miller, K. L. Krause, T. Suenobu and S. Fukuzumi, *J. Phys. Chem.*, 1996, **100**, 16 327; (*c*) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, **120**, 9220; (*d*) E. Allard, L. Riviere, J. Delaunay, D. Dubois and J. Cousseau, *Tetrahedron Lett.*, 1999, **40**, 7223; (*e*) E. Allard, J. Delaunay, F. Cheng, J. Cousseau, J. Ordúna and J. Garín, *Org. Lett.*, 2001, **3**, 3503; (*f*) F. Cheng, Y. Murata and K. Komatsu, *Org. Lett.*, 2002, **4**, 2541; (*g*) E. Allard, F. Cheng, S. Chopin, J. Delaunay, D. Rondeau and J. Cousseau, *New J. Chem.*, 2003, **27**, 188; (*h*) E. Allard, J. Delaunay and J. Cousseau, *Org. Lett.*, 2003, **5**, 2239.

8 M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill and C. C. Henderson, *J. Phys. Chem.*, 1994, **98**, 13 093.

9 D. E. Cliffel and A. J. Bard, *J. Phys. Chem.*, 1994, **98**, 8140.

10 M. S. Meier, R. G. Bergosh, M. E. Gallagher, H. P. Spielmann and Z. Wang, *J. Org. Chem.*, 2002, **67**, 5946.

11 (*a*) C. C. Henderson and P. A. Cahill, *Science*, 1993, **259**, 1885; (*b*) C. C. Henderson, C. M. Rohlfing, R. A. Assink and P. A. Cahill, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 786.

12 S. Ballenweg, R. Gleiter and W. Krätschmer, *Tetrahedron Lett.*, 1993, **34**, 3737.

13 W. E. Billups, W. Luo, A. Gonzalez, D. Arguello, L. B. Alemany, T. Marriott, M. Saunders, H. A. Jiménez-Vázquez and A. Khong, *Tetrahedron Lett.*, 1997, **38**, 171.

14 (*a*) R. G. Bergosh, M. S. Meier, J. A. L. Cooke, H. P. Spielmann and B. R. Weedon, *J. Org. Chem.*, 1997, **62**, 7667; (*b*) H. P. Spielmann, G.-W. Wang, M. S. Meier and B. R. Weedon, *J. Org. Chem.*, 1998, **63**, 9865; (*c*) B. R. Weedon, R. C. Haddon, H. P. Spielmann and M. S. Meier, *J. Am. Chem. Soc.*, 1999, **121**, 335; (*d*) H. P. Spielmann, B. R. Weedon and M. S. Meier, *J. Org. Chem.*, 2000, **65**, 2755.

15 M. S. Meier, F. S. Corbin, V. K. Vance, M. Clayton, M. Mollman and M. Poplawska, *Tetrahedron Lett.*, 1994, **35**, 5789.

16 L. Becker, T. P. Evans and J. L. Bada, *J. Org. Chem.*, 1993, **58**, 7630.

17 (*a*) F. Diederich, L. Isaacs and D. Philp, *Chem. Soc. Rev.*, 1994, 243; (*b*) A. Hirsch, I. Lamparth and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 437; (*c*) K. Kordatos, S. Bosi, T. Da Ros, A. Zambon, V. Lucchini and M. Prato, *J. Org. Chem.*, 2001, **66**, 2802.

18 (*a*) F. Bigi, M. L. Conforti, R. Maggi, A. Piccinno and G. Sartori, *Green Chem.*, 2000, **2**, 101; (*b*) S. Y. Kim, P. S. Kwon, T. W. Kwon, S. K. Chung and Y. T. Chang, *Synth. Commun.*, 1997, **27**, 533; (*c*) S. Balalaie and N. Nemati, *Synth. Commun.*, 2000, **30**, 869; (*d*) A. K. Mitra, A. De and N. Karchaudhuri, *Synth. Commun.*, 1999, **29**, 2731.