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Photochemical addition reactions of [60]fullerene with 1,2-ethylenediamine and piperazine

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Abstract—*N*,*N*′-Dimethylethylenediamine and piperazine reacted with [60]fullerene by photoinduced-electron transfer to form the adduct compounds in a short reaction time with a good yield. NMR spectroscopy showed unambiguously that derivatives were C_{2v} symmetric structures with a 6,6 junction, and a single-electron transfer intermediate was suggested. © 2002 Elsevier Science Ltd. All rights reserved.

Since the discovery of C_{60} and its large scale preparation,[1,2] much work has been devoted to this research field.[3–5] Photo-induced functionalization of [60]fullerene has recently attracted considerable interest,[6–11] because [60]fullerene is a more effective photosensitizer than rose bengal, methylene blue or eosin yellowish (tetrabromo-fluorescein sodium salt).[12] [60]Fullerene can be easily excited into its triplet state by direct excitation or by sensitization,[13] and radical ions generated by single-electron transfer from neutral compounds by means of photoinduced electron transfer (PET) are known as important intermediates in the reaction of functionalization of [60]fullerene.[7]

1. Results and discussion

Kampe reported[14] on the synthesis of diamino derivatives of [60]fullerene from the addition of secondary diamines to [60]fullerene by thermal reaction for five days, and in their report,[14] compound **2** once was characterized by ^{13}C NMR spectroscopy. Their ^{13}C NMR spectrum exhibited just 15 resonance signals for the [60]fullerene skeleton. This was printed as Fig. 1 on the paper and no explanation about the data was given.[14] Kampe previously reported[15] the ^{13}C NMR spectral characterization of compound **4** and the ^{13}C NMR spectrum showed just 14 signals in the aromatic area of C_{60}. A ^{13}C NMR peak at 142.56 ppm was characterized as 6 carbons (6C) and it seems that it should have been characterized as a peak of trapped C_{60}, since only free C_{60} has a ^{13}C NMR peak at 142.6 ppm. The ^{1}H NMR spectrum (compound **4**) is not a first order spectrum. This system should have been described as $AA'A''A'''BB'B''B'''$ system not explained by Kampe et al.[15] We think the addition products (compounds **2** and **4**) should be a C_{2v} symmetric structure with a 6,6 junction.[16–23] A C_{2v} symmetric structure with a 6,6 junction should have exhibited 16 resonance signals in the aromatic area of C_{60}, and altogether should have exhibited 17 resonance signals for [60]fullerene skeleton (including one signal relating to two bridgehead carbons at aliphatic area like compounds **2** and **4** Many research papers[16–23] had reported the ^{13}C NMR spectrum characterization of C_{2v} symmetric structure of C_{60} derivatives. The ^{13}C NMR spectrum exhibited 17 resonance signals for [60]fullerene skeleton, of which four (including one signal from two bridgehead carbons correspond to two carbon atoms and 13 correspond to four carbon in aromatic area). Our experiment was unambiguously diagnostic for the ^{13}C NMR spectrum pattern of C_{2v} symmetric structure with a 6,6 junction.

In order to research its physical chemical and photochemical character, we prepared a diamino [60]fullerene derivatives by stirring the reaction mixture under N_2 at 50°C for five days. The yield was just 15%. In contrast by repeating the reaction under photoinduced electron transfer condition we obtained a higher yield (32%) in just 70 min (Scheme 1, Fig. 1).

By a similar procedure, piperazine was used in place of *N*,*N*-dimethylethylene-diamine (Scheme 2, Fig. 2)

Photochemical reaction of C_{60} with piperazine gave a higher yield of addition product than the reaction of C_{60} with *N*,*N*′-dimethylethylenediamine. However, when we tried using *N*,*N*′-dimethyl-1,6-hexanediamine to substitute *N*,*N*′-dimethylenediamine for the fullerene addition reaction, we found the reaction did not proceed, presumably because the product should contain a 10-membered ring which is not stable especially for fullerene addition derivatives. We also tried piperidine and diethylamine as the additive, but neither reacted with C_{60}.

In our photochemical addition, the addition of compounds **1**

Keywords: [60]fullerene; photochemical addition; single-electron transfer.

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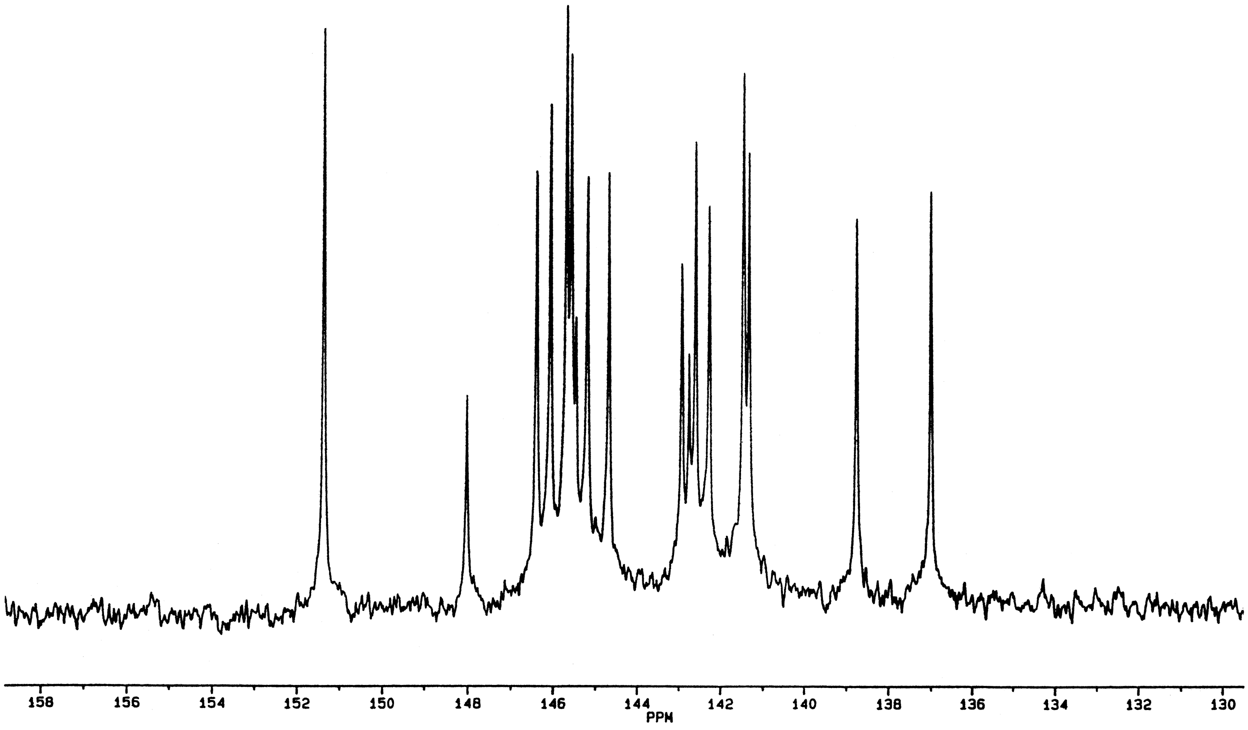
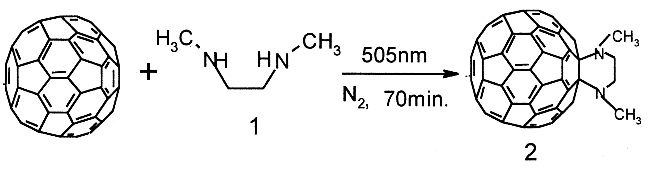


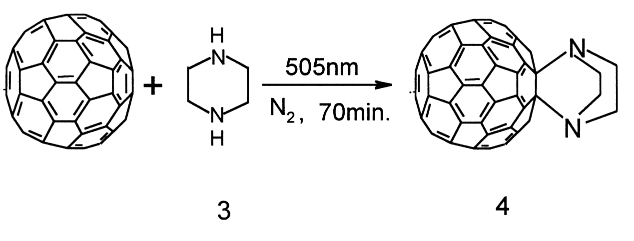
Figure 1. The ^{13}C NMR spectrum of compound **2**.



Scheme 1.

and **3** to [60]fullerene is likely to proceed by single-electron transfer to give an intermediate, $C_{60}^{-\cdot}$ which was generated by PET from *N*,*N*′-dimethylethylenediamine to [60]fullerene, and the activated radical $CH_3N^{\cdot}(CH_2)N^{\cdot}CH_3$ was generated by successive intermolecular proton transfer, which completed the addition reaction with fullerene[60]. The mechanism of single-electron transfer is showed in Scheme 3.

Some results related to the titled compounds have been published,[24,25] however, this focused on their photophysical and nonlinear optical properties. Except for that work, no work of synthesis and characterization has been published.



Scheme 2.

2. Experimental

2.1. Synthesis and characterization of compound 2

To a side-arm Rayonet® photochemical reactor, a solution containing [60]fullerene (580 mg, 0.806 mmol) in toluene (260 mL) was added, the *N*,*N*′-dimethylethylenediamine (517.5 mg, 5.87 mmol) in toluene (40 mL) was added dropwise. Nitrogen was bubbled into the solution for 1 h under a liquid seal. To the vessel inner, potassium chromate aqueous solution (10 g/100 mL) was added to use as a filter cutting off the wavelength of less than 505 nm. Then the stirred mixture was irradiated for 70 min using a 450 W Xenon source under N_2. The solvent was removed, the dried mixture was dissolved in carbon disulfide, and the concentrated solution was purified by chromatography on silica gel column. [60]Fullerene (166.5 mg) was recovered with dichloromethane as eluent, then dichloromethane and methyl alcohol (100:1) was used as eluent, and brown–black compound **2** was eluted from the column, concentrated and precipitated by adding acetonitrile to give pure compound **2** (148.8 mg, yield: 32%). Further elution with dichloromethane and methyl alcohol (100:3.5), gave a mixture of isomeric bisadducts (22 mg) which

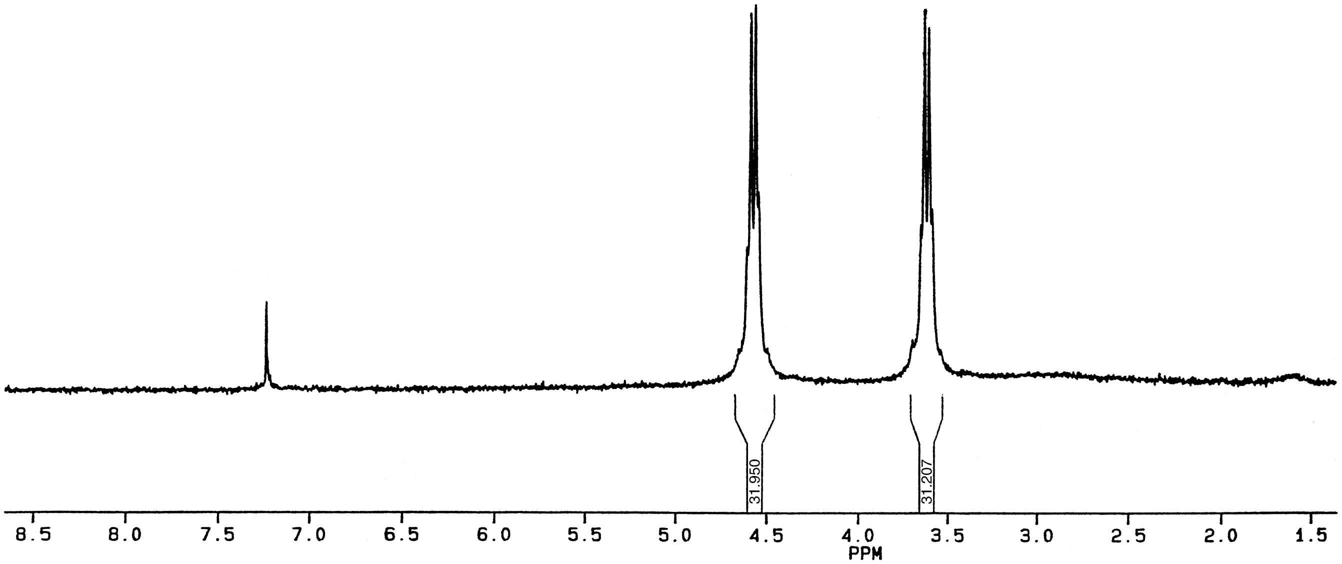
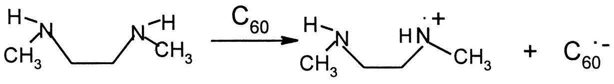


Figure 2. The ^{1}H NMR spectrum of compound **4**.



Scheme 3.

were collected which was purified by treatment with acetonitrile.

2.1.1. Compound 2. ^{1}H NMR (300 MHz, CS$_2$–CDCL$_3$, TMS), δ 3.43 (s, 6H, CH$_3$), 3.92 (s, 4H, CH$_2$). ^{13}C NMR (75.5 MHz, CS$_2$–CDCL$_3$, TMS) δ 151.37(4C), 148.02(2C), 146.39(4C), 146.06(4C), 145.67(4C), 145.56(4C), 145.18(4C), 144.67(4C), 142.92(2C), 142.74(2C), 142.58(4C), 142.26(4C), 141.45(4C), 141.32(4C), 138.75(4C), 136.99(4C), 80.25(2C), 48.33(–CH$_2$–), 44.08(–CH$_3$). FAB-MS (*m/z*): 893(100%), 806(68%). The ^{13}C NMR spectrum exhibited 17 resonance signals for [60]fullerene skeleton, of which four (including two bridgehead carbone at δ 80.25 correspond to two carbon atoms and 13 correspond to four carbon from δ 136.99–157.37, this pattern is unambiguously diagnostic for C_{2v} symmetric structure with a 6,6 junction.[16–23] Isomeric bisadducts exhibited 34 resonance signals at [60]fullerene skeleton, including at δ 78–80 three peaks corresponding to bridgehead carbons. It should be pointed out that, since the isomeric bisadducts were very low, we could not separate them.

2.2. Synthesis and characterization of compound 4

[60]Fullerene (580 mg, 0.806 mmol) was dissolved in toluene (260 mL), then piperazine (465.52 mg, 5.41 mmol) in toluene (40 mL) then was added dropwise, and nitrogen was bubbled into the solution for 1 h. The mixture was irradiated for 70 min under N$_2$ using a 450 W Xenon source (potassium chromate aqueous solution [10 g/100 mL] was added to use as a filter). Unreacted C$_{60}$ (362 mg) was recovered, pure monoadduct product **4** (85 mg, 55%, based on used C$_{60}$) was obtained, as well as isomeric bisadducts (18 mg, 10.6%).

2.2.1. Monoadduct product 4. ^{13}C NMR (75.5 MHz, CS$_2$–CDCL$_3$, TMS) δ 152.01 (4C), 148.15(2C), 146.64(2C), 146.29(4C), 146.03(4C), 145.93(4C), 145.53(4C), 144.89(4C), 143.14(4C), 142.84(4C), 142.89(4C), 142.48(4C), 142.11(4C), 141.28(4C), 140.15(2C), 137.28(4C), 78.49(2C), 47.41(4C, –4×CH2–). FAB-MS (*m/z*): 889(100%), 804(80%). The ^{13}C NMR spectrum (17 resonance signals for C$_{60}$ skeleton) showed that the pattern is also diagnostic for a C_{2v} symmetric structure with a 6,6 junction. ^{1}H NMR (300 MHz, CS$_2$–CDCl$_3$, TMS): δ 4.56 (m, Ha, 4H), 3.62 (m, Hb, 4H). The ^{1}H NMR spectrum of this compound is not a first order spectrum, this system is described as AA$'$A$''$A$'''$BB$'$B$''$B$'''$. Fortunately, the pattern is readily recognized because of its near symmetry and apparent simplicity, under moderate resolution, it resembles an AB pattern of two distorted doublets, with additional splitting. Isomeric bisadducts exhibited 29 resonance signals for the [60]fullerene skeleton.

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