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Photoreactions between [60]Fullerene and Various Aromatic Tertiary Amines

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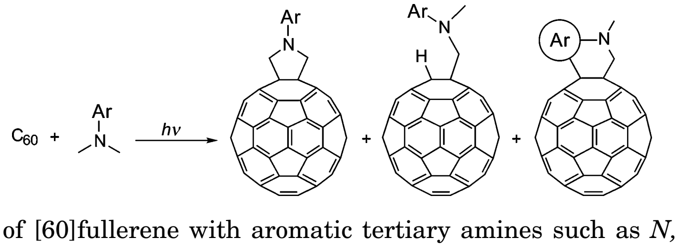
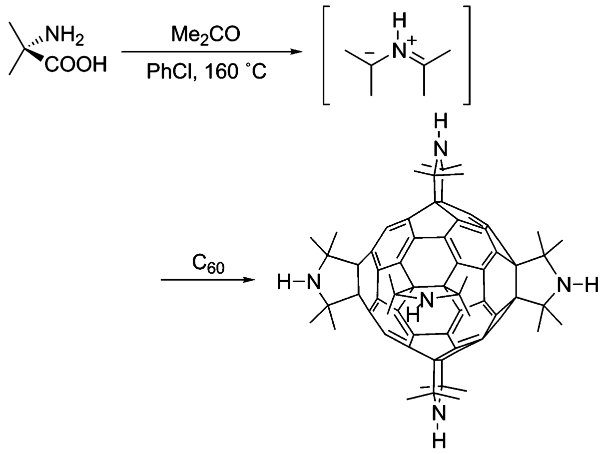


The photoreactions of [60]fullerene with aromatic tertiary amines such as *N,N*-dimethylaniline and *N,N*-dimethyl-1-naphthylamine gave two or three types of [60]fullerene adducts. The reaction efficiency in the series of *p*-substituted *N,N*-dimethylanilines remarkably increased with increasing electron-donating properties of aromatic tertiary amines employed.

Introduction

The fluorescence of [60]fullerene and its monoadducts is generally weak with quantum yields on the order of 10^{-4}.[1-4] However, it has recently been reported that a T_h-symmetrical hexapyrrolidine adduct (THP) displays a strong yellow-green fluorescence, which is atypical of [60]fullerene and its derivatives.[5] Furthermore, the combination of this THP adduct with poly(9-vinylcarbazole) (PVK) and 2,5-bis(4-naphthyl)-1,3,4-oxadiazole (BND) gave a single-layer, white light, organic light-emitting diode, which was the first example of electroluminescence from [60]fullerene derivatives.[6]

In general, [60]fullerene pyrrolidine adducts including THP have been prepared by the Prato reaction, the cycloaddition reaction with azomethine ylide generated from suitable aldehydes or ketones and substituted glycine (eq 1).[5,7] This reaction has been widely applied to the functionalization of fullerene.[8] Nonetheless, it is



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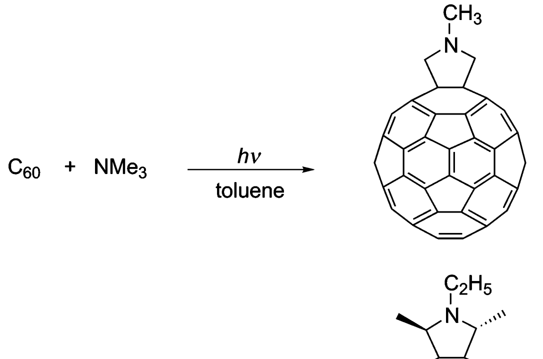

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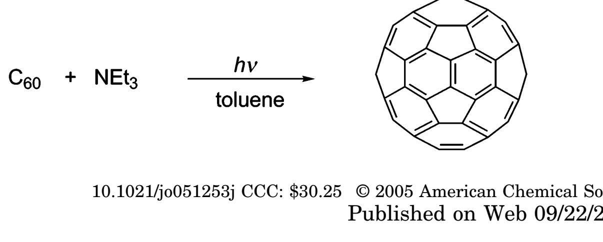

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[1] Ma, B.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2157.

[2] Luo, C.; Fujitsuka, M.; Watanabe, A.; Ito, O.; Gan, L.; Huang, Y.; Huang, C.-H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 527.

[3] Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.

[4] Lin, S.-K.; Shiu, L.-L.; Chien, K.-M.; Luh, T.-Y.; Lin, T.-I. *J. Phys. Chem.* **1995**, *99*, 105.

[5] Schick, G.; Levitus, M.; Kvetko, L.; Johnson, B. A.; Lamparth, I.; Lunkwitz, R.; Ma, B.; Khan, S. I.; Garcia-Garibay, M. A.; Rubin, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3246.

[6] Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *J. Am. Chem. Soc.* **1999**, *121*, 5611.

[7] Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

[8] Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519 and references therein.

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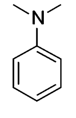
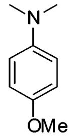
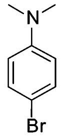
desirable to develop another new and simple methodology for the preparation of [60]fullerene pyrrolidine adducts under mild conditions. It is known that the photoinduced reactions of [60]fullerene with aliphatic tertiary amines such as trimethyl- and triethylamine give pyrrolidine adducts (eqs 2 and 3).[9,10] This reaction, however, has been hardly applied to the aromatic tertiary amines. Only the reaction using *N,N*-dimethylaniline (**1a**) was reported in the literature,[9] but it afforded no pyrrolidine adducts. Thus, we were prompted to examine the photoreactions of [60]fullerene with various aromatic tertiary amines (**1a**−**d**). Here, the results of these photoreactions under various conditions, the characterization of photoproducts obtained, and the proposed reaction mechanism are described in detail.

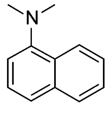

1a



1b



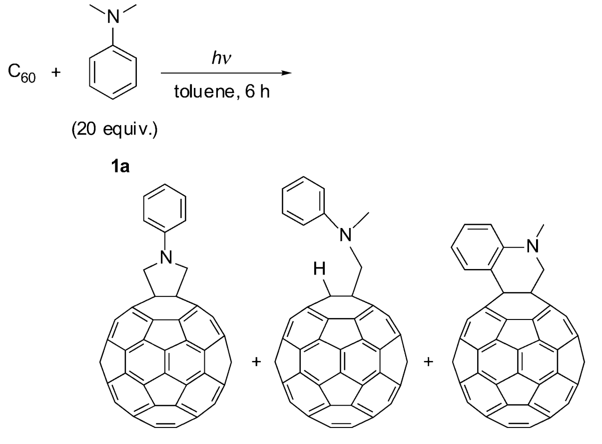
1c


1d

Results and Discussion

Photoreaction between [60]Fullerene and *N,N*-Dimethylaniline (1a). The photoreaction of [60]fullerene with *N,N*-dimethylaniline (**1a**) has already been investigated by Cheng and co-workers.[9] According to their report, this reaction gave only adduct **3a** in 25% yield, and the formation of [60]fullerene pyrrolidine adduct **2a** was not recognized.[9] Thus, this photoreaction was reexamined first. After bubbled with N_2 gas for an hour, a solution of [60]fullerene and **1a** (20 equiv) in toluene (8×10^{-4} M) was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter for 6 h (eq 4). The purification of reaction product by column chromatography on silica gel gave a mixture of three products **2a**, **3a**, and **4a** along with a recovery of [60]fullerene (84%). Each of **2a**−**4a** was successfully separated and isolated by gel permeation chromatography (GPC) and characterized by ^{1}H and ^{13}C NMR, APCI mass, and UV−vis spectroscopies. All of them were found to be [60]fullerene monoadducts as illustrated in eq 4. Their isolated yields were 2−7%, as listed in Table 1 (entry 1). Both **2a** and **4a** have been obtained for the first time in the present study. In our experiments, the irradiation time (6 h) is shorter and the amount of **1a** relative to [60]fullerene (20 equiv) is smaller than those (12 h, 50 equiv) in the report by Cheng et al.[9] Such differences in experimental conditions enabled the formation of **2a** and **4a**, although the total product yields decreased.

The APCI mass spectrum of **3a** afforded a molecular ion peak of $m/z = 841$, which corresponds to the sum of [60]fullerene and **1a**. In **2a** and **4a**, a molecular ion peak of $m/z = 839$ was observed, suggesting the loss of two hydrogen atoms. The UV−vis spectra of **2a**−**4a** in chloroform were almost the same as one another, showing a sharp peak around 430 nm and a broad band around 700 nm, which are characteristic of [60]fullerene monoadducts.[8,10]



(4)

TABLE 1. Results for Photoreactions of 1a with [60]Fullerene

		yield/%[a]			
entry	conditions[b]	**2a**	**3a**	**4a**	recovery of C_{60}/%
1	N_2 bubbling	2.0	5.0	6.7	84
2	without N_2 bubbling	3.0	5.1	7.8	73

[a] Experimental errors are within 2%. [b] Time, 6 h; **1a**/C_{60} = 20.

The ^{1}H NMR spectra of **2a**−**4a** gave decisive evidence for their identification. The spectrum of **2a** exhibits the simplest spectral pattern among the three; it gives only a singlet (δ 5.14) of methylene protons and three signals of phenyl protons, in agreement with the *N*-phenylpyrrolidine residue. In **3a**, three singlets due to methyl protons, methylene protons, and the proton attached to [60]fullerene are observed at δ 3.51, 5.34, and 6.49, respectively, along with the protons of phenyl group. In the spectrum of **4a**, the [60]fullerene-attached proton is absent, whereas the singlets of methyl and methylene protons are observed at δ 3.34 and 4.70, respectively. The upfield shift of methylene protons relative to those in **2a** and **3a** is quite remarkable. Probably, the deshielding effect onto the methylene protons from the benzene ring in **4a** is smaller than in **2a** and **3a**. Noticeably, the aromatic proton peaks in **4a** reveal a spectral pattern characteristic of ortho-disubstituted benzenes, in contrast with **2a** and **3a**; that is, one of the ortho-protons against the dimethylamino group on benzene ring is abstracted. These observations obviously indicate the novel tetrahydroquinoline-attached [60]fullerene structure, as shown in eq 4.

The photoreaction of [60]fullerene and **1a** was also examined without N_2 bubbling before irradiation. In this case, monoadducts **2a**−**4a** were again obtained, and their isolated yields are comparable to those for the photoreaction after N_2 bubbling, as shown in Table 1 (entry 2). These results suggest that the oxygen molecules dissolved in toluene hardly affect the progress of this photoreaction.

Photoreaction between [60]Fullerene and *N,N*-Dimethyl-*p*-anisidine (1b). *N,N*-Dimethyl-*p*-anisidine (**1b**) carrying an electron-donating methoxy group was next employed as an aromatic tertiary amine to clarify the effect of substituent groups on the photoreaction. The photoreaction of [60]fullerene and **1b** (20 equiv) was carried out after N_2 bubbling, under irradiation conditions similar to those for **1a** (eq 5). The 6-h irradiation,

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(9) Liou, K.-F.; Cheng, C.-H. *Chem. Commun.* **1996**, 1423.

(10) (a) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *Chem. Commun.* **1995**, 2225. (b) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. *J. Org. Chem.* **1999**, *64*, 5913.

followed by purification of the resulting products by column chromatography and GPC, gave monoadducts **3b** and **4b**, corresponding to **3a** and **4a**, respectively. In contrast, the formation of **2b**, corresponding to **2a**, bearing a pyrrolidine moiety was not detected. In addition to **3b** and **4b**, more polar products were also obtained, which are probably bis- and multiadducts resulting from the reaction of two or more molecules of **1b** with one [60]fullerene molecule. These products were not obtained in the photoreaction of **1a**. They were not subjected to further separation, since they were apparently composed of complex mixtures.

Both **3b** and **4b** were characterized by spectroscopic methods similar to **2a**−**4a**. The ^{1}H NMR spectral features of **3b** and **4b** are similar to those of **3a** and **4a**, respectively, except for the pattern of aromatic regions and the presence of methoxy protons. Obviously, the aromatic regions of **3b** and **4b** exhibit the spectral patterns of para-disubstituted and 1,2,4-trisubstituted benzenes, respectively, demonstrating the structures depicted in eq 5. The methoxy proton peaks are detected at δ 3.8 for both **3b** and **4b**.

The isolated yields of **3b** and **4b** are shown in Table 2 (entry 1). The total yields are higher than those of **2a**−**4a** (Table 1, entry 1), and the recovery of unreacted [60]fullerene is much reduced. As described above, bis- and multiadducts were also obtained in the reaction of **1b**, though their yields could not be determined. These results apparently indicate that an electron-donating methoxy group in **1b** enhances the reaction conversion or efficiency. The reason for the absence of **2b** is obscure at the present stage.

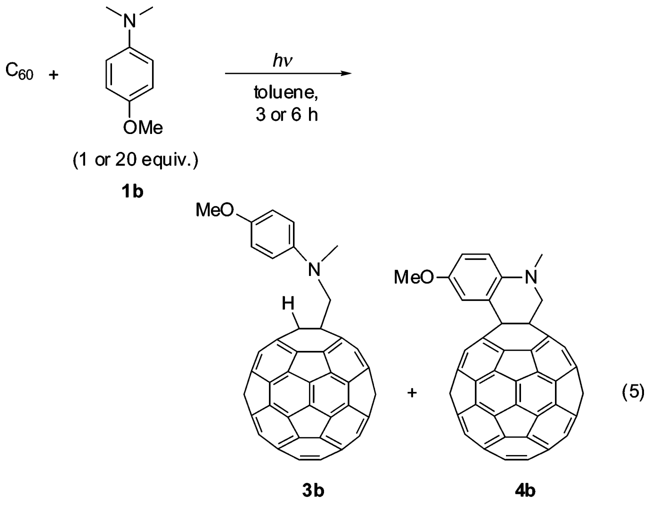

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TABLE 2. Results for Photoreactions of 1b with [60]Fullerene

	conditions			yield/%^{a}		recovery
entry	bubbling	time/h	**1b**/C_{60}	**3b**	**4b**	of C_{60}/%
1	N_2 bubbling	6	20	9.1	11.2	45
2	N_2 bubbling	3	1	0	6.4	86
3	without N_2 bubbling	6	20	1.4	4.3	67

^{a} Experimental errors are within 2%.

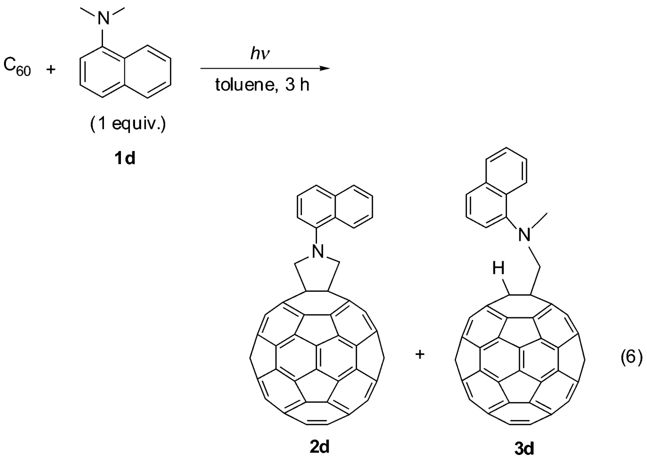
The photoreaction of [60]fullerene with an equimolar amount of **1b** was also performed in a shorter period (3 h) (Table 2, entry 2). These conditions yielded only monoadduct **4b** without the formation of **3b** and bis- or multiadducts, which were obtained under the above conditions using excess of **1b** (Table 2, entry 1 vs entry 2). The yield of **4b** decreased, while the recovery of [60]fullerene much increased. The reaction conversion is significantly lowered by the reduced amount of **1b** and irradiation time.

The photoreaction of [60]fullerene and **1b** (20 equiv) for 6 h was also examined without N_2 bubbling before irradiation. Intriguingly, the yields of both **3b** and **4b** much decreased, while the recovery of [60]fullerene increased, as shown in Table 2 (entry 1 vs entry 3). The oxygen molecules dissolved in toluene highly disturb the progress of this photoreaction, in contrast with the reaction of **1a**.

Photoreaction between [60]Fullerene and *N,N*-Dimethyl-*p*-bromoaniline (1c). The photoreaction using *N,N*-dimethyl-*p*-bromoaniline (**1c**) carrying an electron-withdrawing bromine group was also examined.

After N_2 bubbling, a toluene solution of [60]fullerene and of **1c** (1 or 20 equiv) was irradiated for 3 or 6 h. With the irradiation, the color of solution slightly changed from purple to brownish, suggesting the reaction toward [60]fullerene leading to the formation of some addition products. However, the purification of reaction mixture by column chromatography gave unreacted [60]fullerene (~90%) and **1c** without desired monoadducts such as **2**−**4**. A small amount of rather polar, unidentified products were only obtained. These results apparently reveal that an electron-withdrawing bromine group lowers the reaction conversion or efficiency, contrary to an electron-donating methoxy group.

Photoreaction between [60]Fullerene and *N,N*-Dimethy-1-naphthylamine (1d). Finally, the photoreaction using *N,N*-dimethyl-1-naphthylamine (**1d**) bearing a naphthalene ring instead of benzene ring was investigated.



(6)

The photoreaction between [60]fullerene and **1d** (1 equiv) was carried out for 3 h after N_2 bubbling (eq 6), under irradiation conditions similar to those of Table 2, entry 2. Monoadduct **3d** having a structure analogous to **3a** and **3b** was obtained in 22% yield along with **2d** (~1%) analogous to **2a** and **2b** (Table 3, entry 1). The tetrahydroquinoline-attached adduct similar to **4a** and **4b** was not recognized. A complex mixture of bis- and multiadducts was also obtained. Both **2d** and **3d** were

TABLE 3. Results for Photoreactions of 1d with [60]Fullerene

		yield/%^{a}		
entry	conditions^b	**2d**	**3d**	recovery of C_{60}/%
1	N_2 bubbling	1.0	22.0	30
2	without N_2 bubbling	~1	~1	80

^{a} Experimental errors are within 2%. ^{b} Time, 3 h; **1d**/C_{60} = 1.

identified by spectroscopic methods similar to **2a**−**4a**, **3b**, and **4b**. The ^{1}H NMR spectra of **2d** and **3d** exhibited spectral features similar to those of **2a** and **3a**, respectively. Monoadduct **2d** gives a singlet of methylene protons at δ 3.99, and **3d** exhibits the proton attached to [60]fullerene at δ 7.01.

Compared to the reaction of **1b** (Table 2, entry 2), the total yield of monoadducts is much enhanced and the recovery of unreacted [60]fullerene is much reduced, though the types of main products obtained are different between the two cases (**4b** vs **3d**).

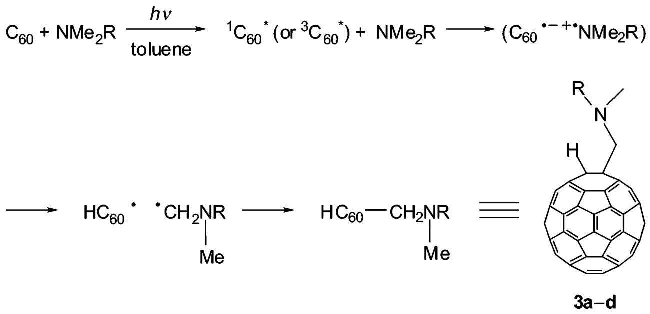
In the photoreaction using a large excess of **1d** (20 equiv) for 6 h, only a complex mixture of bis- and multiadducts was obtained along with a small amount of unreacted [60]fullerene and neither **2d** nor **3d** was obtained.

The photoreaction of [60]fullerene and **1d** (1 equiv) for 3 h was also examined without N_2 bubbling before irradiation. Noticeably, **2d** and **3d** were hardly obtained, and a large amount of [60]fullerene (~80%) was recovered (Table 3, entry 2). The oxygen molecules dissolved in toluene highly disturb the progress of this photoreaction, similar to the reaction of **1b** but in contrast with that of **1a**.

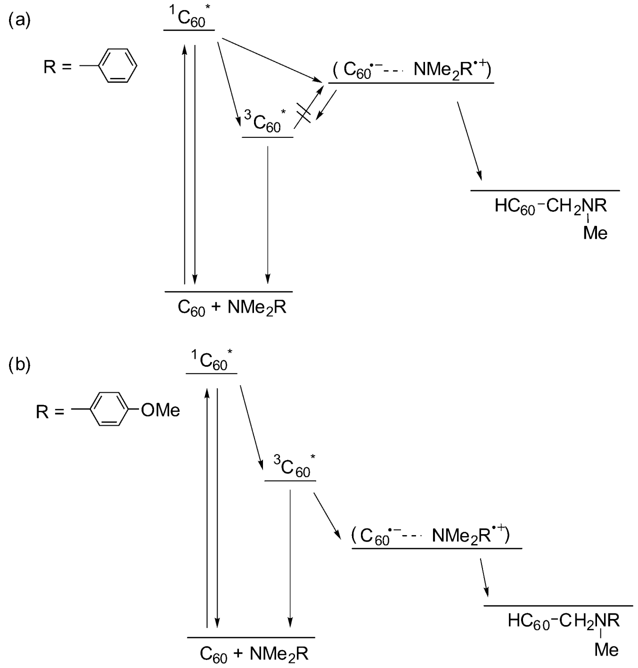
From the examination on the photoreactions of [60]fullerene with four aromatic tertiary amines **1a**−**d**, it is concluded that the order of reactivity is as follows: *N,N*-dimethyl-*p*-bromoaniline (**1c**) < *N,N*-dimethylaniline (**1a**) < *N,N*-dimethyl-*p*-anisidine (**1b**) < *N,N*-dimethyl-1-naphthylamine (**1d**). The electron-donating groups on the benzene ring enhance the reactivity with [60]fullerene, while the electron-withdrawing groups reduce it. The introduction of a naphthalene ring instead of benzene ring also increases the reactivity. In the photoreactions using **1b** and **1d**, however, the yields of products are significantly lowered by the oxygen molecules dissolved in solution.

Mechanistic Consideration of These Photoreactions. For the photoreactions between [60]fullerene and tertiary amines, the previous reports suggest that, upon the excitation of [60]fullerene, the photoinduced electron transfer from an amine to [60]fullerene takes place to give a radical ion pair (Scheme 1).[9,10] This is followed by deprotonation of the amine cation radical by [60]fullerene anion radical to yield an α-aminoalkyl and HC_{60} radical pair. The subsequent combination of radical pair leads to the product such as **3a**−**d**. Thus, the high conversion of photoinduced electron transfer from an amine to [60]fullerene at the initial stage is critical for this photoreaction.

SCHEME 1. Proposed Mechanism of Photoreaction between [60]Fullerene and Tertiary Amines



SCHEME 2. Proposed Energy Diagrams of Photoreaction of C_{60} with (a) *N,N*-Dimethylaniline (1a) and (b) *N,N*-Dimethyl-*p*-anisidine (1b) in Toluene



In the photoreaction of **1a** (eq 4), the product yields are generally low, and the product yield and distribution are almost independent of the presence or absence of oxygen dissolved in toluene. These results can be reasonably explained based on the energy diagram for the photoinduced electron transfer in toluene, which is schematically illustrated in Scheme 2a.[11] Since the electron transfer from **1a** to $^3C_{60}$* is endothermic (ΔG_{et} = ~+0.2 eV) in toluene,[11] this process is virtually excluded. The electron transfer from **1a** to $^1C_{60}$* is less endothermic, and the free energy change (ΔG_{et}) is slightly negative, since the energy difference between $^1C_{60}$* and $^3C_{60}$* is ca. 0.4 eV.[4,16] Hence, the obtained reaction products are almost exclusively derived from the electron

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(11) Sandanayaka, A. S. D.; Araki, Y.; Lou, C.; Fujitsuka, M.; Ito, O. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1313.

(12) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, J. P.; Smith, A. B., III; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075.

(13) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501.

(14) Lee, M.; Song, O.-K.; Seo, J.-C.; Kim, D.; Suh, Y. D.; Jin, S. M.; Kim, S. K. *Chem. Phys. Lett.* **1992**, *196*, 325.

(15) Watanabe, A.; Ito, O.; Watanabe, M.; Saito, H.; Koishi, M. *Chem. Commun.* **1996**, 117.

(16) Arbogast, J. W.; Daymanyan, A. O.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

transfer via $^1C_{60}^*$. The lifetime of $^1C_{60}^*$ is extremely short (~1 ns) due to the fast intersystem crossing (~8×10^8 s^{-1}).[12–15] Such short lifetime of $^1C_{60}^*$ must result in the low possibility of electron transfer despite using excess of **1a** (20 equiv). In addition, the radical ion pair produced via $^1C_{60}^*$ seems to be also short-lived due to the rapid back electron transfer. These facts can reasonably elucidate the low product yields in the photoreaction of **1a**. However, $^1C_{60}^*$ is hardly quenched by oxygen molecules in solution due to the short lifetime, leading to the almost comparable product yields in the presence and absence of dissolved oxygen molecules.

In the photoreaction of **1b**, the reaction conversion was much enhanced relative to that for **1a**, although it was considerably reduced by dissolved oxygen. According to the energy diagram for the photoinduced electron-transfer involving **1b** (Scheme 2b),[11] the electron transfer from **1b** to $^3C_{60}^*$ as well as $^1C_{60}^*$ is exothermic, because the oxidation potential of **1b** is lower than that of **1a** by ca. 0.4 V due to the methoxy group.[19] Hence, the electron transfer via $^3C_{60}^*$, which was impossible in the photoreaction of **1a**, becomes energetically possible. The $^3C_{60}^*$, which is known to have a relatively long lifetime (~50–100 μs),[12,13,16–18] probably gives radical ion pairs in a higher yield via the electron transfer, leading to much higher reaction conversion. The $^3C_{60}^*$ is significantly quenched by oxygen molecules, in contrast to $^1C_{60}^*$. This quenching is responsible for the decreased product yields in the reaction without N_2 bubbling.

On the other hand, in the photoreaction of **1c**, almost no addition products were obtained. The oxidation potential of **1c** is apparently high relative to **1a**, due to an electron-withdrawing bromine group, making the electron-transfer process via $^1C_{60}^*$ more endothermic. For this reason, almost no products were formed from **1c**.

The higher efficiency in the photoreaction of **1d** than that of **1a** is also ascribable to the lower oxidation potential of **1d** than **1a** ($\Delta E = 0.13$ V),[20] which obviously makes the electron-transfer process via $^3C_{60}^*$ favorable relative to **1a**. In this case, $^3C_{60}^*$ can be efficiently quenched by oxygen molecules, resulting in the decreased product yields in the presence of dissolved oxygen. However, despite the lower oxidation potential of **1b** than **1d**, the photoreaction of **1d** proceeds with higher efficiency than that of **1b**. This may be partly ascribed to the charge-transfer complex formation in the ground state of **1d**/C_{60}. In the UV–vis spectra, no appreciable charge-transfer (CT) band was recognized in **1b**/C_{60}, while **1d**/C_{60} afforded a new weak band around 700–800 nm, which is assignable to CT band, under the conditions similar to those for the photoreactions ($[C_{60}] = 8 \times 10^{-4}$ M; **1**/C_{60} = 1–20).

Thus, the observed dependence of the reaction conversion (product yields) on the electron-donating properties (oxidation potentials) of employed aromatic tertiary amines **1a**–**d** can be roughly explained by considering the excited state of [60]fullerene involved in the electron-transfer process. In **1b** and **1d**, the electron-transfer process via $^3C_{60}^*$ as well as $^1C_{60}^*$ is energetically possible, while only the electron transfer via $^1C_{60}^*$ is possible in **1a**. For **1c**, both electron transfer processes are unlikely to proceed.

As illustrated in Scheme 1, monoadduct **3** is first produced following the electron transfer from a tertiary amine to [60]fullerene. In the literature, it is proposed that pyrrolidine adduct **2** is formed via **3**: the photoinduced electron transfer from **3** to [60]fullerene, followed by successive intermolecular proton transfer, hydrogen abstraction, and ring closure, gives **2** and $C_{60}H_2$.[9,10] Thus, to verify this reaction mechanism for the formation of **2** and to disclose the mechanism for formation of **4**, the photoreaction of **3a** isolated was investigated. A toluene solution of **3a** was irradiated for 1.5 h, after N_2 bubbling. In the ^1H NMR spectrum of resulting products, the peaks assigned to **2a** appeared with a decrease in peaks of **3a**,[21] while no peaks of **4a** were detected at all. These observations apparently indicate that **2a** is produced via **3a**. However, the mechanism for the formation of **4** remains unknown. The absence of **2b** is associated with the higher electron-donating property of the anisidine moiety in **3b**. As described below, **3b** allows the efficient *intramolecular* electron transfer even in a nonpolar solvent, so that it hampers the *intermolecular* electron transfer, which are necessary for the formation of **2b**.

Fluorescence Spectra of Obtained Adducts. The fluorescence spectra of obtained [60]fullerene adducts were measured in several solvents at room temperature. In cyclohexane or benzene upon 430-nm excitation, which can exclusively excite the C_{60} moiety, **2a**–**4a**, **2d**, and **3d** exhibited a relatively weak and broad fluorescence with a maximum around 700 nm. These spectral features are characteristic of [60]fullerene monoadducts.[2–4,22,23] The fluorescence of these adducts was significantly quenched in polar benzonitrile (ca. 1/10). This behavior probably suggests the intramolecular electron transfer from the tertiary amine to fullerene moiety, as also demonstrated in similar [60]fullerene adducts.[10b,23] Intriguingly, **3b** and **4b** bearing an anisidine residue exhibited almost no fluorescence even in benzene. It seems that the intramolecular electron-transfer becomes possible in such a nonpolar solvent for **3b** and **4b** due to the higher electron-donating ability of anisidine moiety. More detailed photophysical properties are now in investigation.

The fluorescence spectra of **2d** and **3d** bearing a naphthalene ring were also measured upon 280-nm excitation, which can excite the naphthalene moiety as well as C_{60} moiety. Under the conditions, no fluorescence derived from naphthalene was observed. This is probably ascribed to the fast intramolecular energy transfer from naphthalene to C_{60} moiety, as reported for similar [60]fullerene adducts in the literature.[22]

Summary

The photoreactions of *N,N*-dimethylaniline (**1a**), *N,N*-dimethyl-*p*-anisidine (**1b**), and *N,N*-dimethyl-1-naphthyl-

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(17) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886.

(18) Tanigaki, K.; Ebbesen, T. W.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *185*, 189.

(19) Goto, Y.; Watanabe, Y.; Fukuzumi, S.; Jones, J. P.; Dinnocenzo, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 10762.

(20) Lee, Y.; Kitagawa, T.; Komatsu, K. *J. Org. Chem.* **2004**, *69*, 263.

(21) We have tried to detect the formation of $C_{60}H_2$ several times, but somehow all the attempts failed.

(22) Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351.

(23) Nakamura, Y.; Minowa, T.; Hayashida, Y.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 377.

amine (**1d**) with [60]fullerene gave two or three types of [60]fullerene adducts, whereas *N,N*-dimethyl-*p*-bromoaniline (**1c**) afforded no isolable adducts. The reaction efficiency remarkably increased with increasing electron-donating properties of the aromatic amines employed, though the photoreactions using **1b** and **1d** were significantly disturbed by the oxygen molecules dissolved in solution. These observations can be reasonably explained based on the excited state of [60]fullerene involved in the photoreactions; only the electron transfer via $^1C_{60}$* is involved in **1a**, while the electron transfer via $^3C_{60}$* is also involved in **1b** and **1d**.

Experimental Section

Spectroscopic data of **2a**−**4a**, **3b**, **4b**, **2d**, and **3d** are as follows.

2a: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (t, J = 8.0 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 7.7 Hz, 1H), 5.14 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.2, 147.7, 146.1, 145.9, 145.7, 145.5, 145.4, 144.4, 142.5, 142.1, 141.9, 141.8, 140.1, 136.0, 129.5, 128.9, 128.1, 125.2, 120.5, 116.4, 69.6, 62.9; APCI-MS: *m/z* 839 (M^-).

3a:[9] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.49 (s, 1H), 5.34 (s, 2H), 3.51 (s, 3H). APCI-MS: *m/ z* 841 (M^-).

4a: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.39 (d, J = 6.8 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 7.06 (t, J = 7.7 Hz, 1H), 4.70 (s, 2H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.6, 153.8, 151.4, 150.3, 147.6, 147.5, 146.32, 146.26, 146.1, 146.0, 145.8, 145.3, 145.24, 145.15, 144.6, 143.0, 142.5, 142.4, 142.2, 142.1, 141.9, 141.8, 141.6, 141.5, 141.4, 140.2, 139.5, 138.2, 136.7, 134.3, 128.8, 128.2, 126.8, 126.6, 115.6, 111.1, 56.9, 54.6, 40.0; APCI-MS: *m/z* 839 (M^-).

3b: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.21 (d, J = 9.2 Hz, 2H), 6.96 (d, J = 9.2 Hz, 2H), 6.55 (s, 1H), 5.27 (s, 2H), 3.82 (s, 3H), 3.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.8, 153.9, 152.5, 147.33, 147.29, 147.11, 147.08, 146.38, 146.35, 146.2, 146.1, 145.8, 145.5, 145.41, 145.35, 144.61, 144.56, 144.5, 143.2, 142.60, 142.57, 142.2, 142.1, 142.0, 141.8, 141.73, 141.65, 140.3, 140.1, 136.3, 135.6, 115.2, 114.9, 68.8, 68.1, 58.2, 55.8, 42.1; APCI-MS: *m/z* 871 (M^-).

4b: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (s, 1H), 7.18 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 6.1 Hz, 1H), 4.68 (s, 2H), 3.85 (s, 3H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.7, 147.8, 147.7, 146.49, 146.46, 146.23, 146.20, 146.0, 145.8, 145.53, 145.45, 145.42, 145.35, 144.8, 144.7, 143.2, 142.7, 142.3, 142.2, 142.1, 142.0, 141.7, 141.6, 140.4, 137.7, 116.0, 114.2, 112.9, 68.4, 67.0, 64.5, 55.7, 40.7; APCI-MS: *m/z* 869 (M^-).

2d: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.76 (d, J = 8.5 Hz, 1H), 8.53 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.74−7.63 (m, 3H), 3.99 (s, 4H); APCI-MS: *m/z* 889 (M^-).

3d: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.91 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.0 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.61−7.57 (m, 2H), 7.01 (s, 1H), 5.28 (s, 2H), 3.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.0, 154.4, 151.5, 147.4, 147.3, 147.2, 146.5, 146.4, 146.3, 146.2, 146.1, 145.8, 145.42, 145.39, 145.37, 145.3, 144.7, 144.5, 144.2, 142.6, 142.3, 142.1, 142.0, 141.8, 141.61, 141.60, 140.2, 140.1, 136.3, 136,2, 135.0, 130.6, 128.6, 126.4, 126.3, 126.0, 125.3, 124.1, 119.5, 70.5, 68.0, 58.3, 48.1; APCI-MS: *m/z* 891 (M^-).

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Supporting Information Available: The general experimental procedure and ^{1}H NMR and UV−vis spectra of **2a-4a**, **3b**, **4b**, **2d**, and **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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