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# Intramolecular Charge-Transfer Interaction in a New Dyad Based on $C_{60}$ and Bis(4′-*tert*-butylbiphenyl-4-yl)aniline (BBA) Donor

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A novel dyad **2** based on $C_{60}$ and bis(4′-*tert*-butylbiphenyl-4-yl)aniline (BBA) donor has been synthesized and characterized. Cyclic voltammetry (CV) and UV−vis spectra of **2**, 61-phenyl-1, 2-methanofullerene[60] **4**, 1,2-methanofullerene[60] **5**, and BBA were measured and analyzed. CV measurements showed that a reversible oxidation wave of **2** was positively shifted by 40 mV compared to that of BBA. More remarkably, comparing UV−vis spectra of **2** and **5** shows the big hyperchromic effect of **2** on a broad band at 500 nm despite lacking of more than 400 nm of absorbance for BBA. These results indicate obvious evidence of intramolecular charge-transfer interactions between $C_{60}$-moiety and BBA.

## Introduction

Buckminsterfullerene $C_{60}$ and its derivatives exhibit a number of distinctive electronic and photophysical properties and have been investigated for the application as novel molecular electronic devices.[1,2] In one of the most attractive strategies, various electron donors have been covalently linked to the $C_{60}$ cage by different synthetic procedures to attain efficient intramolecular energy and electron transfer and to generate long-lived charge-separated states in these $C_{60}$−donor dyads with the intention of developing artificial photosynthetic systems.[1,3] $C_{60}$ is expected to be a potential electron acceptor in artificial photosynthesis because of symmetrical shape, large size, and properties of its $\pi$-electron system.[4]

On the other hand triarylamines are one of strong electron donor moieties and an important class of compounds because they form stable aminium radical cations and can be building blocks for high-spin polyradical and conducting polymers as well as the hole-transport layer in electroluminescent devices.[5] In recent years, Shirota et al. reported that tris(oligophenylenyl)amine derivatives as well as a novel class of starburst molecules consisting of a fully conjugated $\pi$-electron system like 4,4′,4″-tris(diphenylamino)triphenylamine have become a new type of low-molecular weight materials that can form stable amorphous glasses, which are attractive for their excellent processability, flexibility, transparency, absence of grain boundaries, and isotropic properties.[6]

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(1) For a recent review on $C_{60}$-based electroactive organofullerenes, see, (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−526. (c) Diekers, M.; Hirsch, A.; Pyo, S.; Rivera, J.; Echegoyen, L. *Eur. J. Org. Chem.* **1998**, 1111−1121. (d) Paddon-Row: M. N. *Fullerene Sci. Technol.* **1999**, *7*, 1151−1173. (e) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695−703. (f) *Carbon*, **2000**, *38*, Fullerenes '99 guest edited by Bernier, P.; Hirsch A. (g) Konarev, D. V.; Lyubovskaya, R. N.; Drichko, N. V.; Yudanova, E. I.; Shul′ga, Y. M.; Litvinov, A. L.; Semkin, V. N.; Tarasov, B. P. *J. Mater. Chem.* **2000**, *10*, 803−818.

(2) (a) Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617−618. (b) Imahori, H.; Azuma, T.; Ozawa, S.; Yamada, H.; Ushida, K.; Ajavakom, A.; Norieda, H.; Sakata, Y. *Chem. Commun.* **1999**, 557−558. (c) Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611−5612. (d) Mattoussi, H.; Rubner, M. F.; Zhou, F.; Kumar, J.; Tripathy, S. K.; Chiang, L. Y.; *Appl. Phys. Lett.*, **2000**, *77*, 1540−1542. (e) Roman, L. S.; Inganas, O.; Granlund, T.; Nyberg, T.; Svensson, M.; Andersson, M. R.; Hummelen, J. C. *Adv. Mater.* **2000**, *12*, 189−195.

(3) (a) Liu, S.-G.; Shu, L.; Rievera, J.; Liu, H.; Raimundo, J.-M.; Roncali, J.; Gorgues, A.; Echegoyen, L. *J. Org. Chem.* **1999**, *64*, 4884−4886 and literature cited therein. (b) Guldi, D. M. *Chem. Commun.* **2000**, 321−327. (c) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445−2457. (d) Jolliffe, K. A.; Langford, S. J.; Ranasinghe, M. G.; Shephard, M. J.; Paddon-Row: M. N. *J. Org. Chem.* **1999**, *64*, 1238−126. (d) Yamada, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *Chem. Lett.* **1999**, 895−896. (e) Martín, N.; Sánchez, L.; Guldi, D. M. *Chem. Commun.* **2000**, 113−114. (f) Guldi, D. M.; Luo, C.; Prato, M.; Dietel, E.; Hirsch, A. *Chem. Commun.* **2000**, 373−374. (g) Guldi, D. M.; Luo, C.; Ros, T. D.; Prato, M.; Dietel, E.; Hirsch, A. *Chem. Commun.* **2000**, 375−376. (h) Guldi, D. M.; Gonzalez, S.; Martín, N.; Antón, A.; Garín, J.; Orduna, J. *J. Org. Chem.* **2000**, *65*, 1978−1983.

(4) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row: M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055−5062.

(5) (a) Wienk, M. M.; Janssen, R. A. *Chem. Commun.* **1996**, 267−268. (b) Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448−449. (c) Ishikawa, M.; Kawai, M.; Ohsawa, Y. *Synth. Met.* **1995**, *40*, 231−238.

(6) (a) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145−1148. (b) Higuchi, A.; Inada, H.; Nakano, H.; Shirota, Y. *Adv. Mater.* **1991**, *3*, 549−540. (c) Ishikawa, W.; Inada, H.; Nakano, H.; Shirota, Y. *Chem. Lett.* **1991**, 1731−1734. (d) Ishikawa, W.; Inada, H.; Nakano, H.; Shirota, Y. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 431−438. (e) Inada, H.; Shirota, Y. *J. Mater. Chem.* **1993**, *3*, 319−320. (f) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677−679. (g) Ueta, E.; Nakano, H.; Shirota, Y. *Chem. Lett.* **1994**, 2397−2400. (h) Higuchi, A.; Shirota, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *242*, 395−401. (i) Kageyama, H.; Itano, K.; Ishikawa, W.; Shirota, Y. *J. Mater. Chem.* **1996**, *6*, 675−676. (j) Shirota, Y.; Kuwabara, Y.; Okuda, D.; Okuda, R.; Ogawa, H.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y. *J. Lumin.* **1997**, *72−74*, 985−991. (k) Higuchi, A.; Ohnishi, K.; Nomura, S.; Inada, H.; Shirota, Y. *J. Mater. Chem.* **1992**,*2*, 1109−1110. (l) Inada, H.; Ohnishi, K.; Nomura, S.; Higuchi, A.; Nakano, H.; Shiorta, Y. *J. Mater. Chem.* **1994**, *4*, 171−177. (m) Inada, H.; Yonemoto, Y.; Wakimoto, T.; Imai, K.; Shirota, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A.* **1996**, *280*, 331−336. (n) Shirota, Y.; Kuwabara, H.; Inada, H.; Wakimoto, T.; Nakada, Y.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807−809. (o) Yoshiiwa, M.; Kageyama, H.; Shirota, Y.; Wakaya, F.; Gamo, K.; Takai, M. *Appl. Phys. Lett.* **1996**, *69*, 2605−2607. (p) Nomura, S.; Nishimura, K.; Shirota, Y. *Thin Solid Films* **1996**, *273*, 27−34. (q) Kageyama, H.; Ohnishi, K.; Nomura, S.; Shirota, Y. *Chem. Phys. Lett.* **1997**, *277*, 137−141. (r) Katsuma, K.; Shirota, Y. *Adv. Mater.* **1998**, *10*, 223−226. (s) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714−9715. (t) Shirota, Y.; Moriwaki, K.; Yoshikawa, S.; Ujiike, T.; Nakano, H., *J. Mater. Chem.* **1998**, *8*, 2579−2581. (u) Noda, T., Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283−285.

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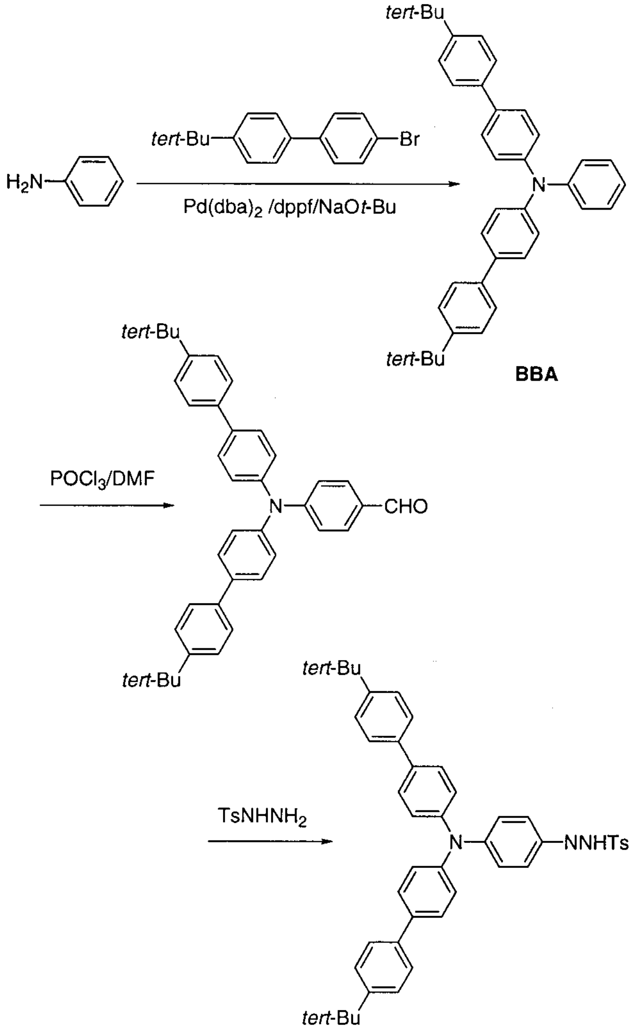
On this basis, we report herein the synthesis and properties of a methanofullerene having a triarylamine consisting of a fully conjugated $\pi$-electron system as a donor moiety in the $C_{60}$−donor dyad. Furthermore, obvious evidence of intramolecular charge-transfer interactions are shown for the first time, though it was very difficult to estimate the degree of charge-transfer interactions between the $C_{60}$ moiety and donor in the ground state because it was, in general, very small in the $C_{60}$−donor dyads.[1a, 7]

## Results and Discussion

Among various types of functionalization of $C_{60}$,[8] 1,3-dipole addition of diazo compounds to $C_{60}$ plays a important role.[9] We have selected the synthetic approach for the target molecule **2**. The tosylhydrazone **1** was prepared as illustrated in Scheme 1.

**Scheme 1**



The treating of $C_{60}$, **1** (1.4 equiv), and $NaOCH_3$ (1.6 equiv) in *o*-dichlorobenzene (ODCB) gave a monoadduct **2** and bis-adduct **3** after flash chromatography as illustrated in Scheme 2. Yields of **2** and **3** depended on the reaction temperature (Table 1). Yield of **2** was highest (48% yield (87%: based on consumed $C_{60}$)) when the reaction was carried at 50 °C for 10 h (run 2). Notably, addition of **1** to $C_{60}$ gave, of the three possible [5, 6]- and [6, 6]-isomers, essentially only [6,6]-isomer even at 40 °C. It is likely that [6,6]-methanofullerene is thermodynamically more stable than [5,6]-fulleroid because of the electron-donating properties of the *p*-diarylamine substituent.

The solubility of **2** was much better than that of $C_{60}$ in toluene, ODCB, $CH_2Cl_2$, and $CHCl_3$ as expected. The structure of a compound **2** (Figure 1) was supported by analytical and spectroscopic data. FDMS spectra exhibited a parent ion + 1 peak at *m*/*e* 1242 (100%). $^1H$ NMR spectrum of **2** in $CDCl_3$ solution shows that the signal of methine proton of cyclopropane ring appears at 5.35 ppm. It agreed closely with the data of 61-(4-isopropoxyphenyl)-1,2-methanofullerene (5.33 ppm).[11] The assignment of **2** to the methanofullerene structure is strengthened by $^{13}C$ NMR as well as $^1H$ NMR. The signals of 43.12 and 75.74 ppm indicate the presence of cyclopropane ring on [6,6] junction showing a bridge and two bridge heads of signals, respectively.[10]

The redox behavior of the newly synthesized compounds has been investigated using cyclic voltammetry (CV). Figure 3 shows the cyclic voltammograms of bis(4′-*tert*-butylbiphenyl-4-yl)aniline (BBA), methanofullerenes **2**, **4**, **5** (Figure 2), and $C_{60}$ in ODCB with 0.05 M $(n\text{-}Bu)_4NPF_6$. 61-Phenyl-1,2-methanofullerene **4**[11] and 1, 2-methanofullerene **5**[12] were prepared according to literature. In this solvent, the first three reductions of **2** are found to be reversible one electron processes with an anodic to cathodic peak separation, $\Delta E$ of ca. 60 mV. These processes are located at $E_{1/2} = -1.20$, $-1.56$, and $-2.03$ V vs $F_c/F_c^+$ (ferrocene/ferrocenium couple), respectively, and are negatively shifted by 70 to 130 mV compared to the corresponding electroreductions of $C_{60}$ (Table 2). As Wudl reported that the CV data of diphenylmethanofullerenes with electron-donating groups and electron-withdrawing groups in the *p*,*p*′ positions of the phenyl groups are independent of the functional groups,[13] the difference among the CV data of methanofullerenes **2**, **4**, and **5** was very small. However, $E_1$ and $E_2$ of **2** might be negatively shifted by 10 to 20 mV compared to those of **4** and **5**. More salient is the observation of a reversible oxidation wave $E_{ox}$ of

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(7) (a) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093−4099. (b) Saricifti, N. S.; Wudl, F.; Heeger, A. J.; Maggini, M.; Scorrano, G.; Prato, M.; Bourassa, J.; Ford, P. C. *Chem. Phys. Lett.* **1995**, *247*, 510−514. (c) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandona, G.; Farniá, G. *Tetrahedron* **1996**, *52*, 5221−5234. (d) Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C.; *J. Org. Chem.* **1997**, *62*, 5690−5695.

(8) As some reviews, (a) Hirsch, A. *Synthesis* **1995**, 895−913. (b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−526. (c) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123-2165. (d) Hirsch, A.; Nuber, B. *Acc. Chem. Res.* **1999**, *32*, 795−804. (e) Diederich, F.; Kessinger, R. *Acc. Chem. Res.* **1999**, *32*, 537−545. (f) Kikan Kagaku Sosetsu, 43 (Furaren no Kagaku) **1999**, Nippon Kagakkai. (g) Taylor, R. *Synlett* **2000**, *6*, 776−793.

(9) Hummelen, J. C.; Knight, B.; LePeq, F.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 532−538 and literature cited therein.

(10) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl. E.; Scorrano, G. *J. Am. Chem. Soc.* **1993**, *115*, 8479−8480.

(11) (a) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157−161. (b) Prato, M.; Bianco, A., Maggini, M.; Scorrano, G.; Toniolo, C.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 5578−5580.

(12) (a) Suzuki, T.; Li, Q. C.; Khemani, K. C.; Wudl, F.*J. Am. Chem. Soc.* **1992**, *114*, 7301−7302. (b) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C *J. Am. Chem. Soc.* **1993**, *115*, 5829−5830. (c) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C *J. Am. Chem. Soc.* **1995**, *117*, 5492−5502.

(13) Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q. C.; Maggini, M.; Martín, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591−1594.

**Scheme 2**

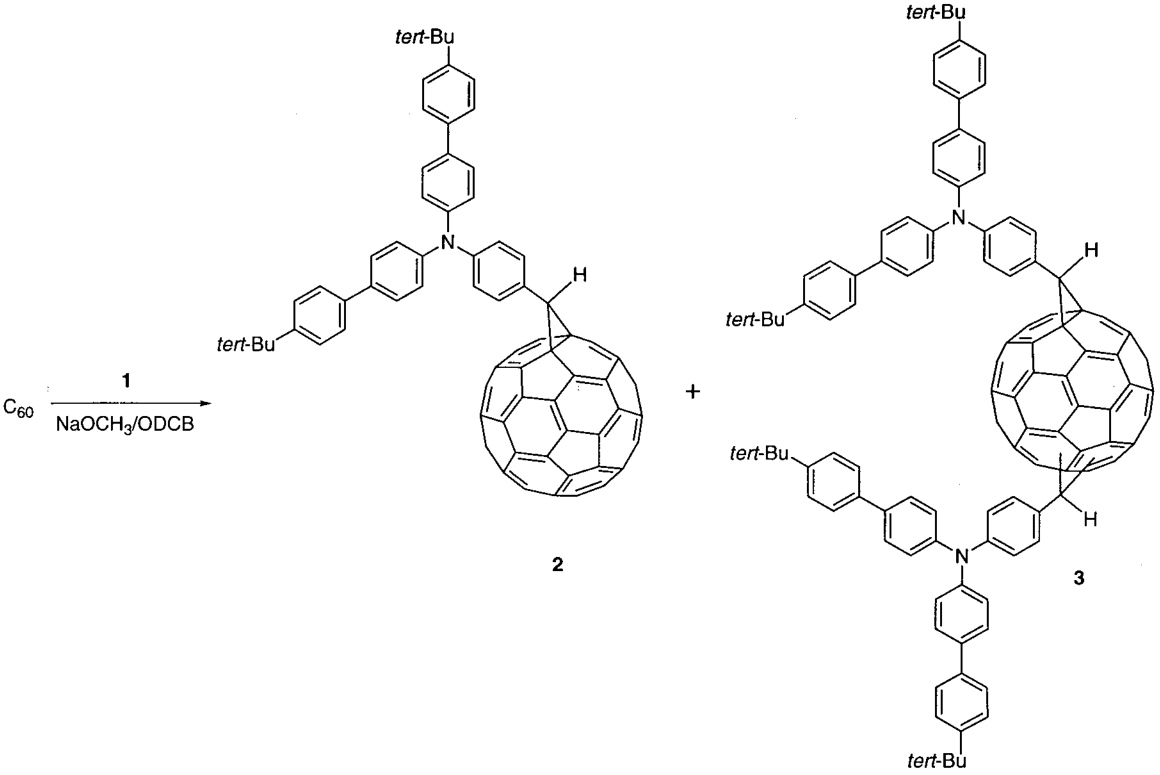

**Table 1. Conditions[a] and Yields of 2 and 3**

| run | temp (°C) | time (h) | conversion (%) | yield of **2** (%) | yield of **3** (%) |
|---|---|---|---|---|---|
| 1 | 40 | 26 | 50 | 17 (35)[b] | 7 |
| 2 | 50 | 10 | 64 | 48 (87)[b] | 15 |
| 3 | 90 | 3 | 84 | 46 (55)[b] | 25 |

[a] Tosylhydrazone **1**; 1.4 equiv to $C_{60}$, $NaOCH_3$; 1.6 equiv to $C_{60}$, ODCB. [b] Based on consumed $C_{60}$.

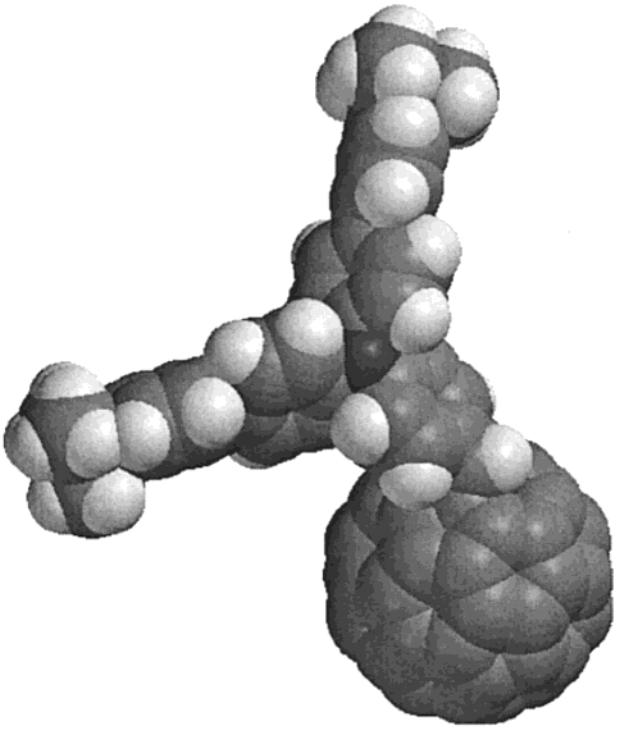

**Figure 1.** Most stable conformation of **2** on the basis of PM3 calculations.

**2** at 0.43 V vs $F_c/F_c^+$, it was positively shifted by 40 mV compared to that of BBA. These results clearly indicate the small electronic interactions between the $C_{60}$ and BBA addend in covalently linked $C_{60}$−BBA dyad **2**.

Though it was reported that various types of $C_{60}$-based dyad did not show intramolecular charge transfer in the ground state,[1a,7] weak broad bands between 450 and 520 nm were observed in some cases, and they have been ascribed to weak electronic interactions between donor and acceptor moieties.[14] However, unequivocal evidences of intramolecular charge-transfer interactions are still lacking. Therefore, the UV−vis spectra of $C_{60}$−BBA dyad **2**, 1,2-methanofullerene **5**, and BBA in toluene were measured (Figure 4). Methanofullerenes exhibited a sharp small band at 432 nm as characteristic of [6,6]-closed ring bridged methanofullerenes. Comparing UV−vis spectra of **2** and **5** shows the big hyperchromic effect of **2** on a broad band at 500 nm despite lacking of more than 400 nm of absorbance for BBA. Incidentally, the UV−vis spectra of a mixture of a large excess of BBA and **5** ([BBA]:[**5**] = 100:1) was measured to know the degree of intermolecular interaction between BBA and **5**. Though it showed very small hyperchromic effect in comparison with UV−vis spectra of **5**, it was too little to find the presence.[15,16] The UV−vis spectra for **2** in solvents more polar than toluene ($CH_2Cl_2$, benzonitrile) were measured, and it was confirmed that shapes of the broad band were changed depending on solvents (Figure

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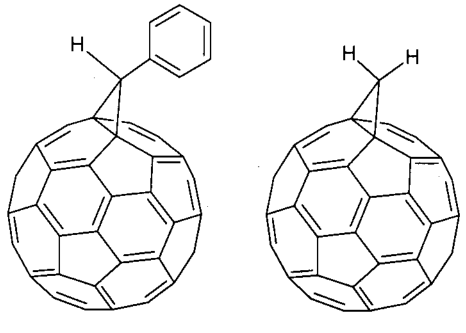
(14) (a) Matsubara, Y.; Tada, H.; Nagase, S.; Yoshida, Z. *J. Org. Chem.* **1995**, *60*, 5372−5373. (b) Guldi, D.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974−980. (c) Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351−2357. (d) Llacay, J.; Veciana, J.; V.-Gancedo, J.; Bourdelande, J. L.; G.-Moreno, R.; Rovira, C. *J. Org. Chem.* **1998**, *63*, 5201−5210.



**4** **5**

**Figure 2.** Methanofullerenes **4** and **5**.

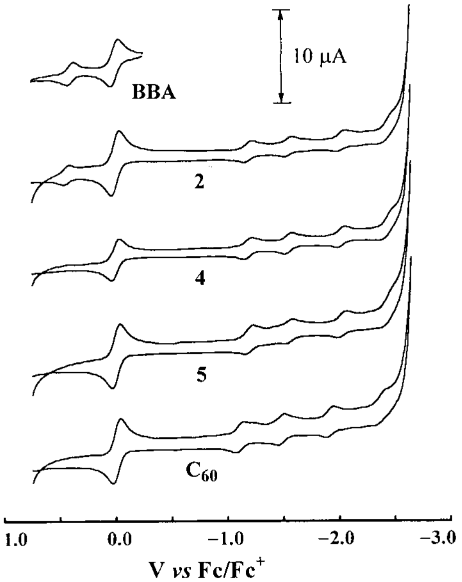


**Figure 3.** Cyclic voltammograms of BBA, methanofullerenes **4**, **5**, and $C_{60}$. V vs $F_c/F_c^+$ (ferrocene/ferrocenium couple). $(n\text{-Bu})_4NPF_6$ (0.05 M) in ODCB. Scan rate = 20 mV/s.

**Table 2. Half-Wave Potentials of BBA, Methanofullerenes 2, 4, 5, and $C_{60}$ by Cyclic Voltammetry**[a]

| compound | $E_{ox}$ | $E_1$ | $E_2$ | $E_3$ |
|---|---|---|---|---|
| BBA | 0.39 | | | |
| 2 | 0.43 | −1.20 | −1.56 | −2.03 |
| 4 | | −1.19 | −1.54 | −2.03 |
| 5 | | −1.19 | −1.56 | −2.03 |
| $C_{60}$ | | −1.11 | −1.49 | −1.90 |

[a] V vs $F_c/F_c^+$, $(n\text{-Bu})_4NPF_6$ (0.05 M) in ODCB, scan rate = 20 mV/s. The values were measured to three places of decimals. To make them accurate they are expressed in three significant figures.

5). These results indicate obvious evidence of intramolecular charge-transfer interactions between the $C_{60}$ moiety and BBA.

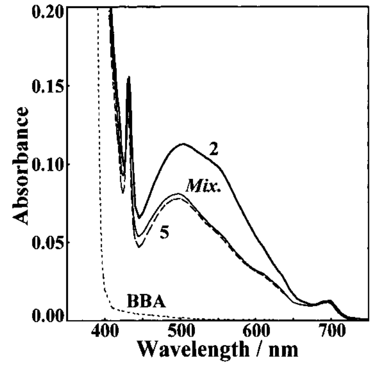


**Figure 4.** Electronic absorption spectra of BBA, **2** , **5**, and *Mix* (a mixture of BBA and **5** ([BBA]:[**5**] = 100:1)) in a toulene solution ([BBA] = [**2**] = [**5**] = 5 × $10^{-5}$ M).

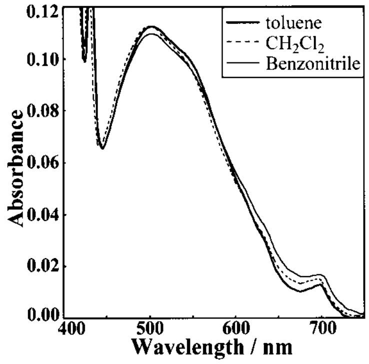


**Figure 5.** Electronic absorption spectra of **2** in some solvents ([**2**] = 5 × $10^{-5}$ M).

In conclusion, a novel new dyad based on $C_{60}$ and bis-(4′-*tert*-butylbiphenyl-4-yl)aniline (BBA) donor has been synthesized and characterized. Obvious evidence of intramolecular charge-transfer interactions between the $C_{60}$ moiety and BBA in the ground state was presented by CV and UV−vis measurements. Work is now underway to study the amorphous properties, photoinduced charge separation, and recombination in this novel $C_{60}$−BBA dyad molecule.

## Experimental Section

**General Details.** Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Dry THF and toluene were distilled from sodium−benzophenone ketyl. $Pd(DBA)_2$ (bis(dibenzylideneacetone)palladium (0)) was prepared according to literature procedure.[18] $C_{60}$ was purchased from MER corporation (Tucson, AZ). Tetra-*n*-butylammonium hexaflurophosphate $(n\text{-Bu})_4NPF_6$ was recrystallized three times from EtOH and dried in a vacuum oven at 100 °C overnight. Dry 1,2-dichlorobenzene (ODCB) was distilled from $CaH_2$. BBA was prepared according to the modified procedure of literature.[18] Aniline was distilled before use.

$^1H$ NMR and $^{13}C$ NMR spectra were recorded with a 300 MHz apparatus in $CDCl_3$. FD-Mass spectra were obtained on a JEOL JMS-DX303HF. Cyclic voltammetry measurements were performed at ambient temperature under an argon

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(15) Due to the various contributions of Sun et al. the charge-transfer properties of fullerene/donor mixtures are well established.[16] Especially, they reported about the CT band (540 nm) between $C_{60}$ and *N*,*N*-dimethylaniline (DMA) or *N*,*N*-diethylaniline (DEA).[16a] The observed molar absorptivities of the CT band increases from 940 $M^{-1}$ $cm^{-1}$ in neat toluene ([DMA]:[$C_{60}$] = 0:1) to 5300 $M^{-1}$ $cm^{-1}$ in neat DMA ([DMA]:[$C_{60}$] = 16000:1). That is, intermolecular interaction is present but small without the presence of an extreme excess of donor.

(16) (a) Sun, Y.-P.; Bunker, C. E.; Ma, B. *J. Am. Chem. Soc.* **1994**, *116*, 9692−9699. (b) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2225−2226. (c) Bunker, C. E.; Rollins, H. W.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1307−1309. (d) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. *J. Org. Chem.* **1999**, *64*, 5913−5920.

(17) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253−266.

(18) (a) As a review, Hartwig, J. F. *Synlett* **1997**, 329−340. (b) Louis, J.; Hartwig, F. *J. Am. Chem. Soc.* **1997**, *119*, 11695−11696. (c) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694−3703. (d) Marcoux, J.-F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1568−1569.

atmosphere in a 0.05 M ODCB solution of $(n\text{-Bu})_4NPF_6$ using a glassy carbon electrode as a working electrode, and a platinum wire as a counter electrode. The concentrations of samples were approximately $2.5 \times 10^{-4}$ M. The reference electrode was an Ag/0.01 M $AgNO_3$ electrode filled with 0.1 M $(n\text{-Bu})_4NClO_4$ in $CH_3CN$. All potentials are referenced to the ferrocene/ferrocenium couple ($F_c/F_c^+$) as the internal standard. All cyclic voltammograms were run at a scan rate of 20 mV/s.

**Bis(4′-*tert*-butylbiphenyl-4-yl)aniline (**BBA**).** A reaction flask was charged with aniline (2.0 g, 21 mmol), 4-bromo-4′-*tert*-butylbiphenyl (12 g, 41 mmol), $NaO^tBu$ (5.0 g, 52 mmol), $Pd(DBA)_2$ (120 mg, 0.2 mmol), dppf (1,1′-bis(diphenylphosphino)ferrocene) (200 mg, 0.3 mmol), and 120 mL of dry toluene under Ar atmosphere. The reaction mixture was refluxed for 15 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product. The purified product, 6.1 g, was obtained in 56% isolated yield by flash chromatography using a 30% hexane in toluene as the eluent:

white solid; mp 88−90 °C; MS (EI): *m*/*z* 509 ($M^+$); $^1H$ NMR $\delta$ 1.36 (s, 18H), 7.01−7.30 (m, 9H), 7.42−7.57 (m, 12H); $^{13}C$ NMR $\delta$ 31.4, 34.5, 123.0, 124.1, 124.6, 125.7, 126.3, 127.7, 129.3, 135.3, 137.8, 146.8, 147.6, 149.8; IR (KBr): 2367, 1589, 1498, 1327, 1290, 1269, 1215, 1162, 1113, 1005, 825 $cm^{-1}$. Anal. Calcd for $C_{38}H_{39}N$: C, 89.54; H, 7.71; N, 2.75. Found: C, 89.52; H, 7.64; N, 2.76.

**4-(Bis(4′-*tert*-butylbiphenyl-4-yl)amino)benzaldehyde.** To 10 mL of DMF was added 4 mL of $POCl_3$ (6.4 g, 41.7 mmol) at 0 °C and stirred for 1 h. To the Vilsmeier reagent was added a solution of BBA (3 g, 5.9 mmol) in 30 mL of DMF at 0 °C and heated at 80 °C for 4 h. After the reaction mixture was cooled to room temperature, it was poured into 1000 mL of 2 wt % NaOH aqueous solution and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product. The purified product, 2.5 g, was obtained in 79% isolated yield by flash chromatography using a 30% hexane in toluene as the eluent.

yellow solid: mp 117−119 °C; $^1H$ NMR: $\delta$ 1.27 (s, 18H), 7.03 (d, 2H, $J = 8.72$ Hz), 7.14 (dd, 4H, $J = 8.44$, 1.65 Hz), 7.37 (dd, 4H, $J = 7.52$, 1.84 Hz), 7.45 (dd, 4H, $J = 7.52$, 1.84 Hz), 7.47 (dd, 4H, $J = 8.44$, 1.65 Hz), 7.62 (d, 2H, $J = 8.72$ Hz), 9.73 (S, 1H); $^{13}C$ NMR: $\delta$ 31.33, 34.51, 119.86, 129.75, 126.26, 126.48, 128.12, 129.35, 131.30, 137.29, 137.70, 145.02, 150.31, 153.13, 190.34; IR (KBr): 2964, 1697, 1596, 1495, 1323, 1298, 1273, 1218, 1159, 1113, 824, 547 $cm^{-1}$. Anal. Calcd for $C_{39}H_{39}NO$: C, 87.11; H, 7.31; N, 2.60. Found: C, 87.35; H, 7.58; N, 2.84.

**4-(Bis(4′-*tert*-butylbiphenyl-4-yl)amino)benzaldehyde Tosylhydrazone 1.** To *p*-toluenesulfonehydrazide (0.346 g, 1.86 mmol) suspended in 20 mL of cold ethanol was slowly added the solution of aminobenzaldehyde (1.0 g, 1.86 mmol) in a mixture of 40 mL of ethanol and 10 mL of ether. The reaction mixture was stirred for 3 days at ambient temperature. After checking TLC (hexane:$CH_3CO_2Et$ = 7:3) and filtration, the solid was recrystallized from ethanol (1.14 g, 86.8%).

yellow solid: mp 181−183 °C; $^1H$ NMR; $\delta$ 1.36 (s, 18H), 2.41-(s, 3H), 7.07 (d, 2H, $J = 8.41$ Hz), 7.17 (d, 4H, $J = 8.41$ Hz), 7.31 (d, 2H, $J = 8.11$ Hz), 7.42−7.53 (m, 14H), 7.71 (s, 2H), 7.87 (d, 2H, $J = 8.11$ Hz), $^{13}C$ NMR: $\delta$ 21.57, 31.34, 34.49, 122.08, 125.24, 125.72, 126.38, 126.53, 127.87, 127.97, 128.47, 129.63, 135.38, 136.47, 137.48, 144.10, 145.81, 148.26, 149.69, 150.07; IR (KBr): 3030, 2962, 2904, 2863, 1600, 1496, 1325, 1289, 1171, 1108, 1054, 941, 829, 666 $cm^{-1}$. Anal. Calcd for $C_{46}H_{47}N_3O_2S$: C, 78.26; H, 6.71; N, 5.95; S, 4.54. Found: C, 78.58; H, 6.46; N, 5.90; S, 4.37.

**61-[4-(Bis(4′-*tert*-butylbiphenyl-4-yl)amino)phenyl]-1,2-methanofullerene[60] 2. General Procedure.** $C_{60}$ (50 mg, $6.94 \times 10^{-5}$ mol) was dissolved in 5 mL of ODCB by ultrasonic for 20 min at 30 °C under $N_2$. Into the solution, 1.4 equiv of tosylhydrazone (68.6 mg, $9.71 \times 10^{-5}$ mol), 1.6 equiv of $NaOCH_3$ (6.0 mg, $1.11 \times 10^{-4}$ mol), and 0.5 mL of pyridine were added. The mixture was stirred at 50 °C for 10 h. After removal of the solvent by distillation, the residue was chromatographed with 20% of $CS_2$ in hexane to get 22.4 mg of unreacted $C_{60}$, and with 20% of toluene in hexane to get 41.4 mg of **2** in 48% (87%; based on consumed $C_{60}$).

FDMS; *m*/*z* 1242 (M + 1); UV−vis (toluene) $\lambda_{max} = 334$ nm ($\epsilon = 89900$), 432 nm ($\epsilon = 3240$), 501 nm ($\epsilon = 2270$), 697 nm ($\epsilon = 237$); $^1H$ NMR: $\delta$ 1.37 (s, 18H), 5.36 (s, 1H), 7.28 (d, 4H, $J = 8.63$ Hz), 7.31 (d, 2H, $J = 8.26$ Hz), 7.46 (d, 4H, $J = 8.62$ Hz), 7.55 (d, 4H, $J = 8.62$ Hz), 7.56 (d, 4H, $J = 8.62$ Hz), 7.85 (d, 2H, $J = 8.26$ Hz); $^{13}C$ NMR: $\delta$ 31.33, 34.43, 43.12, 75.74, 122.85, 125.04, 125.64, 126.35, 127.73, 131.72, 136.03, 136.28, 137.45, 138.46, 140.79, 140.96, 141.99, 142.07, 142.36, 142.64, 142.83, 142.88, 142.99, 143.64, 143.66, 144.10, 144.29, 144.32, 144.50, 144.60, 144.72, 144.99, 145.03, 145.05, 145.10, 145.48, 145.63, 145.95, 147.30, 147.75, 149.82, 149.93; IR (KBr): 2960, 2921, 2851, 2364, 1601, 1494, 1461, 1427, 1320, 1261, 1096, 1029, 802, 526 $cm^{-1}$. Anal. Calcd for $C_{99}H_{39}N$: C, 95.71; H, 3.16; N, 1.13. Found: C, 93.84; H, 3.04; N, 1.34.

**62-Bis[4-(Bis(4′-*tert*-butylbiphenyl-4-yl)amino)phenyl]-1,2-methano]fullerene[60] 3:** FDMS; *m*/*z* 1763 (M + 1); $^1H$ NMR: $\delta$ 1.26−1.27 (m, 36H), 4.48−5.84 (m, 2H), 6.75−7.92 (m, 40H); $^{13}C$ NMR: $\delta$ 31.37, 34.47, 43.12, 74.83−75.17(m), 122.90−124.95(m), 125.28, 125.70, 127.82, 128.20, 129.01, 131.20−132.02, 135.88, 137.56, 140−149(m), 146.3, 149.9; IR (KBr): 3028, 2957, 2865, 1600, 1494, 1317, 1266, 1180, 1112, 1004, 818, 728, 568, 528 $cm^{-1}$. Anal. Calcd for $C_{138}H_{78}N_2$: C, 93.95; H, 4.46; N, 1.59. Found: C, 92.84; H, 4.22; N, 1.36.

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