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# Synthesis and Fast Electron-Transfer Reactions of Fullerene-Carbazole Dendrimers with Short Linkages

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((Dedication, optional))

Fast electron-transfer reactions of newly synthesized  $(carbazole)_n$  dendrimers (n = 1, 3 and 7), which are connected with C<sub>60</sub> with a short linkage, have been investigated in polar benzonitrile. The  $(carbazole)_n$ -C<sub>60</sub> dendrimers were spectroscopic, computational characterized and by electrochemical methods. The geometric and electronic structures of the C<sub>60</sub>-(carbazole)<sub>n</sub> dendrimers were examined by using ab initio B3LYP/6-311G method. The distribution of the highest occupied frontier molecular orbital (HOMO) was found over the carbazole (Cz) entities, whereas the lowest unoccupied molecular orbital (LUMO) was located over the fullerene entity, suggesting the formation of the chargeseparated (CS) states  $(C_{60}$  --(carbazole)<sub>n</sub> +). The redox measurements revealed that the charge separation from carbazole to the singlet-excited state of C<sub>60</sub> is

#### Introduction

Photoinduced electron-transfer processes in donor-acceptor systems have attracted considerable interest because of the most critical aspects in photosynthesis and solar energy conversion.<sup>1-6</sup> In this line, great efforts have been done in the last years from different research groups to prepare simple donor-acceptor molecules (dyads, triads and tetrads).<sup>1-6</sup> Recently, there is growing interest to prepare and characterize novel donor-acceptor dendrimers that have abilities to convert the sunlight to chemical energy.<sup>7-10</sup> Dendrimers are known to be three-dimensional treelike molecules processing well-defined structures composed of a core and various numbers of dendrons.<sup>7-12</sup>

In the most of the successful donor-acceptor models, three dimensional electron acceptors, fullerenes in general and C<sub>60</sub> in particular, has be proven to be superior electron acceptors due to their  $\pi$ -electron rich surface, favorable reduction potentials and low reorganization energies in electron-transfer reactions.<sup>6,13-16</sup> Accordingly, in fullerene-containing donor-acceptor systems, forward electron transfer occurs in the top portion of the Marcus parabola while charge recombination occurs in the inverted region of the parabola, ultimately producing high charge separation/charge recombination ratio.

Among various electron donors, carbazole, which is a tricyclic molecule with two benzene rings fused on either side of a five-membered nitrogen-containing ring, has attracted

thermodynamically feasible in polar benzonitrile. The femtosecond transient absorption measurements in the visible-NIR region revealed fast charge separation (~  $10^{11}$  s<sup>-1</sup>) from the carbazole to the singlet-excited state of C<sub>60</sub> producing the charge-separated states (C<sub>60</sub><sup>--</sup>-(carbazole)<sup>++</sup>) with lifetimes of 1.25~1.30 ns. The complementary nanosecond transient absorption measurements in the microsecond region revealed that the charge-separated states decayed to populate the triplet states of C<sub>60</sub>, as well as the ground states. The higher charge separation / charge recombination ratios (~ 800) suggested the potential of compounds **1-3** to be light harvesting systems.

Keywords: Fullerene . carbazole . electron transfer . laser flash photolysis

special attention as a component of photoconductive poly-(*N*-vinylcarbazole) (PVCz).<sup>17</sup> Carbazoles have also been used as a light-emitting photosensitizer, charge/hole transport material in OLED applications, and photovoltaic and display devices.<sup>17-21</sup> Despite these unique properties and applications of carbazole, there are only a few examples of electron donor-acceptor systems using carbazole as an electron donor, in which the charge separation is not so efficient.<sup>22</sup> There are many examples of fast charge separation in electron donor-acceptor systems using short linkage.<sup>23-28</sup> However, there is no example of carbazole-linked C<sub>60</sub> dyads with short linkage.<sup>29</sup>

We report herein the synthesis, characterization and electron-transfer reactions of fullerene ( $C_{60}$ )-carbazole dendrimers (Fig. 1), where  $C_{60}$ -cored dendrimers are connected with (carbazole)<sub>n</sub> dendrons (n = 1, 3 and 7) with short linkages.<sup>30</sup> Because of the short linkages between the Cz and  $C_{60}$  units, an extremely fast charge separation

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processes were achieved compared to the reported dendrimers with long linkages.<sup>10</sup> Such fast intramolecular charge separation processes from the carbazole to the singlet-excited state of  $C_{60}$  were suggested from the steady-state emission, and confirmed from the femtosecond transient absorption measurements. The energies of the charge-separated states were obtained from the cyclic voltammetry technique.



Fig. 1 Molecular structures of  $C_{60}$ -(Cz)<sub>n</sub> 1-3.

#### **Results and Discussion**

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The most straightforward preparation of compounds 1, 2 and 3 can be envisaged to proceed through a reaction sequence of the following steps, i.e., the Ullmann<sup>31</sup> and Prato's 1, 3dipolar cycloaddition reactions<sup>32</sup> as depicted in Scheme 1. Every step of the reaction sequence proceeded smoothly and efficiently to give a good or moderate yield of the product (see Experimental Section for the synthetic details). Commercially available carbazole was iodinated to give 5 in 68% yield and then the subsequent protection of amine proton in 5 was carried out using p-toluenesulfonyl chloride according to the literature procedure<sup>33</sup> to give compound 6 in 73% yield. Compound 6 was reacted with carbazole under Ullmann condition<sup>31</sup> to produce compound **7** in 55.4% yield. The tosyl group in 7 was then deprotected by base hydrolysis to afford compound 8 in 90% vield. To increase the number of carbazole units, Ullmann coupling reaction of compound 8 with compound 6 was repeated to produce 9 in 34% yield. Deprotection of the tosyl group in 9 was then carried out using base hydrolysis to obtain carbazole dendrimer 10 in 90% yield. Carbazole dendrons 4, 8 and 10 were reacted with 4-iodobenzaldehyde under Ullmann conditions to give monoaldehydes 11 (31%), 12 (34%) and 13 (66%), respectively. Finally, aldehyde groups in 11, 12 and 13 were reacted with N-octylglycine and C<sub>60</sub> through Prato's 1, 3dipolar cycloaddition<sup>32</sup> to produce C<sub>60</sub>-cored carbazole dendrimers 1 (30%), 2 (18%) and 3 (23%), respectively.

 $C_{60}$ -(carbazole)<sub>n</sub> dendrimers **1-3** and their precursor compounds are very soluble in aromatic solvents (i.e., toluene, *o*-dichlorobenzene and benzonitrile) and other common organic solvents (i.e., acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and THF). The structures and purity of the newly synthesized

compounds were confirmed mainly by <sup>1</sup>H NMR and elemental analysis (see Experimental Section). <sup>1</sup>H NMR spectra of **1**, **2** and **3** are consistent with the proposed structures, showing the expected features with the correct integration ratios, respectively. The MALDI-TOF mass spectra provided a direct evidence for the structures of **1**, **2** and **3** showing a singly charged molecular ion peaks at m/z = 1116.37 for **1**, m/z = 1446.52 for **2** and m/z = 2108.62 for **3** (Figs. S1-S3). Further confirmation of **1**, **2** and **3** was obtained from the steady-state UV/vis measurements as shown in the forthcoming sections.



Fig. 2 shows the steady-state absorption spectra of dendrimers **1-3** along with the reference compounds in benzonitrile (PhCN). The spectral features of **1-3** in the visible range exhibited a strong absorption in the UV region and the characteristic absorption bands of fulleropyrrolidine ( $C_{60}$ -ref) at 698 and 432 nm. The absorption maxima of the carbazole entities are located at 296 nm as a main band and shoulder bands at 323 and 336 nm. The absorption bands in the UV range (<400 nm) correspond to both fullerene and carbazole entities were also recorded. The absence of new absorption bands in the visible-near IR region indicating no interaction between Cz and  $C_{60}$  moieties in the ground states of **1-3**.

The photoinduced intramolecular events of **1-3** were investigated by the steady-state fluorescence measurements in benzonitrile by using 430 nm excitation light, which excited mainly the C<sub>60</sub> entity. Fig. 2 shows extremely weak fluorescence intensities of the singlet excited state of C<sub>60</sub> ( $^{1}C_{60}^{*}$ ) at 710 nm of **1-3** compared to that of C<sub>60</sub>-ref suggesting that the emission of the  $^{1}C_{60}^{*}$  was heavily quenched by the appended carbazole entities because of the electron transfer from Cz to the singlet C<sub>60</sub> ( $^{1}C_{60}^{*}$ ), by taking into account that the energy transfer from  $^{1}C_{60}^{*}$  (1.75 eV) to the singlet Cz (3.43 eV)<sup>20b</sup> is excluded due to the energetic considerations.



**Fig. 2** (Left) Steady-state absorption spectra of dendrimers **1-3** (1.0 x 10<sup>-4</sup> M), along with C<sub>60</sub>-ref and Cz-ref in PhCN. (Right) Fluorescence spectra of C<sub>60</sub>-(Cz)<sub>n</sub> and C<sub>60</sub>-ref in PhCN. Concentrations are kept at  $5.0 \times 10^{-5}$  M;  $\lambda_{ex} = 430$  nm.

Femtosecond transient absorption spectroscopy was employed to obtain further insight into the excited state interactions in **1-3** to corroborate the proposed electrontransfer process. Toward this end, compounds **1-3** were probed with 390 nm laser light to selectively excite the  $C_{60}$ entity. Fig. **3** shows the transient spectral response for representative **1**. The spectral absorption features in the visible region and NIR region, which are seen immediately (i.e., 5 ps) upon excitation of **1** in deaerated benzonitrile, correspond to the singlet-excited state of  $C_{60}$  ( ${}^{1}C_{60}$ \*). With increasing the time window from 5 to 40 ps, one can see clearly the decay of the <sup>1</sup>C<sub>60</sub>\* accompanied with the formation of the characteristic absorption bands of C<sub>60</sub> radical anion  $(C_{60}^{-})$  at 1000 nm<sup>6,13-16</sup> and the Cz radical cation (Cz<sup>+</sup>) at 600 nm.34 This clear observation indicates the occurrence of electron transfer from Cz to the singlet-excited of C<sub>60</sub> affording the charge-separated state (C<sub>60</sub> - Cz<sup>+</sup>). The characteristic absorption band of  $C_{60}$  in the near-IR region was employed as a reliable probe to determine the rate constants of the charge separation  $(k_{CS})$  and charge recombination ( $k_{CR}$ ), because the fingerprint absorption band of C60° band at 1000 nm does not overlap with the bands of other species.<sup>10,13-16</sup> By fitting the rise time profile of  $C_{60}$  at 1000 nm (Fig. S4), the rate constant of charge separation  $(k_{\rm CS})$  was determined to be 4.64 × 10<sup>11</sup> s<sup>-1</sup>. The short distance between the centre of C<sub>60</sub> and carbazole entities (11.2 Å) may facilitate such fast electron-transfer process. By fitting the decay time profile of  $C_{60}$ , the rate constant of charge recombination ( $k_{CR}$ ) was found to be 7.99 × 10<sup>8</sup> s<sup>-1</sup>, from which the lifetime of charge-separated state  $(\tau_{CS})$  was determined as 1.25 ns. By checking the absorption bands in the visible and NIR (Fig. 2), one can see clearly that the decay of the  $C_{60} \dot{\ }$  at 1000 nm is accompanied by the formation of a new absorption band at 700 nm, which corresponds to the triplet state of  $C_{60}$  ( ${}^{3}C_{60}$ ) with a rate constant of 6.40  $\times$  10<sup>8</sup> s<sup>-1</sup>. This finding may suggest that the radical-ion pairs recombine to populate the triplet C<sub>60</sub>, as well as the ground states.



**Fig. 3** (Upper figure) Differential absorption spectra obtained upon femtosecond flash photolysis ( $\lambda_{ex}$  = 390 nm) of **1** (1.0 ×10<sup>-4</sup> M) in PhCN at the indicated time intervals. (Lower figures) Decay time profile of  $C_{60}^{--}$  (1000 nm) and rise time profile of  ${}^{3}C_{60}^{+}$  (700 nm), monitoring the charge recombination and formation of the triplet  $C_{60}$ , respectively.

When turning to **2** and **3** (Figs. 4 and S5), the femtosecond transient absorption spectra in benzonitrile showed similar charge separation features as those of **1**. By fitting the rise and the decay time profiles of  $C_{60}$ , we determined the rates of charge-recombination and lifetimes of the charge-separated states as  $7.87 \times 10^8$  s<sup>-1</sup> and 1.27 ns (for **2**) and  $7.69 \times 10^8$  s<sup>-1</sup> and 1.30 ns (for **3**).

In dimethylformamide (DMF), similar spectral features were observed as those in benzonitrile (Fig. S6). By fitting the decay time profiles of  $C_{60} \dot{-}$  at 1000 nm, we determined the rates of charge recombination as 2.00  $\times$  10<sup>9</sup>, 1.93  $\times$  10<sup>9</sup> and  $1.80 \times 10^9$  s<sup>-1</sup> for **1**, **2** and **3**, respectively. From these values, the lifetimes of charge-separated states were determined as 0.50, 0.52 and 0.55 ns for 1, 2 and 3, respectively. The finding that the lifetimes of charge-separated-states of 1-3 in the polar benzonitrile and dimethylformamide are not largely dependent on the number of carbazole dendrons suggests that the charge recombination between the closely spaced  $C_{60}$  and Cz decurs in competition with the hole migration among the carbazole units. This behavior is different from our previously reported SiPc- $(C_{60})_n$  dendrimers with long linkers (where the  $\tau_{CS}$  value increased with increasing the number of C<sub>60</sub> dendrons).<sup>10a</sup> This difference may be explained by the short distance between the donor and acceptor (11 Å) of the examined dendrimers 1-3 compared with the long distance (25 Å) of the reported SiPc- $(C_{60})_n$  dendrimers.<sup>10a</sup> From this comparison, it seems that the charge recombination in the radical ion pairs occurs faster than the hole migration in 1-3, while the hole migration seems to occur faster than charge recombination in the reported SiPc-(C<sub>60</sub>)<sub>n</sub> dendrimers.<sup>10a</sup>

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**Fig. 4** (Upper figure) Differential absorption spectra obtained upon femtosecond flash photolysis ( $\lambda_{ex}$  = 390 nm) of **3** (1.0 × 10<sup>4</sup> M) in PhCN at the indicated time intervals. (Lower figures) Rise and decay time profiles of C<sub>60</sub> at 1000 nm, monitoring charge-separation and charge-recombination processes, respectively.

The charge-separation processes via <sup>1</sup>C<sub>60</sub>\* were supported from the viewpoint of thermodynamics of the electron-transfer processes. The cyclic voltammograms of 1-3 in deaerated benzonitrile (Figs. 5 and S7-S9) showed the first reduction potentials (E<sub>red</sub>) of the C<sub>60</sub> moiety at -570, -560 and -555 mV vs. SCE for 1, 2 and 3, respectively. On the other hand, the first oxidation potentials  $(E_{ox})$  of the Cz moiety were located at 1020, 980 and 966 mV vs. SCE for 1, 2 and 3, respectively, indicating that the oxidation potential of Cz entity is changed by increasing the Cz generation of the dendrimer.<sup>35</sup> Based on the first oxidation potential of the Cz moiety ( $E_{ox}$ ), the first reduction potential of the C<sub>60</sub> moiety ( $E_{red}$ ), the coulombic term ( $E_c$ ) and energy of the  ${}^{1}C_{60}^{*}$  ( $\Delta E_{0-0}$ ), the driving forces for charge recombination (- $\Delta G_{CR}$ ) and charge separation (- $\Delta G_{CS}$ ) were calculated according to equations 1 and 2:36

$$\Delta G_{CR} = e (E_{ox} - E_{red}) + E_c$$
(1)  
$$\Delta G_{CS} = \Delta E_{0.0} - (-\Delta G_{CR})$$
(2)

From equations 1 and 2, the  $-\Delta G_{CR}$  values were found to be 1.65 eV (for 1), 1.60 eV (for 2) and 1.58 eV (for 3), by taking into account that the coulombic term in polar solvents is negligible (~0.06 eV).<sup>37</sup> These values indicate that the energy levels of the CS states of compounds 1-3 are lower than the energy of the singlet C<sub>60</sub> (1.75 eV) and higher than the triplet C<sub>60</sub> (1.55 eV).<sup>10-14</sup> The negative  $\Delta G_{CS}$  values (-0.10 eV for 1, -0.15 eV for 2 and -0.17 eV for 3) suggest that the electron transfer via the singlet excited state of C<sub>60</sub> is thermodynamically feasible in polar benzonitrile.



**Fig. 5** Cyclic voltammogram of 1  $(1.0 \times 10^{-4} \text{ M})$  in deaerated PhCN with TBAPF<sub>6</sub> (0.1 M) as support electrolyte. Scan rate = 20 mV/s.

Moreover, the charge-separation process from Cz to  $C_{60}$  was supported by studying the molecular geometries and electronic structures of **1-3** on the basis of molecular orbital calculation using density functional method (DFT) at B3LYP/6-311G level (Figs. 6, S10 and S11). The structures were optimized to stationary point on the Born-Oppenheimer potential surface. The centre-to-centre distance between  $C_{60}$  and the nitrogen atom of Cz entity of **1** was 11.2 Å. In compounds **1-3**, the orbital distribution of the highest occupied molecular orbitals (HOMO and HOMO-1) was located on the Cz entities, while the orbital distribution of lowest unoccupied molecular orbital (LUMO) was located on the  $C_{60}$  unit, possible charge separation takes place first between the electron-donating Cz and the  $C_{60}$  unit as an electron acceptor.

The absence of LUMOs on the Cz unit and HOMO on the  $C_{60}$  moiety proposes weak or no charge-transfer interactions between the electron donor and acceptors in the ground state in compounds **1-3**.



Fig. 6 The frontier HOMO, HOMO-1, and LUMO orbitals of 3 obtained by using *ab initio* B3LYP/6-311G method.

The complementary nanosecond transient absorption measurements of 1-3 in PhCN with 430 nm laser excitation, which selectively excites the  $C_{60}$  moiety, exhibited absorption bands in the visible region with maxima at 700 nm, which correspond to the triplet-excited state of  $C_{60}$  ( ${}^{3}C_{60}^{*}$ ) (Figs. 7, S12 and S13).  $^{10,13\text{--}16}$  The decay rate constant of  $^3C_{60}{}^{\star}$  was determined to be  $5.50 \times 10^4 \text{ s}^{-1}$ . Such formation of the triplet C<sub>60</sub> may arise from the relaxation process of portion of the singlet-excited state of C<sub>60</sub> to its lower triplet state by intersystem crossing process. The charge recombination process of the radical-ion pair to populate the triplet state of C<sub>60</sub>, as well as the ground state can be also considered in 1-3 from the following observations: (i) the rise of  $C_{60}^*$  ( $\lambda_{max}$  = 700 nm) with the decay of the  $C_{60}$  radical anion (Figs. 2 and 3) and (ii) the higher energy levels of the charge-separated states (1.58-1.65 eV) compared with the  ${}^{3}C_{60}{}^{*}$  (1.55 eV).  ${}^{10-14}$ 



Fig. 7 Nanosecond transient absorption spectra of 3 (1.0 ×10<sup>4</sup> M) obtained by 430 nm laser excitation light in deaerated PhCN. Inset: Decay time profile of  ${}^{3}C_{60}{}^{*}$  at 700 nm.

Fig. 8 summarized the intramolecular events for  $C_{60}$ -(Cz)<sub>n</sub> dendrimers in PhCN. Upon excitation by the 390 nm laser light, the  $C_{60}$  is excited to its singlet state ( ${}^{1}C_{60}$ \*), which in turn accept an electron from the electron-donating Cz to yield the charge-separated state  $C_{60}$ <sup>--</sup>-(Cz)<sub>n</sub><sup>++</sup>. The charge separated states, with their high energy levels, decayed to populate the triplet states of  $C_{60}$ , as well as the ground states.



Fig. 8 Energy level diagram depicting the photoinduced intramolecular events of  $C_{60-}(Cz)_n$  **1-3** in PhCN.

#### Conclusion

Photoexcitaion of newly synthesized (carbazole)<sub>n</sub> dendrimers (n = 1, 3 and 7), which are connected with C<sub>60</sub> with short linkages, resulted in fast electron transfer from the carbazole to the singlet-excited state of  $C_{60}$  generating  $C_{60}$  -(Cz)<sup>+</sup> in polar solvents. The electron-transfer process was suggested from the steady-state emission, CV measurements and MO calculations. The femtosecond laser photolysis confirmed the occurrence of fast charge separation (~  $5.0 \times 10^{11} \text{ s}^{-1}$ ) in the closely spaced 1-3, which is nearly 800 times faster than the rates of charge recombination (~  $6.0 \times 10^8 \text{ s}^{-1}$ ). This finding suggests the usefulness of the examined compounds 1-3 as light harvesting systems. Unlike the donor-acceptor dendrimers with long linkages,<sup>10</sup> the  $\tau_{CS}$  values observed for the examined compounds are not largely dependent on the number of carbazole dendrons. This may rationalized by the competition between the fast charge recombination between the closely spaced  $Cz^{+}$  and  $C_{60}^{-}$ , and the charge delocalization among the carbazole units. Another explanation for this finding may arise from the larger solvent reorganization energy of electron transfer due to an increase in the distance between the plus and minus charges in dendrimer 3. Such an increase in the solvent reorganization energy of electron transfer is known to result in an increase in the rate of back electron transfer in the Marcus inverted region.28,38

#### **Experimental Section**

#### Materials and instruments

Reagents and solvents were purchased as reagent grade and used without further purification. Compound  $\mathbf{8}^{39}$  and *N*-octylglycine<sup>40</sup> were synthesized according to the published methods. All reactions were performed using dry glassware under nitrogen atmosphere.

Analytical TLC was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230-400 mesh). Melting points were determined on an Electrothemal IA 9000 series melting point apparatus, being uncorrected. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with TMS peak as reference. UV/Vis spectra were recorded on a Jasco V-550 spectrometer. MALDI-TOF MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer.

Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region. Cyclic voltammograms were carried on a BAS CV-50W Voltammetric Analyzer. A platinum disk electrode was used as working electrode, while a platinum wire served as a counter electrode. SCE electrode was used as a reference electrode. All measurements were carried out in o-dichlorobenzene containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) as the supporting electrolyte. The scan rate was 20 mV/s.

Density-functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. The computational calculations were performed by using the Becke3LYP functional and the 6-311G basis set, with the restricted Hartree-Focck (RHF) formalism implemented in the GAUSSIAN 03 program.<sup>41</sup> The frontier HOMO and LUMO were generated by using Gauss View software program (ver. 3.09) developed by Semichem, Inc.

The studied compounds were excited by a Panther optical parametric oscillator (OPO) pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at  $\lambda$  = 432 nm with the powers of 1.5 and 3.0 mJ per pulse. The transient absorption measurements were performed using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS which has optical frequency mixers resulting in tunable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at 298 K. The transient spectra were recorded using fresh solutions in each laser excitation.

#### Syntheses

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**3,6-Diiodo-9H-carbazole (5).** Carbazole (10.0 g, 59.8 mmol) was dissolved in acetic acid (50 mL) and then warmed to 801. To this solution were added potassium iodide (13 g, 78.3 mmol) and potassium iodate (10 g, 46.7 mmol). The mixture was refluxed for 24 hours and cooled to room temperature. The crude product was diluted with water and filtered. The brown precipitates were stirred in 5% bisulfate solution for 2 hours and filtered. The product was recrystallized from dichloromethane to give **5** (17.2 g, 68%) in a brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.20 (d, 2H), 7.66 (d, 2H), 8.10 (s, 1H), 8.30 (s, 1H). Anal. Calcd for C<sub>12</sub>H<sub>7</sub>NI<sub>2</sub>: C, 34.39%; H, 1.68%; N, 3.35%. Found: C, 34.48%; H, 1.77%; N, 3.28%.

**3,6-Diiodo-9-tosyl-9H-carbazole (6).** To a solution of compound **5** (10.0 g, 23.8 mmol) in *N*,*N*-dimethylformamide (25 mL) was added sodium hydride (2.40 g, 100 mmol) at 0I , and stirred 10 minutes. Subsequently, *p*-toluenesulfonyl chloride (2.40 g, 100 mmol) was added to this mixture and stirred at 0I for 4 hours. The mixture was diluted with water and the precipitates were filtered. The crude product was recrystallized from dichloromethane to afford **6** (10.1 g, 73%) in a brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.30 (s, 3H), 7.10 (d, 2H), 7.60 (d, 2H), 7.79 (d, 2H), 8.05 (d, 2H), 8.16 (s, 2H). Anal. Calcd for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>Sl<sub>2</sub>: C, 39.81%; H, 2.29%; N, 2.44%. Found: C, 39.69%; H, 2.38%; N, 2.36%.

**3,6-Di(9H-carbazol-9-yl)-9-tosyl-9H-carbazole (7).** To a solution of **4** (2.92 g, 17.5 mmol) and **6** (5.0 g, 8.72 mmol) in *N*,*N*-dimethylacetamide (10 mL) was added copper oxide (2.50 g, 17.4 mmol). The mixture was refluxed for 48 hours, cooled to room temperature, and diluted with water. The precipitates were filtered, and recrystallized from dichloromethane/hexane (1:1) to produce **7** (3.15 g, 55.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.40 (s, 3H), 7.20-7.70 (m, 15H), 7.70 (d, 2H), 7.90 (d, 2H), 8.00 (d, 4H), 8.10 (d, 4H), 8.59 (d, 2H). Anal. Calcd for C4<sub>3</sub>H<sub>2</sub><sub>9</sub>N<sub>3</sub>O<sub>2</sub>S: C, 79.24%; H, 4.48%; N, 6.45%. Found: C, 79.11%; H, 4.59%; N, 6.37%.

**3,6-Di(9H-carbazol-9-yl)-9H-carbazole (8).** To a solution of compound **7** (3.00 g, 4.60 mmol) in tetrahydrofuran (9 mL) were added dimethyl sulfoxide (4.5 mL) and water (1.5 mL), and the mixture was stirred for 10 minutes. Subsequently, potassium hydroxide (1.50 g, 26.7 mmol) was added to this mixture, and the reaction mixture was refluxed for 4 hours, cooled to room temperature and diluted with water. After neutralization with dilute HCl solution (6 N), the crude product was filtered and recrystallized from dichloromethane/hexane (1:1) to give **8** (2.07 g, 90%). Mp. 285 I. <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz):  $\delta$  = 7.20-7.40 (m, 13H), 7.60 (d, 2H), 7.70 (d, 2H), 8.14 (d, 3H), 8.19 (s, 2H), 8.46 (s, 1H). Anal. Calcd for G<sub>38</sub>H<sub>23</sub>N: C, 92.08%; H, 4.94%; N, 2.98%. Found: C, 92.25%; H, 4.88%; N, 2.87%.

**3,6-Di{3,6.di(9H-carbazol-9-yl)-9H-carbazol-9-yl}-9-tosyl-9Hcarbazole (9).** To a solution of **6** (600 mg, 1.04 mmol) and **8** in *N*,*N*dimethylacetamide (10 mL) was added copper oxide (300 mg, 2.09 mmol). The mixture was refluxed for 48 hours, cooled to room

mmol). The mixture was refluxed for 48 hours, cooled to room temperature and diluted with water. The precipitates were filtered and then recrystallized from dichloromethane/hexane (1:1) to give **9** (450 mg, 34%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.20-7.40 (m, 25H), 7.60 (m, 10H), 7.92 (d, 2H), 8.00 (d, 2H), 8.12 (d, 8H), 8.28 (s, 3H), 8.32 (s, 2H), 8.76 (d, 2H). Anal. Calcd for C<sub>91</sub>H<sub>57</sub>N<sub>7</sub>O<sub>2</sub>S: C, 83.27%; H, 4.38%; N, 7.47%. Found: C, 83.12%; H, 4.46%; N, 7.39.

**3,6-Di{3,6-di(9H-carbazol-9-yl)-9H-carbazol-9-yl}-9H-carbazole (10).** To a solution of **9** (350 mg, 0.266 mmol) in tetrahydrofuran (2 mL) were added dimethyl sulfoxide (0.9 ml), water (0.4 ml) and potassium hydroxide (0.25 g, 44 mmol). The mixture was refluxed for 4 hours, cooled to room temperature, and neutralized with dilute HCI (6 N). The crude product was filtered, and recrystallized from dichloromethane/hexane (1:1) to afford **10** (280 mg, 90%). Mp. 293 I . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.20-7.30 (m, 8H), 7.30-7.40 (m, 16H), 7.58-7.62 (m, 10H), 8.82 (m, 3H), 8.14 (d, 8H), 8.28 (s, 3H), 8.44 (s, 2H), 8.62 (s, 1H). Anal. Calcd for C<sub>84</sub>H<sub>51</sub>Nr<sup>-</sup> C, 87.10%; H, 4.44%; N, 8.46%. Found: C, 86.94%; H, 4.59%; N, 8.47%.

**4-(9H-carbazol-9-yl)benzaldehyde (11).** To a solution of **4** (300 mg, 1.29 mmol) and 4-iodobenzaldehyde (220 mg, 1.31 mmol) in *N*,*N*-dimethylacetamide (10 mL) was added copper oxide (370 mg, 2.58 mmol). The mixture was refluxed for 48 hours, cooled to room temperature and diluted with water. The precipitates were filtered and chromatographed on silica gel with dichloromethane/hexane (1:1) to afford **11** (230 mg, 66%) in a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.30-6.35$  (t, 2H), 7.40-7.52 (m, 4H), 7.75-7.82 (d, 2H), 8.08-8.21 (m, 4H), 10.10 (s, 1H). Anal. Calcd for C<sub>19</sub>H<sub>13</sub>NO: C, 84.11%; H, 4.83%; N, 5.16%. Found: C, 84.04%; H, 4.96%; N, 5.07%.

#### 4-(9H-carbazol-9-yl)-1-(1-N-octyl-3,4-fulleropyrrolidin-2-

**yl)]benzene (1).** To a solution of **11** (25 mg, 0.092 mmol) and *N*-octylglycine (35 mg, 0.186 mmol) in 1,2-dichlorobenzene (10 mL) was added fullerene C<sub>60</sub> (70 mg, 0.097 mmol). The mixture was refluxed for 24 hours, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel with toluene to remove unreacted fullerene, and then with dichloromethane/carbon disulfide (40:1) to produce **1** (31 mg, 30%) in a reddish black solid. Mp. 152 I . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): *δ* = 1.00 (m, 3H), 1.40 (m, 3H), 1.50 (m, 3H), 1.80 (m, 2H), 1.90-2.10 (m, 3H), 2.72 (m, 1H), 3.40 (m, 1H), 4.20 (d, 1H), 5.20 (d, 1H), 5.21 (s, 1H), 7.20-7.40 (m, 8H), 7.59-7.62 (d, 2H), 8.10 (d, 2H). Anal. Calcd for C<sub>88</sub>H<sub>32</sub>N<sub>2</sub>: C, 94.60%; H, 2.89%; N, 2.51%. Found: C, 94.49%; H, 2.98%; N, 2.53%.

**4-{3,6-Di(9H-carbazol-9-yl)-9H-carbazol-9-yl}benzaldehyde (12).** To a solution of **8** (150 mg, 0.301 mmol) and 4-iodobenzaldehyde (93 mg, 0.402 mmol) in *N*, *N*-dimethylacetamide (10 ml) was added copper oxide (172 mg, 1.26 mmol). The mixture was refluxed for 48

hours, cooled to room temperature and diluted with water. The precipitates were filtered and chromatographed on silica gel with dichloromethane/hexane (2:1) to give **12** (57 mg, 31%) in a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.12-7.20 (m, 4H), 7.25-7.35 (m, 8H), 7.53-7.58 (m, 2H), 7.61-7.63 (d, 2H), 7.82-7.88 (d, 2H), 8.03-8.10 (d, 4H), 8.10-8.15 (d, 2H), 8.16-8.20 (s, 2H), 10.08 (s, 1H). Anal. Calcd for C<sub>43</sub>H<sub>27</sub>N<sub>3</sub>O: C, 85.83%; H, 4.52%; N, 6.98%. Found: C, 85.89%; H, 4.46%; N, 7.07%.

#### 4-{3,6-Di(9H-carbazol-9-yl)-9H-carbazol-9-yl}-1-(1-N-octyl-3,4-

fulleropyrrolidin-2-yl)benzene (2). To a solution of 12 (30 mg, 0.049 mmol) and *N*-octylglycine (20 mg, 0.106 mmol) in 1,2-dichlorobenzene (10 mL) was added fullerene C<sub>60</sub> (50 mg, 0.074 mmol). The mixture was refluxed for 24 hours, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel with toluene to remove unreacted fullerene, and then with dichloromethane/carbon disulfide (40:1) to give 2 (13 mg, 18%) in a reddish black solid. Mp. >350 I . (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  =1.00 (m, 3H), 1.40 (m, 3H), 1.50 (m, 3H), 1.80 (m, 2H), 1.90-2.10 (m, 3H), 2.72 (m, 1H), 3.40 (m, 1H), 4.20 (d, 1H), 5.20 (d, 1H), 5.21 (s, 1H), 7.24-7.29 (m, 6H), 7.36-7.41 (m, 8H), 7.54-7.62 (m, 4H), 7.76-7.81 (d, 2H), 8.12-8.16 (d, 4H), 8.27 (s, 2H). Anal. Calcd for C<sub>112</sub>H<sub>46</sub>N<sub>4</sub>: C, 92.93%; H, 3.20%; N, 3.87%. Found: C, 92.78%; H, 3.09%; N, 4.13%.

#### 4-[3,6-Di{3,6-di(9H-carbazol-9-yl)-9H-carbazol-9-yl}-9H-

**carbazol-9-yi]benzaldehyde (13).** To a solution of **10** (200 mg, 0.173 mmol) and 4-iodobenzaldehyde (80 mg, 0.344 mmol) in *N*,*N*-dimethylacetamide (10 mL) was added copper oxide (80 mg, 0.559 mmol). The mixture was refluxed for 48 hours, cooled to room temperature and diluted with water. The precipitates were filtered and chromatographed on silica gel with dichloromethane/hexane (2:1) to give **12** (73 mg, 33.4%) in a pale yellow solid. Mp. 304 I . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.20-7.30 (m, 10H), 7.30-7.40 (m, 14H), 7.55-7.69 (m. 8H), 7.80-7.90 (s, 4H), 8.00-8.05 (d, 2H), 8.10-8.20 (d, 8H), 8.25-8.31 (s, 6H), 8.50-8.55 (s, 2H), 10.20 (s, 1H). Anal. Calcd for C<sub>91H55</sub>NO: C, 92.75%; H, 4.70%; N, 1.19%. Found: C, 92.58%; H, 4.84%; N, 1.26%.

#### 4-[3,6-Di{3,6-di(9H-carbazol-9-yl)-9H-carbazol-9-yl}-9H-

**carbazol-9-yi]-1-(1-N-octyl-3,4-fulleropyrrolidin-2-yi)benzene (3).** To a solution of **13** (50 mg, 0.039 mmol) and *N*-octylglycine (15 mg, 0.08 mmol) in 1,2-dichlorobenzene (10 ml) was added fullerene C<sub>60</sub> (30 mg, 0.041 mmol). The mixture was refluxed for 24 hours, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel with toluene to remove unreacted fullerene, and then with dichloromethane/carbon disulfide (1:1) to give **3** (19 mg, 23%) in a reddish black solid. Mp. >350 I . (dec.) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.00 (m, 3H), 1.40 (m, 3H), 1.50 (m, 3H), 1.80 (m, 2H), 1.90-2.10 (m, 3H), 2.72 (m, 1H), 3.40 (m, 1H), 4.20 (d, 1H), 5.20 (d, 1H), 5.21 (s, 1H), 7.20-7.40 (m, 26H), 7.70-7.65 (m, 10H), 7.70-7.78 (m, 4H), 8.05 (d, 8H), 8.20 (s, 4H), 8.49 (s, 2H). Anal. Calcd for C<sub>160</sub>/r<sub>4</sub>N<sub>8</sub>: C, 91.15%; H, 3.54%; N, 5.32%. Found: C, 91.00%; H, 3.66%; N, 5.34%.

#### **Supporting Information**

MALDI-TOF mass spectra of compound **1-3**, MO calculations of compounds **1** and **2**, femtosecond transient spectra of compound **2**, CV and DPV for compound **2** and **3**, Optimized structures of **1** and **2**, and nanosecond transient spectra of compounds **1** and **2** in deaerated benzonitrile.

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## Synthesis and Fast Electron-Transfer Reactions of Fullerene-Carbazol Dendrimers with Short Linkers

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Fast and efficient electron-transfer reactions of the closely spaced  $C_{60}$ -(carbazole)<sub>n</sub> dendrimers (n = 1, 3 and 7) were observed by the femtosecond and nanosecond laser photolysis techniques.