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Persistent Photoinduced Electron Transfer from Functionalized Dendrimers to Buckminsterfullerene**

By *René A. J. Janssen,* Johan F. G. A. Jansen, John A. E. H. van Haare*, and *E. W. Meijer**

Both fullerenes and dendrimers exhibit many interesting chemical and physical properties in combination with a fascinating globular molecular architecture.[1,2] While the characteristic soccer-ball shape of Buckminsterfullerene (C_{60}) is constructed from a single layer of interconnected carbon atoms, the tree-like spherical structure of dendrimers results from the increased steric interactions between the bifurcating branches that emit from the central core.

A first study combining these two classes of molecules has recently been reported by Wudl and Fréchet, describing the synthesis of dendritic fullerenes.[3] Here we report that functionalized poly(propylene imine) dendrimers give rise to a remarkably persistent photoinduced electron transfer reaction to C_{60} in solution (Fig. 1). This reaction exhibits

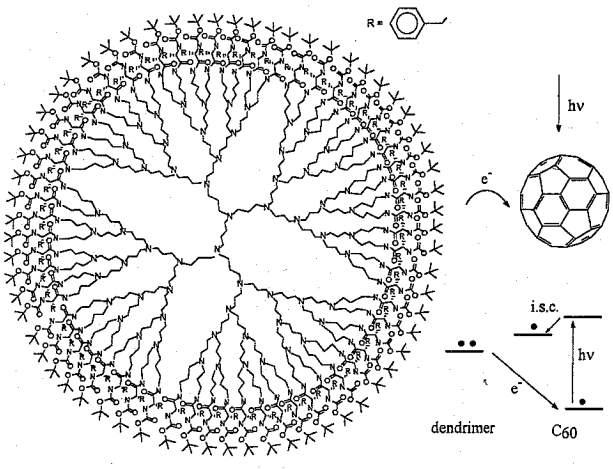

Fig. 1. Schematic illustration of the electron transfer reaction from DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_{64}$ to Buckminsterfullerene and of the energy levels involved.

an interesting size-effect: Persistent photoinduced electron transfer only occurs for dendrimer generations $G \geqq 2$, demonstrating that new properties of dendrimers emerge at higher generations.

The photophysical properties of C_{60} have been actively investigated in recent years. It is well established that after photoexcitation of C_{60} a rapid intersystem crossing occurs to the triplet manifold, producing $^3C_{60}$ in nearly unit quantum yield.[4] Numerous optical and ESR studies have shown that intermolecular reductive quenching of $^3C_{60}$ occurs in the presence of aromatic and aliphatic tertiary amines as donors,[5] and intramolecular quenching by a *N,N*-dimethylaniline moiety coupled to the fullerene has been reported.[6] In these reactions, the forward electron transfer is extremely fast and the charge-separated state is short-lived as a result of a fast geminate back transfer. The electron-transfer reaction is facilitated by increasing solvent polarity, since diffusional separation of products of opposite charge is hindered due to Coulombic effects and a fast rate of back electron transfer.

Surface-functionalized poly(propylene imine) dendrimers with tertiary amine functions in the core may serve as potential electron donors to $^3C_{60}$ in apolar solvents as a result of the intrinsic barrier to back electron transfer formed by the surface shell. Having different generations of poly(propylene imine) dendrimers available from a stepwise repetitive synthetic route using diaminobutane as a central core,[7] we investigated their reactivity after functionalization toward photoexcited C_{60}.

End-group modification of poly(propylene imine) dendrimers (DAB-*dendr*-$(NH_2)_n$; $n = 4, 8, 16, 32, 64$), is accomplished using the *N*-hydroxy-succinimide ester of *N*-(*tert*-butoxycarbonyl)-L-phenylalanine (*N*-*t*-BOC-L-Phe) and produces the corresponding DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$ functionalized dendrimers.[8] The fifth generation structure possesses a strong hydrogen bonded and highly packed shell and is referred to as the dendritic box.[8] In addition to the formation of a surface barrier against back electron transfer, functionalization of the primary amine end groups is necessary to prevent ground-state reactions with C_{60}.[9]

Cyclic voltammetry of DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_{64}$ reveals an irreversible oxidation wave at about 0.85 V vs. SCE (CH_2Cl_2 solution, 0.1 M Bu_4NBF_4). Preliminary studies have shown that DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_{64}$ can serve as an electron donor towards strong electron acceptors like tetracyanoquinodimethane (TCNQ) in dichloromethane, affording $TCNQ^{\odot\ominus}$.[10]

The UV/vis absorption spectrum of a mixture of C_{60} (5×10^{-4}M) and DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$, ($n = 4$, 8, 16, 32, 64; 0.5 mg/ml) in toluene is a linear superposition of the spectra of the two components and no ESR signal can be detected for the mixture. Apparently there is no significant charge-transfer interaction in the ground state at the concentrations employed. After illumination of this mixture with $n = 64$ for only 5 s with filtered light (to remove unwanted UV and IR) of a 500 W mercury lamp, the ESR spectrum (recorded in the dark) reveals the formation of fullerene anions ($C_{60}^{\odot\ominus}$), characterized by a transition at $g \approx 2.000$.[11]

Figure 2 shows the ESR spectra recorded in the dark for the whole series ($n = 4, 8, 16, 32, 64$) after 2 min illumination. Each of the spectra for $n = 8$–64 exhibits two individual absorptions at $g = 2.0005(1)$ ($\Delta H_{pp} = 0.03$ mT) and $g = 2.0001(1)$ ($\Delta H_{pp} = 0.08$ mT). Surprisingly, these ESR

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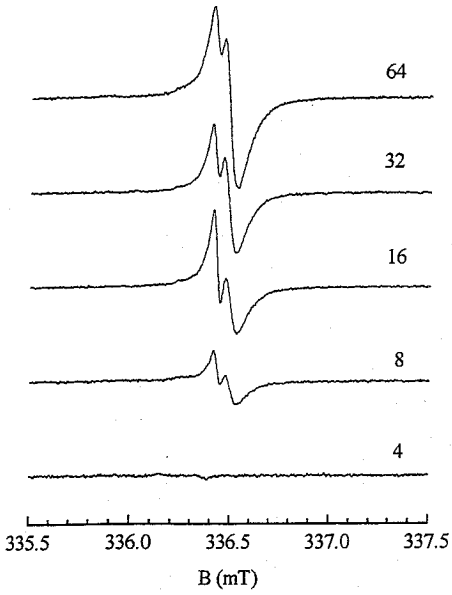

Fig. 2. ESR spectra observed after 2 min photoexcitation of a solution of functionalized poly(propylene imine) dendrimers (0.5 mg/ml DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$, n = 4, 8, 16, 32, 64) in toluene containing 5×10^{-4}M C_{60} at 295 K. All spectra were recorded with the light switched off, 2 mW microwave power, and modulation amplitude 0.025 mT. Spectra recorded at different frequencies were shifted horizontally to align g factor.

signals are not detected for $n = 4$. The ESR spectra for $n = 8$–64 are virtually identical to those recently reported by Stasko et al. in electron transfer reactions to C_{60} after photoexcitation of colloidal TiO_2 toluene/methanol solutions:[12] the $g = 2.0001$ signal was attributed to $C_{60}^{\odot\ominus}$ and the $g = 2.0005$ signal was tentatively assigned to $C_{60}^{2\ominus}$, although for the latter no definite identification was reached. Figure 2 reveals that the relative intensity of the two ESR signals varies somewhat with dendrimer generation. Slight variations were also observed among different samples of the same dendrimer, depending on concentration, irradiation time, and the time that passed before the ESR spectrum was recorded. In closed ESR tubes both signals are very persistent and no decay was detected over several days.

Recently, there has been discussion of the ESR spectra of fulleride anions $C_{60}^{\odot\ominus}$ and $C_{60}^{2\ominus}$.[12–16] While it is undisputed that the g factor associated with fulleride anions is considerably less than that of the free electron ($g = 2.0023$), strongly different opinions exist on the line width (or inverse spin relaxation time T_2) associated with $C_{60}^{\odot\ominus}$ at room temperature in solution. In particular, it has been argued that the sharp signals observed in solutions containing $C_{60}^{\odot\ominus}$, similar to the signals observed in the present study, are due to an as yet unidentified species with lower symmetry and slower molecular rotation than $C_{60}^{\odot\ominus}$.[13]

Unambiguous evidence for the persistent photoinduced formation of $C_{60}^{\odot\ominus}$ in the presence of functionalized dendrimers, however, comes from the anisotropic ESR spectrum recorded at 5 K and low microwave power (Fig. 3). Nearly identical spectra have been observed for

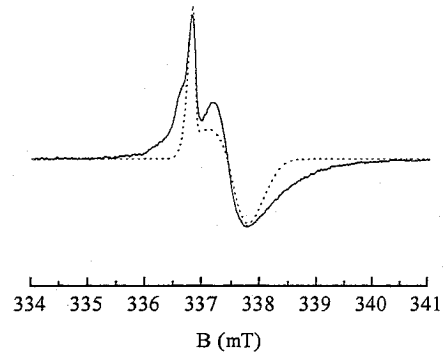

Fig. 3. ESR spectrum observed after 2 min photoexcitation of a dendrimer solution (0.5 mg/ml DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_{64}$) in toluene containing 5×10^{-4}M C_{60}. The spectra were recorded with the light switched off with parameters: Temperature 5 K, microwave power 20 μW, modulation amplitude 0.032 mT. The dotted line is a simulation of the anisotropic spectrum using $g_\perp = 1.9943$ and $g_\parallel = 1.9993$ with ($\sigma_\perp = 0.61$ mT and ($\sigma_\parallel = 0.10$ mT [13].

electrochemically generated $C_{60}^{\odot\ominus}$ in frozen toluene-acetonitrile[13] and for sodium(dibenzo-18-crown-6) $^{\oplus}C_{60}^{\odot\ominus}$ in 2-methyltetrahydrofuran.[14] The anisotropic spectrum can be simulated by an axially symmetrical g tensor, but the agreement is not perfect in the outer wings of the spectrum, possibly due to g-strain.[13,14] Our experiments confirm the observation reported by Eaton et al. that the small shoulder on the low-field edge of the 5 K spectrum evolves to the sharp signal with increasing temperature.[13]

In order to assess the mechanism of the photoinduced electron transfer reaction, we performed ESR experiments under continuous illumination. In the absence of functionalized dendrimers, continuous irradiation of C_{60} in toluene produces the ESR spectrum of $^3C_{60}$ (Fig. 4), consisting of a single narrow line ($\Delta H_{pp} = 0.015$ mT when recorded with a modulation amplitude of 0.0063 mT) centered at $g = 2.0013(1)$.[17] This signal can no longer be detected when

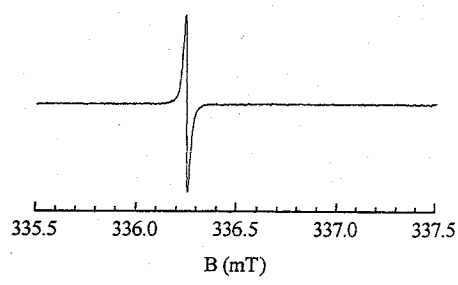

Fig. 4. ESR spectrum of $^3C_{60}$ in toluene recorded during photoexcitation of a 5×10^{-4}M toluene solution of C_{60} at 295 K. The spectrum was measured with 2 mW microwave power and a modulation amplitude of 0.025 mT.

the light is switched off, consistent with the reported life time of $^3C_{60}$ in toluene (about 40 s).[4] Continuous illumination of a solution of C_{60} in the presence of DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$ (n = 8–64) produces the ESR signals of both $^3C_{60}$ and $C_{60}^{\odot\ominus}$. Under these conditions, the intensity of $^3C_{60}$ is considerably less than that of a sample without dendrimers

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present, while the intensity for $C_{60}^{\odot\ominus}$ is continuously increasing with illumination time. These observations are consistent with the mechanism shown in Figure 1 in which photoexcitation of C_{60} and subsequent intersystem crossing to the triplet manifold is followed by a reductive quenching of the resulting $^3C_{60}$ state by DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$.

Recent ESR studies have shown that metastable $C_{60}^{\odot\ominus}$ ($t_{1/2}$ of the order of minutes) can be formed in solution after photoexcitation of C_{60} using triethylamine (TEA) as a donor.[18] In these experiments the concentration of $C_{60}^{\odot\ominus}$ formed after irradiation was shown to depend critically on solvent polarity, being two orders of magnitude larger in a polar solvent (1:1 acetonitrile/toluene) as compared to an apolar solvent (toluene).

To further check that in our experiments the persistent formation of $C_{60}^{\odot\ominus}$ in toluene has to be associated with the functionalized dendrimer as a donor, we performed light-induced ESR experiments on C_{60} in toluene (5×10^{-4}M) in the presence of 0.5 mg/ml tripropylamine (TPA, representing the interior of the dendrimer) or 0.5 mg/ml propylamine substituted with *N*-(*tert*-butoxycarbonyl)-L-phenylalanine ($CH_3CH_2CH_2NH$-*t*-BOC-L-Phe, representing the shell of the dendrimer) as donors. In both cases, the ESR spectrum, recorded under continuous illumination and with identical spectrometer settings as employed for the functionalized dendrimers, showed the transient signal of $^3C_{60}$ only (although of low intensity in case of TPA). No ESR signal was observed after stopping the illumination. In the more polar solvent mixture 1:1 acetonitrile/toluene, we do observe the formation of $C_{60}^{\odot\ominus}$ with TEA, in agreement with the results reported by Stasko et al.[18]

We conclude that the functionalized dendrimers are more effective donors by at least two orders of magnitude than small model compounds representing their core or shell. Additionally, this size effect of the donor in $C_{60}^{\odot\ominus}$ formation is illustrated by the generation-dependent donor properties of DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_n$ dendrimers (Fig. 2): persistent photoinduced electron transfer to C_{60} requires a higher generation dendrimer ($n \geqq 8$; $G \geqq 2$).

The persistence of the $C_{60}^{\cdot\ominus}$ ESR spectrum over several days at room temperature in toluene can be explained by a fast intramolecular fragmentation and/or disproportionation reaction of initially formed aminium radicals, that ensures that the photochemical electron transfer is irreversible and provides for a diamagnetic counter ion. This intramolecular reaction is consistent with the absence of $C_{60}^{\odot\ominus}$ after irradiation of DAB-*dendr*-(NH-*t*-BOC-L-Phe)$_4$ or of small model compounds that represent various parts of the functionalized dendrimer.

In conclusion, we have shown that functionalized dendrimers can serve as a efficient electron donors in quenching photoexcited states. The generation-dependent persistence of the electron-transfer reaction nicely demonstrates that dendrimers develop new properties at higher generations.

Experimental

The preparation of poly(propylene imine) dendrimers and the procedure for functionalization with *N*-*t*-BOC-L-Phe have been described elsewhere [7,8]. High purity C_{60} (99.9 %) was obtained from Syncom b.v. (Groningen, The Netherlands). Samples were prepared under dry and oxygen-free nitrogen atmosphere in degassed toluene. ESR spectra were recorded on a Bruker ER200D X-band spectrometer. Optical excitation was provided by a 500 W Hg lamp (Müller-Osram) and light was focused on the sample in a TE_{102} X-band cavity after passing a 50 mm water filter, a Pyrex glass filter, and a 50 % transmission grid. *g*-Factors were determined versus DPPH ($g = 2.0036$) as an external reference attached to the outside of the sample tube. Temperature was controlled by a Bruker ER4111 VT variable temperature unit between 100 K and 300 K, or by an Oxford 3129 temperature controller combined with an ESR900 continuous flow cryostat in the range from 3.8–100 K.

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Design of Conducting Redox Polymers: A Polythiophene-Ru(bipy)$_3^{n\oplus}$ Hybrid Material**

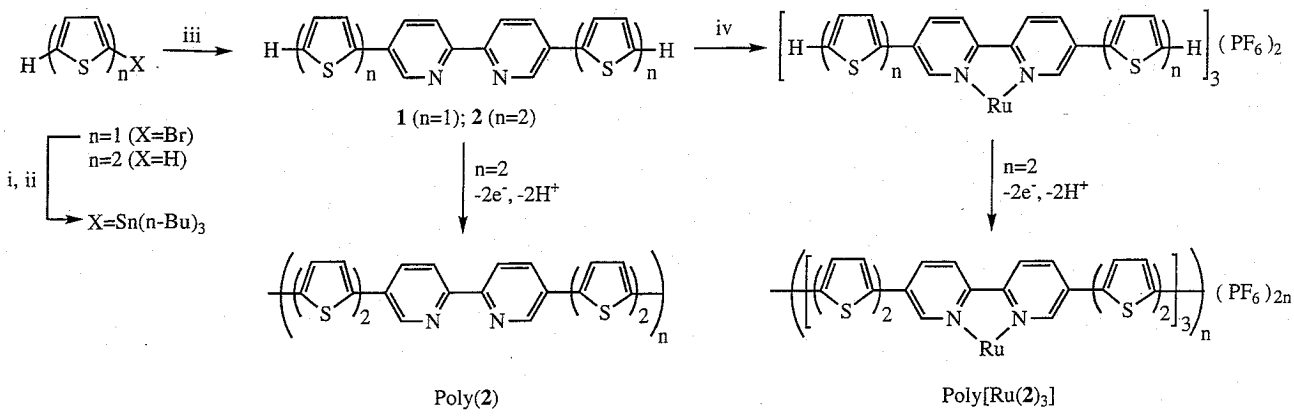
By *S. Sherry Zhu* and *Timothy M. Swager**

Many metal oxides and halides derive their conducting and magnetic properties from rapid self-exchange between metals in mixed oxidation states or from delocalized fractional valence states.[1] Hence, hybrid molecular systems derived from conjugated organic polymers which incorporate redox-active transition metal centers represent a promising approach to materials which display similar properties.

Although there have been extensive investigations of polymers with redox-active metal centers,[2,3] there have been few examples of materials in which the metal-free organic portion is delocalized and electronically conductive.[4] The notion that a conductive polymer should be an efficient conduit for the electron transport makes intuitive sense. However, there is much to learn about how the degree of electronic communication between the redox centers and the polymer can influence the conductive and electrochemical properties of such materials. This understanding is certain to be useful for the development of materials for electrocatalytic,[5] sensory, and magnetic applications. Toward this end, we report herein the synthesis of a conducting polythiophene–Ru$^{2\oplus}$(bipy)$_3$ hybrid material as well as the polymers derived from the non-metallated ligand. We find that this hybrid system exhibits high redox conductivity involving self-exchange between localized Ru$^{n\oplus}$ sites and thereby confirms the merits of this approach.

Our choice of Ru$^{2\oplus}$(bipy)$_3$ centers as the redox component is the result of the broad manifold of reversible electrochemical activity displayed by this type of complex.[6] To achieve a maximum interaction between the polymer and the metal, the bipyridine ligands are incorporated directly into the polymer backbone. The thiophene residues were chosen to allow the polymer synthesis by electrochemical oxidation.[7] The first ligand investigated was 5,5′-bis(2″-thiophene)-2,2′-bipyridine, **1** (Scheme 1), which is produced as a yellow solid by palladium-catalyzed Stille coupling.

Speculating that maximal delocalization is desirable, we chose all-*para* substitution in the bipyridyl group, which yields a conjugated path between the thiophene residues of **1**. The red Ru$^{2\oplus}$(**1**)$_3$ complexes can be readily isolated by standard methods,[8] and these complexes were found to display electrochemical behavior (Table 1) typical of Ru$^{2\oplus}$(bipy)$_3$ except that the redox potentials are more positive. Unfortunately, neither **1** or Ru$^{2\oplus}$(**1**)$_3$ polymerize electrochemically, and in both cases we observe an irreversible ligand-based oxidation at 1.14 V which does not result in polymer deposition.



Scheme 1. i) *n*-BuLi, THF, −78 °C. ii) (*n*-Bu)$_3$SnCl, THF, rt, 6h. iii) 5,5′-dibromo-2,2′-bipyridine [15], Pd(PPh$_3$)$_2$Cl$_2$, DMF, 80–90 °C, 10 h. iv) RuCl$_3$ · *x*H$_2$O, DMF, reflux, 12 h, N$_2$.

Reasoning that extended thiophene units will reduce the potential at which the complexes oxidize and will stabilize the cation radicals, which are presumed to be intermediates

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