Photoinduced electron transfer to C60 across extended 3- and 11-bond hydrocarbon bridges: Creation of a long-lived charge separated state

Williams, R.M.; Koeberg, M.; Lawson, J.M.; An, Y-Z.; Rubin, Y.; Paddon-Row, M.N.; Verhoeven, J.W.

Published in:
Journal of Organic Chemistry

DOI:
10.1021/jo960678q

Link to publication

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)
Photoinduced Electron Transfer to C₆₀ across Extended 3- and 11-Bond Hydrocarbon Bridges: Creation of a Long-Lived Charge-Separated State

René M. Williams,§ Mattijs Koebert,† James M. Lawson,† Yi-Zhong An,† Yves Rubin,§ Michael N. Paddon-Row,§,† and Jan W. Verhoeven,§

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, School of Chemistry, University of New South Wales, Sydney, New South Wales 2052, Australia, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received April 12, 1996

Two new, rigid donor–bridge–C₆₀(acceptor) dyads are presented. In one system (C₆₀[3]TMPD) a 3-α-bond bridge separates the fullerene from a powerful tetraethyl-p-phenylenediamine donor; in the other (C₆₀[11]DMA) the bridge comprises an extended array of 11 bonds, while the donor unit is a dimethylaniline group. Photoexcitation of the 3-bond system induces fast (Kₛ ≥ 1.6 × 10¹⁰ s⁻¹) and virtually complete intramolecular charge separation, irrespective of solvent polarity. It is concluded that this charge separation occurs under nearly “optimal” conditions. Charge recombination, however, is also very fast, preventing the detection of the charge-separated state on a nanosecond time scale. For the 11-bond system, photoinduced charge separation only occurs in polar solvents, reaching Kₛ = 5.5 × 10⁸ s⁻¹ in benzonitrile, which still implies a charge separation yield of ~90%. Interestingly, charge recombination is now slowed down considerably, thereby allowing easy detection of the “giant dipolar” charge-separated state of C₆₀[11]DMA with a lifetime of ca. 0.25 μs. The experimental results, together with semiempirical MO calculations, indicate that the special symmetry properties of the fullerene σ-system may cause it to enter into very strong electronic coupling with the hydrocarbon bridge to allow fast photoinduced charge separation, while at the same time the electronic coupling relevant for charge recombination remains small.

Introduction

Fullerenes¹–² are characterized by remarkably strong electron-accepting properties.³ Stable multianions can be generated,⁴ in contrast to the corresponding cationic species, which are very unstable.⁵ The electron-accepting properties of fullerenes, in combination with their electronic absorption characteristics⁶ extending over most of the visible region, make them promising chromophores. Photophysical properties of the fullerenes, see: Foote, C. S. In Advances in Chemistry 1993, 5055, 1.6 × 10¹⁰ s⁻¹


to 11 bonds in C_{60}[11]DMA,\(^{11}\) in an effort to increase the lifetime of the charge-separated state. This "norbornyllogous" bridge comprises linearly fused norbornane and bicyclo[2.2.0]hexane units and is well-known to be an efficient mediator of through-bond coupling.\(^{12}\) We have, in fact, previously demonstrated\(^{13}\) that separation of an electron donor and acceptor by longer extended hydrocarbon bridges can be applied as a tool to decrease the rate of charge recombination while still maintaining a sufficiently high rate of charge separation.

### Experimental Section

#### Syntheses

The syntheses of the systems C_{60}[3]DMA, C_{60}[11]DMA, and C_{60}[11]TMD have been previously reported.\(^{14}\) The system C_{60}[3]TMPD was synthesized in a similar manner as C_{60}[3]DMA, using an in situ generation of N-(4-(dimethylamino)phenyl)glycine from its ethyl ester, followed by a two-phase water/toluene reaction system for decarbonylation and addition to C_{60} (see supporting information).

#### Photophysical Measurements

Fluorescence emission and excitation spectra were recorded on a SPEX Fluorolog 2 instrument equipped with a red sensitive GaAs photomultiplier (RCA C31034, Peltier cooled) for which the spectral response extends to 890 nm and is known to be quite flat from the UV to about 860 nm.

Fluorescence spectra were measured on dilute solutions (10^{-4} M) using a 570 nm (emission path) cutoff filter. Excitation and emission bandwidths of 4.5 nm were employed, and no corrections were applied to the fluorescence spectra. Long integration times (10 s) and small increments (0.2 nm) were used.

For the determination of the fluorescence quantum yields, C_{60} in non-degassed methycyclohexane (\(\Phi_r = 2 \times 10^{-3}\)) was used as a standard.\(^{7a}\) The excitation wavelength was 470 nm, and the absorbance of both the reference and the sample was adjusted to 0.1 (1 cm) at this wavelength.

Temperature dependent fluorescence measurements were performed with an Oxford Instruments liquid nitrogen DN 1740 cryostat, equipped with an ITC4 control unit. Samples were degassed with three freeze–pump–thaw cycles at ca.

#### Results and Discussion

### Photophysical Properties of Fulleren Adducts. C_{60}[3]TMPD System

The UV−vis absorption of C_{60}[3]TMPD is very similar to that reported earlier\(^{7a}\) for C_{60}[3]DMA. However, while the spectral shape of its fluorescence spectrum is also typical for fullerene adducts [see ref 7a, and the next section], the quantum yield is strongly reduced, compared to that of, for example, C_{60}[3] in all solvents investigated (see Table 1). As we reported earlier,\(^{7a}\) such a reduction in fluorescence quantum yield occurs for C_{60}[3]DMA only in polar solvents. Intramolecular charge separation was implied as the quenching mechanism in the latter system, and this mechanism also appears to be operating in C_{60}[3]TMPD, irrespective of solvent polarity. In accordance with this deduction, the quenched local fluorescence of the fullerene chromophore in C_{60}[3]TMPD is fully restored upon addition of trifluoroacetic acid (TFA) to a solution of C_{60}[3]TMPD in dichloromethane. Protonation of the nitrogen atoms of the TMPD unit reduces its electron-donating capacity and thus prevents charge transfer (see Table 1).

### Table 1. Fluorescence Quantum Yields (Absolute and Relative to Acceptor Reference System C_{60}[3]) of C_{60}[3]TMPD in Various Solvents of Increasing Dielectric Constant (\(\varepsilon\)) and the Rate of Photoinduced Charge Separation (k_{cs}) As Estimated via eq 1

<table>
<thead>
<tr>
<th>solvent</th>
<th>(\varepsilon)</th>
<th>(\Phi_r) (relative in %)</th>
<th>(k_{cs}) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>methycyclohexane</td>
<td>2.07</td>
<td>1.3 \times 10^{-5} (3)</td>
<td>2.5 \times 10^{10}</td>
</tr>
<tr>
<td>toluene</td>
<td>2.38</td>
<td>1.6 \times 10^{-5} (4)</td>
<td>1.9 \times 10^{10}</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>8.93</td>
<td>2.0 \times 10^{-5} (4)</td>
<td>1.9 \times 10^{10}</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>25.20</td>
<td>3.2 \times 10^{-5} (7)</td>
<td>1.0 \times 10^{10}</td>
</tr>
<tr>
<td>dichloromethane/TFA</td>
<td>4.4 \times 10^{-4} (100)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

10^{-5} mbar. Relative fluorescence intensities were determined by spectral integration.

Absorption spectra were recorded on a CARY 3 spectrophotometer, using a 0.5 nm bandwidth.

Transient absorption (TA) spectra were obtained using a gated optical multichannel analyzer, from EG&G instruments, as described earlier.\(^{15}\) For excitation and white probe sources, the third harmonic of a Nd-YAG laser (355 nm, nanosecond pulses) and a 450 W high-pressure Xe arc (white light 300–880 nm) coupled to a Müller Elektronik MSP05 pulser were used, respectively. The excitation beam is at right angles to the probing beam. The probing path length is 1 cm. Samples were adjusted to an absorption of 1.5 (1 cm) at the excitation wavelength. Laser power was 7 mJ per pulse (0.2 cm²).

For the determination of the lifetime of the charge-separated state, the sample was degassed with several freeze–pump–thaw cycles.

Fluorescence lifetimes were measured with time-correlated single photon counting using a Hamamatsu microchannel plate (R 3809) detector in a setup slightly modified from that previously described,\(^{16}\) employing a frequency-doubled DCM dye laser which is synchronously pumped with a mode-locked argon ion laser resulting in 317 nm 20 ps FWHM pulses of 16 nJ. Decays were analyzed with a home-written deconvolution program.

Spectroscopy grade solvents were used in all determinations. Benzonitrile was distilled over P₂O₅ before use.

Semiempirical calculation were performed with a Silicon Graphics Indigo using the package Spartan.\(^{17}\)
constant \((k_{cs})\) can be made via eq 1:

\[
k_{cs} = \frac{\Phi_{ref}/\Phi - 1}{\tau_{ref}}
\]

The results of this estimate are compiled in the last column of Table 1.

Interestingly, in contrast to \(C_{60}\)[3]DMA, the rate of photoinduced charge separation in \(C_{60}\)[3]TMPD displays only a minor solvent dependence (if any) even tends to decrease in more polar solvents. As we have discussed previously,\(^{13b}\) this implies that charge separation occurs under nearly optimal conditions in the sense of the Marcus theory. Under such conditions, the effect of increasing the driving force by moving to more polar solvents can be fully compensated, or even slightly overcompensated, by the concomitant increase in solvent reorganization energy.

While an increase in the donor strength at constant bridge length resulted in optimization of the charge separation process, nanosecond time scale TA measurements performed on \(C_{60}\)[3]TMPD in various solvents did not allow any transient to be observed. Thus in all solvents the lifetime of the charge-separated state is below the nanosecond time scale, as observed earlier for the \(C_{60}\)[3]DMA system,\(^{7a}\) as well as for other donor-bridge-\(C_{60}\) systems involving a short bridge\(^{10}\) in polar solvents.

The \(C_{60}\)[11]DMA and \(C_{60}\)[11] Systems. The absorption and fluorescence spectra of \(C_{60}\)[11]DMA in methylcyclohexane at room temperature (Figures 2A, full range; 2B, expansion above 550 nm).

Figure 2. Vis absorption and fluorescence emission spectra of compound \(C_{60}\)[11]DMA in methylcyclohexane at room temperature (A, full range; B, expansion above 550 nm).

Table 2. Fluorescence Quantum Yields (Absolute and Relative) of \(C_{60}\)[11]DMA in Solvents with Various Dielectric Constants

<table>
<thead>
<tr>
<th>solvent</th>
<th>(\epsilon)</th>
<th>(\Phi_{fl}) (relative in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane</td>
<td>2.07</td>
<td>4.37 \times 10^{-4} (100)</td>
</tr>
<tr>
<td>toluene</td>
<td>2.38</td>
<td>4.26 \times 10^{-4} (97)</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>2.21</td>
<td>2.32 \times 10^{-4} (53)</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>9.93</td>
<td>1.35 \times 10^{-4} (30)</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>25.20</td>
<td>0.56 \times 10^{-4} (12)</td>
</tr>
</tbody>
</table>

The absorption spectra of \(C_{60}\)[11]DMA in methylcyclohexane.

Absorption maxima are observed at 406 (sh), 434, 480 (sh), 548 (sh), 609, 614, 638, 670, 682 (sh), 692, 703, 717 nm (which is presumably a hot band). Fluorescence maxima are observed at 690 (hot band), 706.6, 718, 742, and 787 nm. The system has a very minor Stokes shift (56 cm\(^{-1}\)) and an \(\epsilon_{\text{ex}}\) of 1.76 eV (705 nm).

The fluorescence excitation spectra for \(C_{60}\)[11]DMA are in excellent agreement with its absorption spectra, indicating "normal" photophysical behavior and the absence of interfering impurities.

Fluorescence quantum yields of \(C_{60}\)[11]DMA in different solvents are given in Table 2. Interestingly, and in analogy to \(C_{60}\)[3]DMA, the fluorescence intensity decreases markedly on going to more polar solvents (see Table 2).

By contrast, \(C_{60}\)[11] displays a virtually solvent independent fluorescence (quantum yield = \(4.05 \times 10^{-4}\)), analogous to the behavior of \(C_{60}\)[3]DMA. Both the fluorescence of \(C_{60}\)[11]DMA and its TA spectrum show a marked solvent dependence. Thus, in nonpolar solvents the nanosecond TA spectra of \(C_{60}\)[11]DMA and \(C_{60}\)[11] are identical and are very similar to that described earlier\(^{7a}\) for \(C_{60}\)[3]DMA. These spectra stem from the triplet state of the fullerene unit which is populated via the fast and almost quantitative intersystem crossing in the \(C_{60}\) chromophore. While \(C_{60}\)[11] and \(C_{60}\)[3] still display the same TA spectra in polar media, the TA spectrum of \(C_{60}\)[11]DMA changes drastically. Thus, in benzonitrile (see Figure 3) a characteristic absorption around 460 nm is observed, and this is attributed to the radical cation of the dimethylaniline chromophore, with a lifetime of 0.25 \(\mu\)s!

Furthermore, absorptions at 750 and especially at 590 nm, which can be attributed to the radical anion of the fullerene moiety,\(^{9c}\) possess the same lifetime as the radical cation of the dimethylaniline chromophore.

The ratio of signal intensities for the \(C_{60}\)[11]DMA samples in methylcyclohexane and benzonitrile (taken...
under similar conditions) is almost equal to the ratio of the extinction coefficients of, respectively, the triplet–
triplet absorption of the fullerene moiety (16700 L mol⁻¹ cm⁻¹ at 692 nm) and the dimethylaniline radical cation (4800 L mol⁻¹ cm⁻¹ at 460 nm). This indicates that the yield of charge transfer state formation in benzonitrile is ≥ 90%.

The solvent dependence of the fluorescence and the TA spectra for C₆₀[11]DMA clearly indicate that in polar solvents an intramolecular charge separation occurs that quenches the locally excited state, thereby creating a long-lived charge transfer state.

While earlier preliminary time-resolved fluorescence experiments on C₆₀[11]DMA, in which the DMA chromophore was excited, indicated that the UV emission emerging from this chromophore is strongly quenched by energy (or electron) transfer, the fluorescence decays now observed for the red emission at 707 nm of the fullerene using single photon counting in methylcyclohexane give a fluorescence lifetime of 1344 ± 10 ps for both C₆₀[11]-DMA and C₆₀[11]. In the polar solvent benzonitrile, in which both luminescence and population of the triplet state for C₆₀[11]DMA are strongly quenched, fluorescence decay from the fullerene unit displays a major fast component of 160 ± 10 ps.

The rate of charge separation for C₆₀[11]DMA in benzonitrile is estimated from eq 2 to be k₀ = 5.5 × 10⁹ s⁻¹:

\[ k_0 = 1/\tau - 1/\tau_{ref} \]  

In this equation, the lifetime of C₆₀[11]DMA (or C₆₀[11]) in methylcyclohexane is taken to be equal to \( \tau_{ref} \). Application of eq 1 to the quantum yield data from Table 2 gives a quite similar value for \( k_0 \): 5.1 × 10⁹ s⁻¹.

From these data the quantum yield for charge separation via the excited singlet state of the fullerene unit is estimated to be k₀[1/τ[ref] + k₀] × 100 = 87–88%, which is in excellent agreement with the estimate made from the transient absorption spectra.

In order to determine the barrier for electron transfer experimentally, the temperature dependence of the fluorescence quantum yield of C₆₀[11]DMA in benzonitrile was investigated (see Table 3 for primary data). As a reference, C₆₀[11] was employed, for which the fluorescence quantum yield is virtually temperature independent. From these measurements, electron transfer rates were derived via eq 1. Linear regression for a plot (see Figure 4) of the natural logarithm of the electron transfer rates multiplied by the square root of \( T \), as a function of 1/T, leads to an intercept of 28.64 (= ln k₀[ref] (s⁻¹ K⁰.⁵)) and a slope of 103.81 (= ΔG[ref](K)). The barrier of electron transfer is therefore determined to be ΔG# = 0.09 eV, and the charge separation rate under barrierless conditions (k₀[ref]) is 2.75 × 10¹² s⁻¹ (K⁰.⁵).

The conformation of the adduct C₆₀[11]DMA obtained by energy minimization with semiempirical AM1 calculations is shown in Figure 5. The center-to-center distance between the two chromophores is estimated to be ca. 18 Å; the edge-to-edge distance is ca. 12.6 Å.

With these geometrical data in hand, together with the electrochemical and photophysical data for the constituent chromophores, the barrier to photoinduced electron transfer can also be predicted, in principle, from the Marcus equation (3):

\[ \Delta G# \text{cs} = (\Delta G_{cs} + \lambda)^2/4\lambda \]  

Here, ΔG₆₀ is the Gibbs free energy change and \( \lambda \) the total reorganization energy. The former can be approximated as proposed by Weller et al. via

\[ \Delta G_{cs} = \sigma(E_{ox}(D) - E_{rad}(A)) - E_0 - \epsilon^2/4\pi\epsilon_0 R_c - \epsilon^2/8\pi\epsilon_0(1/r^+ + 1/r^-)(1/37.5 - 1/\epsilon_s) \]  

Calculation of ΔG₆₀ from eq 4 requires, in addition to the donor and acceptor redox potentials (+0.71 V and −0.57 V vs SCE) and the singlet or triplet state energy (1.76 eV and 1.50 eV), knowledge of the center-to-center distance (Rc) and the effective ionic radii of the donor and acceptor radical cation and anion (r⁺ and r⁻, respectively). A value of 18 Å was estimated for Rc from our modeling results (Figure 5). Values for r⁺ and r⁻ were calculated from the apparent molar volumes of N,N-dimethylaniline (density = ρ = 0.956) and of C₆₀ (density 1.65), using a spherical approach.

\[ 4/3\pi R^3 = M/\rho \]  

Here, M is the molecular weight and N is Avogadro’s number. This gives r⁺ = 3.7 Å and r⁻ = 5.6 Å. The

---

(18) Shida, T. Electronic absorption spectra of radical ions (physical science data); Elsevier Science Publishers: Amsterdam, 1988.
(19) In n-hexane an energy or electron transfer rate of ca. 1.2 × 10¹⁰ s⁻¹ was observed; private communication from A. H. A. Clayton and K. P. Ghiggino, 1995.

---

**Table 3. Primary Data Used for the Determination of the Barrier to Charge Separation for C₆₀[11]DMA in Benzonitrile Relative Emission Yield (Φₒₒ) at Temperature (T) Together with the Rate of Electron Transfer Obtained via eq 1**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Φₒₒ</th>
<th>k₀ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.05</td>
<td>4.74 × 10⁸</td>
</tr>
<tr>
<td>290</td>
<td>1.09</td>
<td>4.47 × 10⁸</td>
</tr>
<tr>
<td>285</td>
<td>1.14</td>
<td>4.27 × 10⁸</td>
</tr>
<tr>
<td>280</td>
<td>1.20</td>
<td>4.04 × 10⁸</td>
</tr>
<tr>
<td>275</td>
<td>1.26</td>
<td>3.82 × 10⁸</td>
</tr>
<tr>
<td>270</td>
<td>1.32</td>
<td>3.59 × 10⁸</td>
</tr>
<tr>
<td>265</td>
<td>1.34</td>
<td>3.33 × 10⁸</td>
</tr>
</tbody>
</table>

---

**Figure 4.** Modified Arrhenius plot ln(kₒₒ × √T) = ln(kₒₒ) − (ΔGₒₒ/K₀) × 1/T for C₆₀[11]DMA obtained in benzonitrile.
Photoinduced ET to C₆₀ across Hydrocarbon Bridges

Table 4. Reorganization Energy (μ = λᵣ + 0.3 eV), Gibbs Free Energy Change (ΔGᵣ), and Barrier (ΔGₛᵣ) for Charge Separation in Various Solvents (Dielectric Constant ϵ, Refractive Index n) from Both the Singlet and Triplet (T) State of the Fullerene Chromophore in C₆₀[11]DMA, As Calculated via eqs 3, 4, and 6

<table>
<thead>
<tr>
<th>solvent</th>
<th>ϵ</th>
<th>n</th>
<th>λ(eV)</th>
<th>ΔGᵣ(eV)</th>
<th>ΔGₛᵣ(eV)</th>
<th>ΔGᵣ(T)(eV)</th>
<th>ΔGₛᵣ(T)(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane</td>
<td>2.07</td>
<td>1.423</td>
<td>0.33</td>
<td>0.61</td>
<td>0.58</td>
<td>0.87</td>
<td>1.09</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>2.209</td>
<td>1.422</td>
<td>0.36</td>
<td>0.53</td>
<td>0.40</td>
<td>0.79</td>
<td>0.80</td>
</tr>
<tr>
<td>toluene</td>
<td>2.38</td>
<td>1.497</td>
<td>0.40</td>
<td>0.50</td>
<td>0.48</td>
<td>0.72</td>
<td>0.35</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>4.20</td>
<td>1.35</td>
<td>1.01</td>
<td>0.01</td>
<td>0.25</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>9.93</td>
<td>1.552</td>
<td>1.02</td>
<td>-0.32</td>
<td>0.12</td>
<td>-0.06</td>
<td>0.23</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>25.20</td>
<td>1.528</td>
<td>1.20</td>
<td>-0.47</td>
<td>0.11</td>
<td>-0.21</td>
<td>0.20</td>
</tr>
</tbody>
</table>

A units, which may even be sufficiently strong to bring the electron transfer processes into the adiabatic regime.

The high rate of photoinduced charge separation, as opposed to the relatively slow recombination in C₆₀[11]DMA, is surprising because both the calculated and experimentally determined barriers to charge separation (0.11 and 0.09 eV, respectively) are significantly higher than in systems for which we have previously observed fast photoinduced charge separation across bridges of similar length. It is therefore interesting to compare the electronic coupling matrix element (V*) involved in the excited state charge separation process for C₆₀[11]DMA with that determined earlier for other bridged systems. This can be done readily using the nonadiabatic expression for electron transfer processes given by eq 7:

\[ kₛ = \frac{2\pi^{3/2}}{hV^*} \exp\left(-\frac{\Delta Gₛ}{kₜT}\right) \]  

Substitution of \( kₛ(5.5 \times 10^9 \text{ s}^{-1} \text{ at 300 K}) \) and \( \Delta Gₛ(0.09 \text{ eV}) \), together with an estimated total reorganization energy of 1.2 eV (see Table 4), leads to \( V^* = 28 \text{ cm}^{-1} \). Table 5 presents a compilation of values of coupling matrix elements for excited state electron transfer (V*) and for thermal electron transfer (V) in a variety of donor–bridge–acceptor systems possessing effective bridge lengths ranging from four to ten \( \sigma \) bonds. In Figure 6, the V* and V values are plotted semilogarithmically against the number, \( n \), of \( \sigma \) bonds in the bridge for each series of systems. The plots display the expected (approximate) exponential decay of V and V* with bridge length (n).

In spite of the fact that the data compiled in Table 5 refer to a variety of bridges and D/A chromophores, it is evident that the V* value of ca. 30 cm⁻¹ determined for C₆₀[11]DMA is exceptionally large, and in fact exceeds the expected value for an 11-bond bridge by about an order of magnitude. The only report of similarly large V values refers to extrapolation of the work of Penfield et al., who measured the intervalence absorption bands in the anion radicals of the DMN[6]DCV series of molecules, arising from through-bond electronic coupling between the 1,1-dicyanovinyl (DCV) radical anion and the 1,4-dimethoxy-naphthalene (DMN) unit, across 4-, 6-, and 8-bond

The reorganization energy \( \lambda_r \) may be partitioned into internal \( (\lambda_i) \) and solvent \( (\lambda_s) \) contributions. The internal reorganization energy was set at \( \lambda_i = 0.3 \text{ eV} \), while \( \lambda_s \) was calculated using the Born–Hush approach (eq 6):

\[ \lambda_s = \frac{\varepsilon}{4\pi\epsilon_0}(1/\bar{r} - 1/R)(1/n^2 - 1/e_s) \]  

It is important to note that, due to the relatively small \( S_1 - T_1 \) energy gap of the fullerene tetramer, photoinduced charge separation from the \( T_1 \) state becomes possible in solvents more polar than diethyl ether. Furthermore, the calculated barrier (0.11 eV) for electron transfer in benzonitrile is in reasonable agreement with the experimental value (0.09 eV). As we have shown earlier, this agreement and the high linearity of the Arrhenius plot obtained (see Figure 4) are typical for electron transfer processes taking place in the "normal" Marcus region if performed in polar media.

It is to be noted that, due to the relatively small \( S_1 - T_1 \) energy gap of the fullerene tetramer, photoinduced charge separation from the \( T_1 \) state can also become exergonic in sufficiently polar media such as benzonitrile (see Table 4). As discussed above, however, charge separation from the \( S_1 \) state is so rapid in this solvent that it accounts for ca. 90% of the fullerene's \( S_1 \) decay modes, thereby overwhelming the otherwise efficient intersystem crossing of the fullerene chromophore \( (k_{isc} \approx 7.5 \times 10^8 \text{ s}^{-1}) \).

Evaluation of the Electronic Coupling Matrix Element for Charge Separation in C₆₀[11]DMA. The high rates of charge separation and recombination in C₆₀[3]DMA and C₆₀[3]TMPD are not surprising in view of the fact that bridges with an effective length of three \( \sigma \) bonds are known to provide quite strong through-bond and through-space electronic coupling between the D and

Figure 5. Structure of C₆₀[11]DMA obtained with AM1.

calculated \( \Delta G \) values in various solvents are listed in Table 4 for both singlet and triplet charge separation.

The reorganization energy \( \lambda \) may be partitioned into internal \( (\lambda_i) \) and solvent \( (\lambda_s) \) contributions. The internal reorganization energy was set at \( \lambda_i = 0.3 \text{ eV} \), while \( \lambda_s \) was calculated using the Born–Hush approach (eq 6):

\[ \lambda_s = \frac{\varepsilon}{4\pi\epsilon_0}(1/\bar{r} - 1/R)(1/n^2 - 1/e_s) \]  

In agreement with the fluorescence data discussed above, it is found that the driving force for charge separation \( (\Delta G_r) \) from the fullerene \( S_1 \) state becomes positive in solvents more polar than diethyl ether. Furthermore, the calculated barrier (0.11 eV) for electron transfer in benzonitrile is in reasonable agreement with the experimental value (0.09 eV). As we have shown earlier, this agreement and the high linearity of the Arrhenius plot obtained (see Figure 4) are typical for electron transfer processes taking place in the "normal" Marcus region if performed in polar media.

It is to be noted that, due to the relatively small \( S_1 - T_1 \) energy gap of the fullerene tetramer, photoinduced charge separation from the \( T_1 \) state can also become exergonic in sufficiently polar media such as benzonitrile (see Table 4). As discussed above, however, charge separation from the \( S_1 \) state is so rapid in this solvent that it accounts for ca. 90% of the fullerene's \( S_1 \) decay modes, thereby overwhelming the otherwise efficient intersystem crossing of the fullerene chromophore \( (k_{isc} \approx 7.5 \times 10^8 \text{ s}^{-1}) \).

Evaluation of the Electronic Coupling Matrix Element for Charge Separation in C₆₀[11]DMA. The high rates of charge separation and recombination in C₆₀[3]DMA and C₆₀[3]TMPD are not surprising in view of the fact that bridges with an effective length of three \( \sigma \) bonds are known to provide quite strong through-bond and through-space electronic coupling between the D and

(23) It should be noted that the occurrence of charge separation in 1,4-dioxane once more testifies to the high micropolarity of this quadrupolar solvent, see: Suppan, P. J. Photochem. Photobiol. A 1990, 50, 293.
bridges. However, measurements of $V^*$ for photoinduced charge separation in the neutral DMN[\(n]\) DCV compounds by Oevering et al.\(^\text{13}\) gave much smaller values, which are much more in line with results obtained for other systems (see Table 5 and Figure 6). In the context of the Penfield et al. experiment, it should be noted that the radical anion of the DCV group is prone to distort by twisting about the C=C double bond, thereby concentrating the unpaired electron on the carbon atom of the vinyl group that is attached to the bridge. This may well enhance the magnitude of the electronic coupling, $V$, in the anion radicals of these systems and it is, therefore, even more striking that with the very diffuse $C_{60}$ acceptor an even stronger coupling in $C_{60}[11]$DMA is achieved.

We tentatively propose that the large $V^*$ for $C_{60}[11]$DMA is mainly related to the special orbital symmetry properties of the fullerene $\pi$-system. Preliminary semiempirical MO calculations are presented in the next section which lend support to this view.

Molecular Orbital Calculations. A simple frontier molecular orbital (FMO) description of photoinduced electron transfer in a D/A system in which the acceptor has the lowest excited state is given in Figure 7.

The HOMOs and LUMOs of D and A are labelled $d$, $d^*$ and $a$, $a^*$, respectively. Local acceptor excitation ($a \rightarrow a^*$) is followed by electron transfer involving orbital interactions between $d$ and $a$, while charge recombination involves interactions between $a^*$ and $d$. The FMO description is undoubtedly an oversimplification, which may, for example, neglect important interactions between charge transfer configurations and locally excited configurations.\(^\text{29}\) Nevertheless, it is a useful starting point for identifying important orbital interactions that contribute to the electronic coupling matrix elements involved in the photoinduced charge separation step, following local acceptor excitation (i.e., $V^*$ is related to $d/a$ interaction), and in the subsequent thermal charge recombination step (i.e., $V$ is related to $a^*/d$ interaction).

The MOs $a$, $a^*$ and $d$ of $C_{60}[11]$DMA are shown in Figures 8–10. These were obtained from AM1 calculations. Although the frontier orbitals are mainly localized on D or on A, it turns out that the highest occupied orbital of A (i.e., $a$) is extensively delocalized into the bridge and tailing out all the way into the donor domain (see Figure 8). Importantly, such delocalization into the bridge is found to a much lesser extent for $a^*$ (see Figure 9) and for $d$ (see Figure 10).

Although the AM1 calculations were performed on the ground state molecule and the electron densities in certain areas will certainly change if UHF calculations on the excited states and anionic or cationic species are performed, we presume that the extensively delocalized character of $a$ is a consequence of the special symmetry properties of the fullerene $\pi$-system. The relevant (pseudo) symmetry planes of the $C_{60}$ $\pi$-system are shown in Figure 11.

For planar $\pi$-systems such as that of naphthalene, plane II coincides with the nodal plane to which all $\pi$ orbitals are antisymmetric. While this is a typical property of any "normal" $\pi$-system, the $\alpha$ orbital of the fullerene system behaves quite atypical in being sym-

metrical with respect to plane II. As schematized in Figure 12 this allows orbital a of the fullerene to interact with the first carbon–carbon bond σ orbitals of the attached bridge (geminal bonds). By contrast, normal π orbitals, such as those of naphthalene, cannot couple with the geminal carbon–carbon orbitals of the bridge but only with the next bonds of the bridge (i.e., the vicinal bonds).

The fullerene–bridge coupling occurs through 12 π–σ interactions, as opposed to only two π–σ interactions for the case of planar π-chromophores. As indicated in the lower part of Figure 12, there are a total of eight vicinal (v) interactions and four geminal (g) interactions. The latter are strongly influenced by the pyramidal character of the C_{60} carbon atoms. Together, these couplings might well amount to a sizeable overall coupling matrix element.

This expectation is borne out by a preliminary natural bond orbital analysis which found that the strengths of the individual v and g couplings in the fullerene–bridge system are 1.0 and 0.7 eV, respectively, and are only slightly smaller than the value of 1.1 eV for each of the v pathways in the naphthalene–bridge system.

It seems important to note that whereas the fullerene HOMO a has the correct symmetry to mix with the bridge σ-HOMO, it cannot interact with the (symmetric) π orbital of the proximate double bond of the cyclohexene ring. Thus no contribution of the latter is found in a (see Figure 8) and the role of this double bond in mediating electron transfer appears to be minor, if any.

While the combination of pyramidalization of the constituent carbon atoms of the fullerene moiety, together with the matching (pseudo)symmetry properties of the fullerene HOMO a and the bridge σ-HOMO, might explain the exceptionally large electronic coupling (V*) for photoinduced charge separation for C_{60}[11]DMA, it should be noted that the orbitals involved in the charge recombination process, a* and d (Figure 7), do not delocalize as strongly into the bridge. Orbital d does
extend into the bridge, in a very skewed way, but it does not extend all the way to the fullerene acceptor. Although the fullerene LUMO a* is (pseudo) symmetric with respect to plane II, it is also symmetric with respect to plane I. The latter symmetry property enables it to mix with the bridge σ*-LUMO (which is symmetric with respect to plane I), but not with the bridge σ-HOMO (which is antisymmetric, Figure 12). Since it is known that π* orbitals couple strongly with the bridge σ orbitals, as well as with the bridge σ* orbitals, through-bond coupling involving the fullerene MO a* might be weaker than that involving the MO a. Consequently, charge recombination is not expected to be unusually fast, and indeed, the long lifetime of the charge-separated state (0.25 µs) appears to substantiate this, making the C_{60}[11]DMA dyad act in a "photodiode" fashion.

Concluding Remarks

The results presented above clearly indicate that excitation of C_{60}[11]DMA in a polar solvent (benzonitrile) gives rise to rapid charge separation, resulting in the formation of a long-lived charge-separated state. The ratio between the rates of charge separation and charge recombination for this system is in fact more than 3 orders of magnitude (k_{cs}/k_{cr} = 1400), where the estimated energy gap between the charge-separated state and the ground state (ΔG_{cr} ≈ −1.29 eV) in benzonitrile solvent is comparable to the total reorganization energy (λ ≈ 1.2 eV). Thus charge recombination cannot be slowed down significantly by "inverted region effects" as clearly is in systems such as those studied by Oevering et al. (see Table 5) in nonpolar media.

The exceptional photodiode properties of the C_{60}[11]-DMA dyad thus seem to be mostly due to the a high ratio of the electronic coupling elements for charge separation and charge recombination (V*/V), which is attributed to a combination of the symmetry properties of the fullerene π-system and the pyramidal nature of the fullerene constituent carbon atoms. This may provide a new approach to the design of donor−bridge−acceptor systems with enhanced k_{cs}/k_{cr} ratios, irrespective of solvent polarity. This goal may be achieved, in part, by replacing the N,N-dimethylaniline donor group in C_{60}[11]DMA with a more powerful donor moiety, such that the charge separation step takes place under essentially barrierless conditions. In view of the results presented for the C_{60}[3]TMPD system, which contains the strong p-phenylenediamine donor, it is likely that systems utilizing the equally potent p-phenylenediamine donor group might lead to systems that display fast and virtually barrierless charge separation, while at the same time maintaining a long lifetime of the charge-separated state, irrespective of solvent polarity. Such covalently functionalized donor−bridge−fullerene (acceptor) systems could then turn out to be interesting molecular building blocks in optoelectronic devices.

Acknowledgment. We thank A. H. A. Clayton and K. P. Ghiggino for making available the results of their measurements [ref 19] on quenching of the DMA singlet state in C_{60}[11]DMA. The present research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Scientific Research (NWO) and the Australian Research Council.

Supporting Information Available: Details of the synthesis and identification of C_{60}[3]TMPD including spectral data (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.