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Photoinduced Intramolecular Electron Transfer in a Bridged C$_{60}$ (Acceptor)—Aniline (Donor) System. Photophysical Properties of the First “Active” Fulleren Diad

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Abstract: A covalently functionalized fullerene comprising an electron donating aniline group coupled to the fullerene unit by a saturated heterocyclic bridge is shown to undergo a photoinduced intramolecular electron transfer process that causes quenching of the fluorescence of the adduct and strong decrease of triplet population in polar solvents. VIS-absorption, fluorescence and phosphorescence at 77 K, triplet—triplet absorption, time resolved fluorescence, and redox potentials of the fullerene adduct are presented. Analysis of the solvent dependence of the energetics of the photoinduced electron transfer is given and is in good agreement with the experimental results.

Table 1. Selected Photophysical Properties of C$_{60}$ and C$_{70}$

| & \( \Phi_0 \) & \( \tau_{1\phi(h)}^b \) & \( \Delta E^{0O}_{0} \) (eV) & \( \Phi_\Delta \) & \( \tau_{T1}^a \) & \( \Delta E^{0O}_{\Delta} \) (eV) |
|---|---|---|---|---|---|---|
| C$_{60}$ & 2 \times 10^{-4} & 1245 \pm 120 & 1.99 & \approx 1 & 325 \pm 20 \text{ ns} & 1.57 |
| C$_{70}$ & 5 \times 10^{-4} & 630 \pm 75 & 1.91 & \approx 1 & 790 \pm 20 \text{ ns} & 1.56 |


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charge separation can be feasible even when D and A are spaced up to 15 Å apart. Through bond interaction via the bridge contributes to the electronic coupling between donor and acceptor that is required for electron transfer.\(^6\)\(^5\) However, although the synthesis of several systems of the donor-bridge fullerene (acceptor) type has been described,\(^4\)\(^6\)\(^7\)\(^8\) no photoinduced intramolecular electron transfer in these covalently functionalized fullerenes has been found until now.

Here we report on the synthesis, characterization, and solvent dependence of the photophysical properties of a new donor-bridge-buckyball compound (I, see Figure 1), that indeed displays photoinduced intramolecular charge separation.

**Experimental Section**

**Syntheses.** The bridged fullerene (acceptor)-aniline(donor) system (1) was obtained by a 1,3 dipolar addition to CS\(_6\) (MER corporation) of the decarboxylated iminium ion formed from 4-(N,N-dimethylaniline)benzaldehyde and N-methylglycine following a procedure slightly modified from that described by Maggini et al.\(^7\)

\[ ^{1}H\text{NMR (400 MHz Bruker ARX 400, CS}_2,\text{ C}_6\text{D}_6 (3:1), 308 K) \delta (ppm) = 2.63, 3H, s, NCH}_3; 2.71, 6H, s, N(CH}_3); 4.04, 1H, d, CH (exo), J = 9.24 Hz; 4.71, 1H, s, CH; 4.74, 1H, d, CH (endo), J = 9.24 Hz; 6.55, 2H, d, CH (arom), J = 8.91 Hz; 7.68, 2H, d (br), CH (arom), J = 7.43 Hz; \]^13C NMR (400 MHz, CS\(_2\), C\(_6\)D\(_6\) (3:1), 300 K, APT) \(\delta \) (ppm) = 40.75, NCH\(_3\); 40.79, N(CH\(_3\)); 69.90, C\(_3\) sp\(_3\) C\(_6\) C\(_6\); 78.74 (C sp\(_3\) C\(_6\)); 84.39, CH; 113.35, CH (arom); 125.05, C\(_6\) (arom); 131.08, CH (arom); 136.73, 136.86, 137.72, 137.75, 140.71, 141.01, 141.12, 141.20, 142.57, 142.68, 142.87, 143.02, 143.03, 143.05, 143.12, 143.16, 143.18, 143.30, 143.34, 143.56, 143.63, 143.69, 144.03, 144.17, 145.40, 145.44, 145.71, 146.21, 146.22, 146.24, 146.27, 146.39, 146.48, 146.49, 146.55, 146.61, 146.81, 146.91, 147.08, 147.12, 147.15, 147.22, 147.32, 147.58, 147.72, 147.99, 148.23, 148.28, 151.06, 155.07, 155.14, 155.15, 157.64, C\(_6\) C\(_6\) and C\(_6\)N (arom); IR (KBr, Perkin-Elmer 1310) v (cm\(^{-1}\)) = 2940 (w), 2905 (w), 2830 (w), 2760 (m), 1605 (s), 1515 (s), 1458 (m), 1438 (m), 1422 (m), 1352 (m), 1328 (m), 1180 (s), 815 (m); Mass spectra were obtained with a JEOL mass spectrometer using field desorption, positive ion: calcd C\(_{71}\)H\(_{16}\)N\(_2\) 896.13134, found 896.1 (and 720 and 176.1).

**Results and Discussion**

Figure 2 shows the fluorescence and the VIS absorption of I in methylcyclohexane.

A beautiful symmetry of vibrational progressions is observed, a very minor Stokes shift (51 cm\(^{-1}\)) and an \(\lambda_E\_0\) of 14 207 cm\(^{-1}\) (704 nm, 1.76 eV). Absorption maxima are observed at (cm\(^{-1}\)) \(14 225, 14 468, 14 671, 14 952, 15 175, 15 708, 18 416 (sh), 20 886 (sh), 23 256, and 24 765. Fluorescence maxima are observed at (cm\(^{-1}\)) \(12 715, 13 504, 13 966, and 14 744. Furthermore a shoulder shows up at 14 440 cm\(^{-1}\) (see Figure 2A) that probably is a "hot band" (it is absent in low temperature emission, see later), and a similar feature can be seen at 13 970 cm\(^{-1}\) in the absorption spectrum.


Figure 2. VIS-absorption and fluorescence of compound 1 in methylcyclohexane at room temperature. The symmetry relation of the emission and absorption is emphasized by the lines in part A.

Vibrational spacings are in reasonable agreement with theoretical and experimental values for native C₆₀.¹¹ Fluorescence excitation spectra are in excellent agreement with the UV–vis absorption spectra, indicating "normal" photophysical behavior (like C₆₀ and C₇₀, see refs 1n–r and 2f), and the absence of interfering impurities.

Fluorescence quantum yields of 1 in different solvents are given in Table 2. Interestingly the adduct shows a sharp
Figure 3. Emission spectra of compound 2 at 77 K, in methylcyclohexane (upper spectrum) and in a methylcyclohexane, methyltetrahydrofuran, ethyl iodide (2:1:1) mixture (lower spectrum). The upper spectrum is vertically shifted. Bandwidth is 2.5 nm.

Table 2. Fluorescence Quantum Yields (Absolute and Relative) and Relative Triplet Quantum Yields of Compound 1 in Various Solvents of Increasing Dielectric Constant:

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\epsilon$</th>
<th>$\Phi_\text{f}$ (relative)</th>
<th>$\Phi_\text{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane</td>
<td>2.07</td>
<td>$6 \times 10^{-4}$ (100)</td>
<td>1</td>
</tr>
<tr>
<td>toluene</td>
<td>2.38</td>
<td>$5 \times 10^{-4}$ (83)</td>
<td></td>
</tr>
<tr>
<td>chloroform</td>
<td>4.70</td>
<td>$2.8 \times 10^{-4}$ (46)</td>
<td>0.85*</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>8.93</td>
<td>$0.2 \times 10^{-4}$ (3)</td>
<td>0.80*</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>9.93</td>
<td>$0.6 \times 10^{-4}$ (10)</td>
<td></td>
</tr>
<tr>
<td>benzonitrile</td>
<td>25.20</td>
<td>$0.2 \times 10^{-4}$ (3)</td>
<td>0.03</td>
</tr>
<tr>
<td>dichloromethane/TFA</td>
<td>6.40</td>
<td>$6 \times 10^{-4}$ (100)</td>
<td></td>
</tr>
</tbody>
</table>

Fluorescence quantum yields in dichloromethane and benzonitrile are near detection limit. Triplet yields in chloroform and dichloromethane (denoted with an asterisk) are estimates due to sample decomposition under laser irradiation.

decrease of fluorescence intensity upon going to more polar solvents. A strong indication that the quenching process responsible for this involves the electron donating substituent dimethylaniline is the fact that addition of 10 $\mu$L of trifluoroacetic acid (TFA) to a solution of 1 in dichloromethane (dcm) results in a sharp increase in the fluorescence intensity restoring it to the level in nonpolar solvents (fluorescence yield of $6 \times 10^{-4}$, see Table 2).

Protonation of the nitrogens results in a slight hypsochromic shift of both the emission (713 nm (in for example toluene) to 696 nm (dcm + TFA)) and absorption maxima (704 nm (dcm) to 686 nm (dcm + TFA)). These shifts and the increase in luminescence can be reversed by addition of a few drops of pyridine. The observation that compound 2 does show fluorescence in benzonitrile, dichloromethane, benzene, and methylcyclohexane with a quantum yield of ca. $6 \times 10^{-4}$ indicates that the pyrrolidine "bridge" moiety is not involved in the quenching process in compound 1.

Emission spectra of 2 at 77 K in methylcyclohexane and in a mixture of methylcyclohexane, methyltetrahydrofuran, and ethyl iodide (2:1:1) are shown in Figure 3. Whereas in the former matrix fluorescence peaks are sharpened and two new emission maxima are observed at 825 and 880 nm, in the latter all fluorescence is absent, and only the maxima at 825 (1.50 eV) and 880 nm are observed. This is a clear indication that the external heavy atom effect caused by ethyl iodide induces enhanced spin-orbit coupling and only phosphorescence is observed in the mixed matrix.1

The triplet energy ($\Delta E_0$) of 1 and 2 is thus determined to be 1.50 eV. Interestingly the singlet–triplet splitting of the C$_{60}$ adducts (i.e., $\Delta(S_1 - T_1) = 0.26$ eV) is smaller than for "native" C$_{60}$ ($\Delta(S_1 - T_1) = 0.42$ eV, see Table 1).

Representative triplet–triplet absorption spectra of 1 and of C$_{60}$ are depicted in Figure 4. Compared to C$_{60}$ the adduct shows a slightly broader transient absorption spectrum with the strongest absorption maximum at a little higher energy and a pronounced T$_1$–T$_2$ absorption at 800 nm (shoulder) indicating a smaller T$_1$–T$_2$ energy gap for 1. Interestingly the relative triplet yields of 1 also show a solvent dependence (see Table 2). Whereas the fluorescence of 1 is fully quenched in dichloromethane, the triplet is still populated for ca. 80% in this solvent. In benzonitrile however also the triplet is strongly quenched.

The solvent dependence of the fluorescence and triplet–triplet absorption of 1 indicates that in polar solvents an extra deactivation path of the excited states (S$_1$ or T$_1$) of 1 becomes available. As the population of a charge transfer state is energetically possible in polar solvents (according to the Weller equation, see below) we attribute this quenching path to an intramolecular electron transfer that deactivates the excited state.

We can so far not attribute any transient to the radical cation and anion of the charge separated state, due to the time resolution of our flash photolysis apparatus. This indicates that the charge separated state has a very short (subnanosecond) lifetime. Picosecond resolved transient absorption spectroscopy will be undertaken in the future.

In contrast to adduct 1, the adduct 2 shows strong triplet–
Figure 4. Comparison of scaled triplet-triplet absorption of compound 1 and C₆₀ in methylcyclohexane.

triplet absorption ($\Phi_t \approx 1$) not only in low polarity but also in high polarity solvents (benzonitrile).

The extinction coefficient of the triplet-triplet absorption ($e^{(T_1-T_0)}$) of 1 at 692 nm is estimated to be 16,700 M⁻¹ cm⁻¹, on the assumption that 1 has a triplet yield near unity in methylcyclohexane. This is obtained by comparison of 1 and C₆₀ under identical experimental conditions and application of

$$P_1/A_1(\lambda_{\text{ex}})C_1l = P_2/A_2(\lambda_{\text{ex}})C_2l$$

$P$ = peak intensity, $A$ = absorbance, $C$ = concentration, $l$ = pathlength, subscript 1 refers to adduct 1, and subscript 2 refers to C₆₀. For C₆₀ a $e^{(T_1-T_0)}$ of 14,500 M⁻¹ cm⁻¹, at 750 nm was used.14

Fluorescence decays obtained with single photon counting in methylcyclohexane and benzonitrile are represented in Figure 5. Monoexponential deconvolution of the decay in the nonpolar methylcyclohexane (in which electron transfer quenching is not exergonic, see below) gives a fluorescence lifetime of 1280 ± 40 ps (i.e., comparable to native C₆₀). In the polar solvent benzonitrile, in which both luminescence and population of the triplet state are strongly quenched, the fluorescence decay is not monoexponential but displays three components: a long living component with a lifetime of 1750 ps and a very low amplitude (0.008) and two fast components of 481 ps and 78 ps with an equal amplitude of 0.032.10a Single photon counting thus indicates that the quenching process in benzonitrile takes place with a rate between $1.3 \times 10^9$ and $1.2 \times 10^{10}$ s⁻¹ by applying one of the fast components as τ and the lifetime of 1 in methylcyclohexane as $\tau_{\text{ref}}$

$$k_{\text{et}} = 1/\tau - 1/\tau_{\text{ref}}$$

The decay in benzonitrile is clearly not monoexponential, which can be attributed to the presence of more conformations10b-e of the compound due to ring inversion of the pyrrolidine ring. However, multiexponential behavior seems to be a problem often encountered in the determination of the time resolved quenching of local fluorescence by intramolecular electron transfer.

Cyclic voltammetry of the adduct 1 in a toluene–acetonitrile mixture (3:1) using glassy carbon (0 to −2 V vs SCE) shows three reduction waves at −0.76, −1.24, and −1.79 V and reoxidation waves at −1.30, −0.83, and −0.38 V vs SCE. The first midpoint reduction potential of the fullerene adduct is thus estimated to be ca. −0.57 V vs SCE, i.e., in good agreement with literature reports for other fullerene adducts.11 A model of the donor (4-(dimethylamino)benzylamine from Aldrich) shows an irreversible oxidation wave of +0.74 V vs SCE in acetonitrile leading to an estimated midpoint potential +0.71 V vs SCE (i.e., comparable to N,N-dimethylparaloiduline12).

The structure of the adduct 1, obtained by minimization with semiempirical AM-1 calculations is shown in Figure 6. The aromatic ring of the donor is in an orthogonal relation to the
Figure 5. Fluorescence decays of compound 1 in methylcyclohexane and in benzonitrile. Laser pulse is also shown.

Figure 6. Structure of compound 1 obtained with AM-1.

plane that bisects the two sp³ carbons of the fullerene. Although the center to center distance of the two chromophores is estimated to be ca. 9 Å, the edge to edge distance is only ca. 5 Å.

Energetic Considerations. An estimate of the driving force for photoinduced charge separation (−ΔG<sub>oc</sub>) in compound 1 was made using the standard Weller-type approach.<sup>13</sup> This requires, in addition to the donor and acceptor redox potentials (+0.71 V and −0.57 V vs SCE, see above) and the singlet or triplet state energy (1<sub>E₀</sub> = 1.76 eV and 3<sub>E₀</sub> = 1.50 eV, see above), substitution of the center to center distance (R<sub>c</sub>) and of the effective ionic radii of the donor and acceptor radical cation and anion (r<sup>+</sup> resp. r<sup>−</sup>). For R<sub>c</sub> a value of 9 Å was estimated.

Table 3. Gibbs Free Energy Change for Charge Separation (ΔGcs), Barrier to Charge Separation (ΔG*), and Gibbs Free Energy Change for Charge Recombination (ΔGcr) and the Reorganization Energy (λ) in Different Solvents (Given with Dielectric Constants (ε) and Refractive Indices (n)) for Both the Singlet and Triplet (T) state, Obtained for Compound 1 with R1 = 9 Å, r2 = 3.7 Å, and r3 = 5.6 Å

<table>
<thead>
<tr>
<th>solvent</th>
<th>ε</th>
<th>n</th>
<th>ΔGcs(eV)</th>
<th>λ(eV)</th>
<th>ΔG* (eV)</th>
<th>ΔGcr(eV)</th>
<th>ΔG(T) (eV)</th>
<th>ΔG*(T) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane</td>
<td>2.07</td>
<td>1.423</td>
<td>0.22</td>
<td>0.63</td>
<td>0.29</td>
<td>-1.98</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>toluene</td>
<td>2.38</td>
<td>1.497</td>
<td>0.12</td>
<td>0.67</td>
<td>0.23</td>
<td>-1.88</td>
<td>0.38</td>
<td>0.41</td>
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<tr>
<td>chloroform</td>
<td>4.70</td>
<td>1.446</td>
<td>-0.22</td>
<td>1.02</td>
<td>0.16</td>
<td>-1.54</td>
<td>0.04</td>
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<tr>
<td>dichloromethane</td>
<td>8.93</td>
<td>1.424</td>
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<td>1.18</td>
<td>0.14</td>
<td>-1.38</td>
<td>-0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>9.93</td>
<td>1.552</td>
<td>-0.40</td>
<td>1.11</td>
<td>0.11</td>
<td>-1.36</td>
<td>-0.14</td>
<td>0.21</td>
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<tr>
<td>benzonitrile</td>
<td>25.20</td>
<td>1.528</td>
<td>-0.50</td>
<td>1.22</td>
<td>0.11</td>
<td>-1.26</td>
<td>-0.24</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Internal reorganization energy (λ) is 0.3 eV.

from our modeling results (Figure 6). The r+ and r− values were calculated from the apparent molar volumes of N,N-dimethylaniline (density 0.956) and of C60 (density 1.65) using a spherical approach. This gives r+ = 3.7 Å and r− = 5.6 Å.

Resulting ΔGcs values in various solvents are listed in Table 3, where furthermore values are given for the barrier to charge separation (ΔG*) as estimated via the classical Marcus equation. For this estimation the solvent reorganisation term (λi) was calculated using the Born−Hush approach, and the internal reorganisation energy (λi) was set at 0.3 eV. The latter value was estimated using the charge transfer absorption maximum of C60 in pure diethylaniline (550 nm) and the charge transfer emission maximum of C60 in methylcyclohexane containing 0.1 M diethylaniline (740 nm). The energy difference between these two maxima equals 2λi, resulting in λi ≈ 0.3 eV. An estimate of the Gibbs free energy change for charge recombination (ΔGcr = −ΔGcs − 1ε0) in compound 1 is also given in Table 3. For the triplet state, only the Gibbs free energy change (ΔGcr(T)) and the barrier for electron transfer (ΔG*(T)) differ from the singlet state.

Important conclusions from the data collected in Table 3 are as follows: (i) The driving force for charge separation (−ΔGcs) from the fullerene S1 state becomes positive in solvents more polar than toluene, in good agreement with the fluorescence data, and from the T1 state it requires solvents more polar than chloroform. The relatively high triplet yield and the absence of fluorescence of 1 in dichloromethane indicates that in this solvent of medium polarity charge recombination to the local triplet is a major decay path of the charge transfer state. (ii) Charge separation is in the normal region (−ΔGcs < λ) for every solvent, but charge recombination in benzonitrile is almost in the optimal region (−ΔGcr ≈ λ), in agreement with the short lifetime of the charge transfer state. (iii) The barrier for electron transfer from S1 is always at least 0.09 eV lower than from T1 (the difference in the barrier is 0.20 eV (4.7 kcal/mol) in methylcyclohexane and 0.09 eV (2.1 kcal/mol) in benzonitrile). This indicates that electron transfer rates from the triplet should always be slower than from the singlet state, and this effect should be strongest in nonpolar solvents, in agreement with the results of Caspar and Wang.

Conclusions

The solvent dependence of the fluorescence and triplet−triplet absorption of 1 indicates that in polar solvents an extra deactivation path of the excited states (S1 or T1) of 1 becomes available. As the population of a charge transfer state is exergonic in polar solvents (according to the Weller equation) we attribute this quenching path to an intramolecular electron transfer that deactivates the locally excited states.

Fluorescence decay data indicate that the singlet state electron transfer quenching process in benzonitrile takes place with a rate between 1.3 × 109 and 1.2 × 1010 s−1.

Because, even at the relatively small edge-to-edge donor−acceptor distance present in 1, the charge transfer state can only be populated in rather polar solvents, our results also imply that fullerences are not very well suited for use as electron accepting chromophores for long range electron transfer in bichromophoric donor−bridge−acceptor systems, unless a significantly stronger donor than N,N-dimethylaniline (e.g. N,N,N'N'-tetramethyl-p-phenylenediamine) is used. One of our previous studies on the solvent dependence of intramolecular charge separation has already shown that optimal (in a Marcus sense) electron transfer interactions (at a given distance) can only be accomplished if already in a nonpolar solvent electron transfer is energetically favorable, i.e., by applying polar solvents one can gain driving force (and make electron transfer energetically possible) but one will never obtain the highest electron transfer rates. Our results thus suggest that high rate photoinduced intramolecular electron transfer in the systems described in ref 4b, c and 5e will not be possible due to the large separation distance or the small driving force, although the different spatial orientation of the donor and acceptor in these systems may be of influence.

Furthermore our results indicate that functionalization of C60 is accompanied by a decrease of the eV0 with ca. 0.23 eV and a shift to a more negative first reduction potential of ca. 0.17 V. Thus, under the same conditions (i.e. donor, distance and solvent), the driving force for charge separation for an adduct of C60, compared to "native" C60, would be ca. 0.40 eV less exergonic. This would mean that C60 adducts are less suited for photoinduced electron transfer systems than "native" C60. It would thus seem preferable to incorporate a C60 unit into an electron transfer system by a supramolecular method, such as complexation by calix[8]arenes or y-cyclodextrins, leaving the C60 unit intact.

Acknowledgment. We hereby thank Martijn Werts and Stijn Berkhout for their experimental contributions. This 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).

Supplementary Material Available: 1H NMR, 13C NMR, and mass spectrum of compound 1 and Cartesian coordinates of the AM-1 optimized structure of 1 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.