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Synthesis, Cyclic Voltammetry, and Photophysical Properties of a Bridged *o*-Phenylenediamine–C_{60} Dyad

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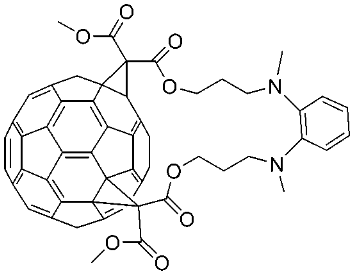
ABSTRACT



The synthesis, complete spectroscopic characterization, cyclic voltammetry, and photophysical measurements of a new *o*-phenylenediamine–C_{60} dyad are described. By using a tether strategy, only a single regioisomer was obtained. Cyclic voltammetry measurements indicate that the two electroactive groups do not interact in their singlet ground states. Photophysical investigations reveal a rapid photoinduced electron transfer between the singlet excited state of the fullerene acceptor and the *o*-phenylenediamine donor, yielding a charge-separated radical pair.

Buckminsterfullerene C_{60} and its derivatives[1] exhibit a number of unique electronic and photophysical properties. In particular, the low reduction potential of C_{60} ($E_{1/2} = -0.44$ V versus SCE) and its singlet ground-state absorption renders them interesting candidates for inter- and intramolecular electron-transfer reactions.[2] The low reorganization energy of C_{60} in electron-transfer reactions stimulated the use of fullerenes as a new building block for the design of multicomponent arrays, which give rise to light-induced electron-transfer processes and yield long-lived charge-separated states. Furthermore, the recent advances in the chemistry of fullerenes provide a powerful tool to change parameters, which are essential to the efficiency of electron-transfer processes. For example, the relative donor−acceptor orientation as well as the distance between the chromophores can be modulated systematically with relative ease. In this context, a variety of donor and acceptor molecules have been covalently attached to C_{60}, and several remarkable electron-transfer phenomena have been disclosed.

Other groups as well as our group have focused on developing chinoid systems as acceptor moieties and porphyrins or *o*-phenylenediamines as sacrificial electron donors.[3] Recently, we have carried out extensive investigations regarding the regiochemistry of multiple addition to C_{60} and have unraveled several principles of fullerene regioselectivity.[4]

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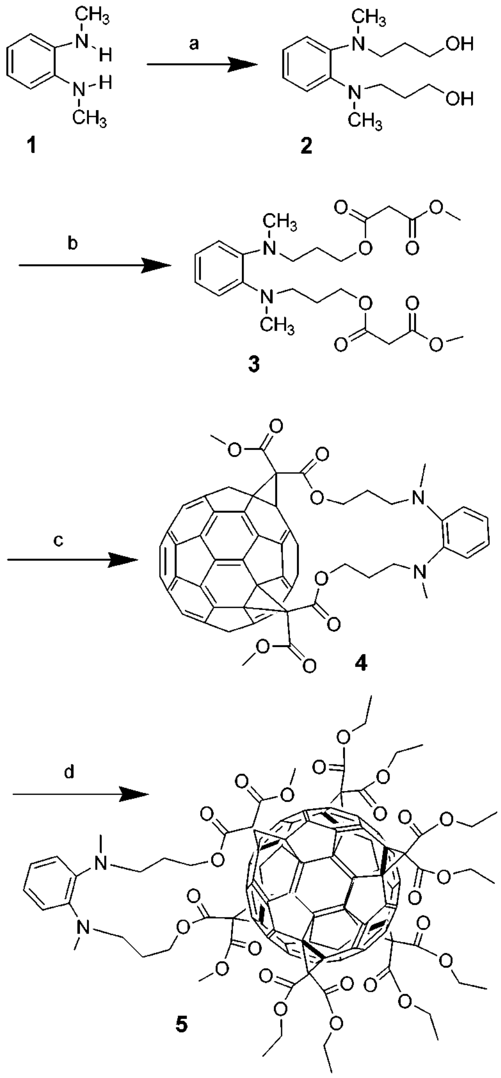
To develop a new C_{60}–donor dyad with the *o*-phenylenediamine moiety as a strong donor, we used *N,N′*-dimethyl-*o*-phenylenediamine, **1**, which is readily available from *o*-phenylenediamine in three steps[5] (Scheme 1). The alkylation of the amino groups leads to diol **2**,[6] which was converted into the corresponding bismalonate **3** and serves as a bifunctional addend for a subsequent tether-functionalization. The nucleophilic cyclopropanation governed the reaction between bismalonate **3** and C_{60}. Only the equatorial isomer **4** was formed upon bisaddition. Bisadduct **4** was isolated by flash chromatography (SiO_2, toluene:triethylamine 19:1 v/v) followed by preparative HPLC (grom-sil amino, toluene). The NMR and UV spectra of **4** reveal the characteristics of an equatorial adduct.[7] Additional proof for the equatorial structure of bisadduct **4** stems from the follow-up synthesis of hexaadduct **5**, using our template mediation technique.[8] Formation of this hexaadduct pattern can only be obtained starting from equatorial bisadducts, which, in turn, leads to the conclusion that bisadduct **4** is an equatorial isomer.

Scheme 1[a]



[a] (a) $Cl(CH_2)_3OH$, $CaCO_3$, H_2O, 100 °C; (b) $ClCOCH_2COOCH_3$, CH_2Cl_2; (c) C_{60}, CBr_4, DBU, toluene; (d) dimethylanthracene, diethyl bromomalonate, DBU, toluene.

Compounds **3**, **4**, and **5** were studied electrochemically using a glassy carbon electrode in a dichloromethane solution (supporting electrolyte: $TBAPF_6$) under argon. Well-resolved and reversible cyclic voltammetric waves were observed in all cases. The results were compared with those of the parent C_{60} and the equatorial bisadduct e-$C_{62}(COOC_2H_4COOC_4H_9)_4$ **6**, carrying alkyl groups, as reference compounds (Table 1).

Table 1. $E_{1/2}$ Values Measured as the Average of the Anodic and Cathodic Peak Potentials vs the Potential for the Redox Couple of Internally Added Fc/Fc^+

compound	E_1	E_2	E_3	E_4
C_{60}			−1.08	−1.48
6			−1.21	−1.58
3	+0.56	+0.20		
4	+0.65	+0.23	−1.19	−1.57
5	+0.67	+0.21	−1.77[a]	

[a] Irreversible.

The reduction potentials of the equatorial bisadduct **6** compared with those of dyad **4** and the oxidation potentials of bismalonate **3** compared with those of dyad **4** and hexaadduct **5** are quite similar. This suggests that no electronic coupling prevails between the two electroactive groups of dyad **4** in their singlet ground state.

The fluorescence quantum yields of the *o*-phenylenediamine–C_{60} dyad **4** were measured in solvents of different polarity and compared with that of the corresponding equatorial reference isomer ($\Phi = 4.2 \times 10^{-4}$). Two dominant features are derived from the data in Table 2: First a strong quenching of the fluorescence is noted in all the solvents

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Table 2. Photophysical Properties of *o*-Phenylenediamine−C_{60} Dyad **4** in Various Solvents at rt[a]

solvent	ϵ	fluorescence quantum yield (Φ)	lifetime (τ) singlet excited state	lifetime (τ) radical pair	quantum yield charge separation (Φ)
toluene	2.39	3.6×10^{-5}	383 ps	*b*	*c*
1-chlorobutane	7.39	1.8×10^{-5}	144 ps	620 ns	0.21
THF	7.6	8.5×10^{-6}	142 ps	447 ns	0.48
benzonitrile	24.8	7.4×10^{-6}	110 ps	683 ns	0.21
dimethylformamide	36.7	5.9×10^{-6}	78 ps	822 ns	0.13

[a] Excitation wavelength: 337 nm. [b] $\tau < 50$ ns. [c] No measurable electron-transfer products on the nanosecond time scale.

investigated. Far more important is the second observation, namely, the solvent dependence, giving rise to a marked increase of the quenching with increasing solvent polarity from toluene ($\epsilon = 2.39$) to DMF ($\epsilon = 36.7$). Since polar solvents decrease the energy of the charge-separated state, a more exothermic driving force ($-\Delta G$) characterizes an intramolecular electron transfer in, for example, benzonitrile and DMF relative to toluene or THF. Thus, the observed trend is a first indication for an electron-transfer mechanism being responsible for the rapid deactivation of the fullerene singlet excited state. On the other hand, an intramolecular energy transfer mechanism from the fullerene singlet excited state ($E_{\text{SINGLET}} = 1.77$ eV) to the *o*-phenylenediamine moiety ($E_{\text{SINGLET}} = 3.97$ eV; $E_{\text{TRIPLET}} = 3.08$ eV)[9] can be ruled out, based on the unfavorable thermodynamics.

To shed further light onto the deactivation processes of the fullerene singlet excited state, time-resolved transient absorption measurements following an 18 ps or a 50 ns laser pulse were carried out. Following the 18 ps laser pulses, the equatorial reference reveals the grow-in of a transient absorption, maximizing around 870 nm. These spectral characteristics are ascribed to the singlet excited-state absorption of the equatorial isomer. On a longer time scale (i.e., 10 ns) the singlet−singlet absorption at 870 nm decays with a lifetime of 3.1 ns. In parallel with this decay, the grow-in of a 650 nm absorption was observed, which corresponds to the fullerene triplet excited-state absorption.[10]

In the case of the *o*-phenylenediamine−C_{60} dyad **4**, the transient absorption changes, recorded immediately after the completion of the picosecond laser pulse, are virtually identical to those of the reference. In particular, the singlet−singlet absorption at 870 nm is evident in all solvents. The lifetime of the singlet excited state absorption is, however, markedly shortened in toluene and decreases further in solvents of higher polarity (see Table 2). These changes are in good resemblance with the steady-state fluorescence measurements and corroborate the electron-transfer mechanism.

Spectral evidence for the hypothesis that an intramolecular electron transfer from the electron-donating *o*-phenylenediamine moiety to the fullerene governs the fate of the photoexcited fullerene systems is derived from complementary nanosecond photolytic experiments. In particular, a sharp maximum found at 1065 nm, shown in Figure 1, resembles an earlier pulse-radiolytic investigation[11] and, in turn, confirms the formation of the one-electron-reduced fullerene π-radical anion.

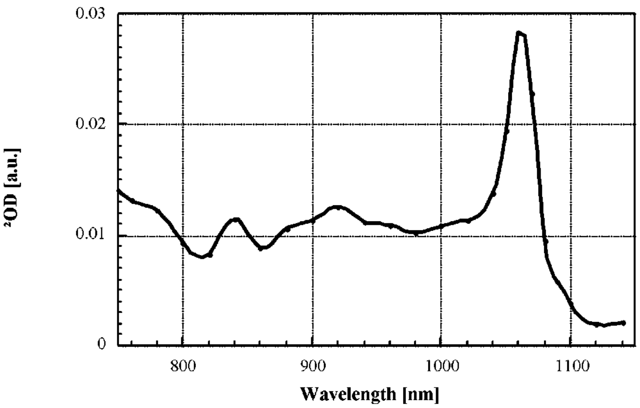

Figure 1. Transient absorption spectrum (near-IR part) recorded 50 ns after flash photolysis of 2.0×10^{-5} M dyad **4** at 337 nm in deoxygenated benzonitrile.

On the other hand, a transient maximum in the visible (i.e., at 440 nm, see Figure 2) corroborates the oxidation of the

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(7) Spectroscopic data of **4**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 1.88 (m, 4 H, CH_2), 2.70 (s, 3 H, NCH_3), 2.80 (s, 3 H, NCH_3), 3.15 (t, 2 H, NCH_2), 3.31 (m, 2 H, NCH_2), 3.99 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 4.18 (m, 1 H, OCH_2), 4.27 (m, 1 H, OCH_2), 4.44 (m, 1 H, OCH_2), 4.63(m, 1 H, OCH_2), 6.92 (m, 4 H, CH). ^{13}C NMR (100.50 MHz, $CDCl_3$, 25 °C): δ [ppm] = 25.35 (1 C, CH_2), 25.55 (1 C, CH_2) 39.36 (1 C, NCH_3), 40.08 (1 C, NCH_3), 50.22 (1 C, NCH_2), 50.44 (1 C, NCH_2), 51.37 (1 C, bridgehead-*C*), 53.85 (1 C, bridgehead-*C*), 53.92 (1 C, OCH_3), 53.98 (1 C, OCH_3), 65.87 (1 C, OCH_2), 66.00 (1 C, OCH_2), 70.35 (1 C, sp^3-C_{60}-*C*), 71.50 (1 C, sp^3-C_{60}-*C*), 71.61 (2 C, sp^3-C_{60}-*C*), 119.44 (1 C, *C*H), 120.43 (1 C, *C*H), 121.85 (1 C, *C*H), 122.60 (1 C, *C*H), 138.64, 138.90, 139.63, 140.71, 141.27, 141.51, 141.66, 141.86, 141.93, 142.08, 142.33, 142.53, 143.06, 143.26, 143.45, 143.56, 143.70, 143.81, 143.85, 143.94, 144.03, 144.09, 144.31, 144.47, 144.60, 144.69, 144.76, 144.87, 144.93, 145.07, 145.18, 145.24, 145.33, 145.55, 145.73, 146.08, 146.13, 146.32, 146.44, 146.50, 146.74, 147.28, 148.44 (sp^2 *C*), 163.16, 163.78, 164.04 ($C{=}O$). UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (ϵ) [nm] = 252 (108000), 306 (41300), 396 (4200), 421 (2400), 478 (3000). MS (FAB): m/z (%) = 1170 (M^+). IR (KBr): ν [cm^{-1}] = 3053, 2950, 2844, 2796, 1749, 1494, 1433, 1384, 1266, 1237, 1212, 1102, 1061, 1024, 746, 708.

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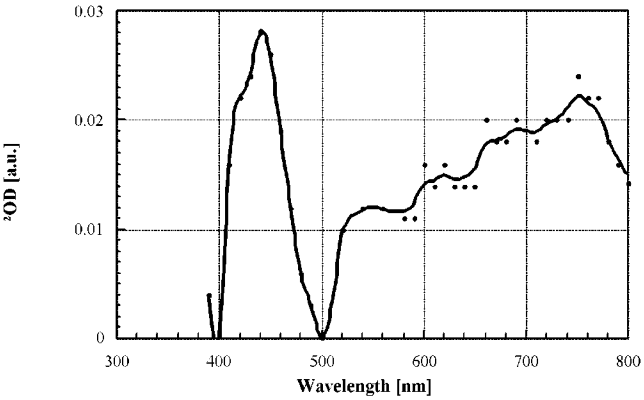

Figure 2. Transient absorption spectrum (UV−vis part) recorded 50 ns after flash photolysis of 2.0 × 10^{-5} M dyad **4** at 337 nm in deoxygenated benzonitrile.

o-phenylenediamine moiety and completes the characterization of the charge-separated radical pair, namely, $C_{60}^{\bullet -}$−(*o*-phenylenediamine)$^{\bullet +}$. Toluene is the only exception, and on the time scale investigated no electron-transfer products were identified. This indicates the low stabilization of the radical pair in this nonpolar solvent and implies a fast back electron transfer.

The strong fullerene π-radical anion absorption at 1065 nm was employed as a reliable probe for (i) measuring the lifetime of the charge-separated state and (ii) determining the overall quantum yield of the charge-separation process. Interestingly, polar solvents slow down the back electron transfer and, consequently, help to stabilize the radical pair. This indicates that the back electron transfer lies in the normal region of the “Marcus Parabola”. Similar lifetimes were also derived from the decay of the one-electron-oxidized aniline absorption in the visible.

The observation that the back electron transfer is apparently located in the normal region, but, nevertheless, slower than forward electron transfer suggests additional stabilization of the charge-separated radical pair. A possible rational explanation implies the formation of a three-electron bond between the two nitrogens of the *o*-phenylenediamine moiety, similar to the case of the radical cation of diazabicyclooctane.[12] This, in turn, helps to slow the back electron transfer dynamics.

The quantum efficiency of the charge separation using 1-chlorobutane as a solvent leads to the highest yields, although the lifetime of the radical pair is apparently not optimized. This observation is consistent with earlier literature reports.[13]

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Supporting Information Available: Experimental procedures and full characterization for compounds **3**−**5**, a figure of compound **6**, and cyclic voltammograms of C_{60} and compounds **3**−**6**. This material is available free of charge via Internet at http://pubs.acs.org.

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