Supporting Information

Electron Transfer through exTTF Bridges in Electron Donor-Acceptor Conjugates

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Table of Contents

General Information: All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum-backed Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded with Bruker Avance 300 spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet. FT-IR spectra were recorded with a Perkin-Elmer 781 spectrometer. UV/Vis spectra were recorded with Varian Cary 50. Steady state fluorescence studies were carried out on a Fluoromax 3 (Horiba) instrument and all the spectra were corrected for the instrument response. The femtosecond transient absorption studies were performed with laser pulses (1Khz 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Mass spectra were recorded with a HP 5989A spectrometer. Cyclic voltammetry was performed using an Autolab PGStat 30. These measurements were made in a double-walled cell (Metrohm EA 876-20). A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (30 μ) for 1 min, and platinum wire was used as the counter electrode. A Ag /Ag^+ electrode was used as reference. Tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte, and dry dichloromethane was used as solvent. The samples were purged with argon prior to measurement. The scan rate was 100 mV/s.

Synthesis

Compound 5. To a solution of **3** (404 mg, 0.94 mmol) and **4** (149 mg, 0.47 mmol) in anhydrous THF (40 mL), $Pd(PPh_3)_4$ (110 mg, 9.4×10^{-2} mmol), CuI (20 mg, 9.4×10^{-2} mmol) and $^iPr_2NH$ (0.5

mL) were added under argon atmosphere. The reaction mixture was refluxed for 1.5 h. After dilution with CH_2Cl_2 (100 mL), the organic layer was sequentially washed with a saturated solution of NH_4Cl in water (3x50 mL), water and brine. The organic layer was then dried ($MgSO_4$) and the solvent eliminated under reduced pressure. The resulting residue was purified by column chromatography (silica gel; hexane/CH_2Cl_2 3/1). Compound **5** (73 mg) was obtained as a red solid in 52% yield. ^{1}H-NMR (200 MHz, $CDCl_3$), δ: 10.03 (s, 1H), 7.89-7.63 (m, 8H), 7.55-7.40 (m, 2H), 6.34 (s, 4H), 3.12 (s, 1H) ppm; ^{13}C-NMR(75 MHz, $CDCl_3$), δ: 191.44, 138.40, 138.18, 135.76, 135.55, 135.39, 135.30, 135.21, 132.11, 129.75, 129.65, 129.57, 129.44, 128.34, 127.96, 125.05, 124.92, 120.36, 120.35, 119.81, 119.54, 117.42, 117.38, 117.29, 93.80, 88.87, 83.71 ppm; FTIR (KBr), υ: 779, 1460, 1598, 1629, 1697, 2206, 2852, 2922 cm^{-1}; MS *m/z* (ESI): 532 (M^+), 294, 293, 275; UV-*vis* (CH_2Cl_2), λ_{max}: 454, 392, 333, 288, 254 nm.

Compound 8. To a solution of **6** (445 mg, 0.88 mmol) and **7** (512 mg, 0.59 mmol) in anhydrous THF (80 mL), $Pd(PPh_3)_4$ (102 mg, 0.088 mmol), CuI (20 mg, 0.094 mmol) and $^iPr_2NH$ (0.5 mL) were added under argon atmosphere. The reaction mixture was refluxed for 1.5 h. After dilution with CH_2Cl_2 (150 mL), the organic layer was sequentially washed with a saturated solution of NH_4Cl in water (3x50 mL), water and brine. The organic layer was then dried ($MgSO_4$) and the solvent eliminated under reduced pressure. The resulting residue was chromatographied over silica (hexane/CH_2Cl_2 3/1). Compound **8** (179 mg) was obtained as a yellow solid in 38% yield. ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 7.85 (d, J = 1.4 Hz, 1H), 7.72-7.70(m, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.44 (dd, J_1 = 8.0, J_2= 1.4 Hz, 1H), 7.31-7.29 (m, 3H), 6.94 (s, 1H), 6.32 (d, J = 4.53 Hz, 4H), 4.03-3.97 (m, 4H), 1.88-1.81 (m, 4H), 1.40-1.33 (m, 12H), 0.93-0.91 (m, 6H); ^{13}C-NMR(125 MHz, $CDCl_3$), δ: 154.84, 152.25, 137.05, 136.94, 135.89, 135.72, 135.61, 129.44, 128.23, 126.48, 125.38, 125.35, 125.31, 124.31, 122.14, 121.72, 121.15, 117.71, 117.61, 117.57, 116.36, 114.21, 95.04, 87.80, 86.23, 70.52, 70.37, 32.09, 31.92, 30.12, 29.79, 29.57, 26.22, 26.17, 23.10, 23.03, 14.55, 14.48 ppm; FTIR (KBr), υ: 653, 758, 1213, 1465, 1485, 1508, 1542, 1629, 2854, 2925, 3065 cm^{-1}; MS *m/z* (FAB): 806.7 (M^+);UV-*vis* (CH_2Cl_2), λ_{max}: 443, 382, 342, 305, 265, 234 nm.

Compound 9. To a solution of **8** (155 mg, 0.29 mmol) and **5** (235 mg, 0.29 mg) in anhydrous THF (150 mL), $Pd(PPh_3)_4$ (34 mg, 0.029 mmol), CuI (6 mg, 0.029 mmol) and $^iPr_2NH$ (0.2 mL) were added under argon atmosphere. The reaction mixture was refluxed for 7 h. After dilution with CH_2Cl_2 (150 mL), the organic layer was sequentially washed with a saturated solution of NH_4Cl in water (3x75 mL), water and brine. The organic layer was then dried ($MgSO_4$) and the solvent eliminated under reduced pressure. The resulting residue was chromatographied over silica (hexane/CH_2Cl_2 3/1). Compound **9** (69 mg) was obtained as a red solid in 20% yield. ^{1}H-NMR (500 MHz, $CDCl_3/CS_2$), δ: 10.03 (s), 7.89-7.87 (m, 5H), 7.73-7.68(m, 7H), 7.49-7.44 (m, 3H), 7.32-7.30 (m, 2H), 7.04 (s, 2H), 6.36-635 (m, 4H), 6.32 (m, 2H), 6.31 (m, 2H), 4.06 (t, 4H, J = 6.4 Hz), 1.91-1.86 (m, 4H), 1.39-1.38 (m, 12H), 1.15-1.10 (m, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$), δ: 189.39, 153.39, 150.39, 146.38, 138.12, 136.81, 135.23, 135.20, 135.08, 134.99, 134.91, 132.08, 131.86, 129.27, 129.16, 129.07, 128.87, 128.76, 128.01, 127.70, 127.51, 127.45, 126.59, 125.90, 124.87, 124.74, 124.65, 124.08, 124.01, 123.70, 118.90, 117.50, 117.38, 117.17, 117.02, 116.47, 116.40, 69.15, 69.11, 37.11, 34.40, 34.00, 32.78, 32.03, 31.79, 31.21, 30.27, 30.16, 29.91, 29.82, 29.50, 27.19, 25.96, 22.96, 14.27 ppm; FTIR (KBr), υ: 1458, 1500, 1544, 1600, 1629, 2206, 2343, 2854, 2925 cm^{-1}; MS *m/z* (MALDI-TOF): calculated. 1210.1839, found 1210.1829; UV-*vis* (CH_2Cl_2), λ_{max}: 451, 394, 314 nm.

Compound 1. To a solution of C_{60} (48.24 mg, 0.067 mmol) in chlorobenzene (13 mL), compound **9** (81 mg, 0.067 mmol) and *N*-octylglycine (62 mg, 0.33 mmol) were added. The reaction mixture was refluxed for 4 h under argon atmosphere. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography over silica gel, employing cyclohexane/toluene 1/1 as the eluent. Triad **1** (29 mg) was obtained in 21% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 7.86-7.83 (m, 5H), 7.72-7.60 (m, 7H), 7.46-7.42 (m, 3H), 7.32-7.29 (m, 2H), 7.03 (s, 2H), 6.33-6.31 (m, 8H), 5.10 (d, J = 9.3 Hz, 1H), 5.07 (s, 1H), 4.12 (d, J = 9.3 Hz,1H), 4.07-4.03 (m, 4H), 3.23-3.16 (m, 1H), 2.60-2.53 (m, 1H), 1.90-1.85 (m, 8H), 1.37-1.26 (m, 20H), 0.93-0.89 (m, 9H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$), δ: 155.89, 154.58, 154.14, 153.76, 153.62, 147.70, 147.10, 146.85, 146.71, 146.61, 146.54, 146.49, 146.31, 146.15, 145.92, 145.72, 145.61, 145.55, 145.11, 145.03, 144.79, 143.55, 143.38, 143.08, 142.93, 142.72, 142.66, 142.51, 142.46, 142.41, 142.30, 142.27, 142.06, 141.94, 140.57, 140.54, 140.30, 139.95, 138.19, 138.08, 137.31, 137.02, 136.91, 136.26, 136.08, 135.88, 135.69, 135.62, 135.48, 132.34, 129.87, 129.61, 129.49, 128.22, 126.47, 125.35, 123.66, 122.18, 121.71, 121.41, 121.25, 121.17, 120.95, 117.73, 117.60, 117.31, 114.48, 114.36, 95.76, 90.74, 89.94, 86.77, 82.71, 70.08, 69.36, 67.26, 53.64, 32.37, 32.13, 31.66, 30.08, 29.84, 29.79, 28.79, 27.99, 26.28, 23.17, 23.13, 14.63, 14.59 ppm; FTIR (KBr), υ: 640, 752, 1461, 1500, 1542, 1654, 2796, 2850, 2923, 3066 cm^{-1}; MS *m/z* (FAB): 2057.5 (M$^+$); UV-*vis* (CH_2Cl_2), λ_{max}: 452, 433, 365, 315, 253, 239, 228 nm.

Compound 11. To a solution of **10** (83.2 mg, 0.36 mmol) and **7** (289 mg, 0.54 mmol) in anhydrous THF (40 mL), $Pd(PPh_3)_4$ (32 mg, 0.036 mmol), CuI (5 mg, 0.036 mmol) and $^{i}Pr_2NH$ (0.15 mL) were added under argon atmosphere. The reaction mixture was refluxed for 1.5 h. After dilution with CH_2Cl_2 (50 mL), the organic layer was sequentially washed with a saturated solution of NH_4Cl in water (3x50 mL), water and brine. The organic layer was then dried ($MgSO_4$) and the solvent eliminated under reduced pressure. The resulting residue was chromatographied over silica (hexane/$CHCl_3$ 4/1). Compound **11** (60 mg) was obtained as a yellow solid in 26% yield. ^{1}H-NMR (300 MHz, acetone-d_6), δ: 7.45 (s, 1H), 6.99 (s, 1H), 6.92 (bs, 1H), 6.66 (bs, 2H), 4.07-4.02 (m, 4H), 1.84-1.75 (m, 4H), 1.57-1.53 (m, 4H), 1.40-1.38 (m, 8H), 0.93-0.91 (m, 6H); ^{13}C-NMR (75 MHz, acetone-d_6), δ: 154.95, 152.30, 125.90, 124.15, 119.99, 119.79, 115.73, 112.36, 88.91, 70.12, 69.89, 31.88, 31.71, 26.07, 26.01, 22.90, 22.80, 13.93, 13.82; FTIR (KBr), υ: 3060, 2921, 2851, 1484, 1463, 1213, 797, 640 cm^{-1}; MS *m/z* (MALDI-TOF): calculated 630.0252, found 630.0266; UV-*vis* (CH_2Cl_2), λ_{max}: 425, 334, 298 nm.

Compound 12. To a solution of **11** (102 mg, 0.16 mmol) and **5** (86 mg, 0.16 mg) in anhydrous THF (50 mL), $Pd(PPh_3)_4$ (19 mg, 0.016 mmol), CuI (3 mg, 0.016 mmol) and $^{i}Pr_2NH$ (0.1 mL) were added under argon atmosphere. The reaction mixture was refluxed for 16 h. After dilution with CH_2Cl_2 (50 mL), the organic layer was sequentially washed with a saturated solution of NH_4Cl in water (3x75 mL), water and brine. The organic layer was then dried ($MgSO_4$) and the solvent eliminated under reduced pressure. The resulting residue was chromatographied over silica (chloroform). Compound **12** (53 mg) was obtained as a red solid in 54 % yield. ^{1}H-NMR (200 MHz, $CDCl_3$), δ: 10.03 (s, 1H), 7.90-7.86 (m, 3H), 7.73-7.67 (m, 5H), 7.49-7.43 (m, 3H), 7.00 (s, 1H), 6.94 (s, 1H), 6.54 (s, 1H), 6.36-6.33 (m, 5H), 4.01 (t, *J* = 6.3 Hz, 4H), 1.86-1.79 (m, 4H), 1.42-1.33 (m, 12H), 0.93-0.88 (m, 6H) ppm; ^{13}C-NMR (50 MHz, $CDCl_3$), δ: 191.38, 153.84, 153.66, 138.18, 137.95, 135.88, 135.51, 135.37, 135.32, 135.17, 132.37, 132.14, 132.00, 131.54, 129.70, 129.57, 129.42, 129.25, 128.61, 128.37, 128.02, 127.84, 127.58, 125.09, 124.97, 124.17, 120.95, 120.66, 119.86, 118.79, 117.49, 117.43, 117.36, 116.84, 116.66, 114.97, 112.53, 95.61, 93.84, 90.33, 88.87, 86.32, 85.72, 69.72, 69.67, 31.67, 31.61, 29.68, 29.37, 29.26, 25.77, 22.67, 14.10 ppm; FTIR (KBr), v: 3066, 2924, 2853, 2205, 1729, 1700, 1497, 1463, 1219, 719 cm^{-1}; MS *m/z* (MALDI-TOF): 1034.2 (M$^+$) ; UV-*vis* (CH_2Cl_2), λ_{max}: 460, 375, 320 nm.

Compound 2. To a solution of C_{60} (191 mg, 0.265 mmol) in chlorobenzene (53 mL), compound **12** (68 mg, 0.066 mmol) and *N*-octylglycine (62 mg, 0.33 mmol) were added. The reaction mixture was refluxed for 6 h under argon atmosphere. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography over silica gel, employing cyclohexane/toluene 1/1 as the eluent. Triad **2** (63 mg) was obtained in 51% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 7.86-7.84 (m, 4H), 7.68 (d, *J* = 8.06 Hz, 2H), 7.63 (d, *J* = 8.06 Hz, 2H), 7.46-7.44 (m, 3H), 7.01 (s, 1H), 6.92 (s, 1H), 6.55 (s, 1H), 6.36-6.34 (m, 5H), 5.14 (d, *J* = 9.3 Hz, 1H), 5.10 (s, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 4.02 (m, 4H), 3.27-3.22 (m, 1H), 2.64-2.60 (m, 1H), 1.89-1.83 (m, 8H), 1.39-1.36 (m, 20H), 0.97-0.92 (m, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$), δ: 156.89, 154.60, 154.23, 153.78, 153.62, 146.73, 147.12, 146.87, 146.73, 146.68, 146.63, 146.56, 146.51, 146.37, 146.34, 146.17, 145.95, 145.75, 145.68, 145.64, 145.58, 145.13, 145.06, 144.82, 143.58, 143.41, 143.11, 143.00, 142.75, 142.69, 142.55, 142.49, 142.44, 142.32, 142.09, 141.97, 140.61, 140.58, 140.33, 138.19, 137.33, 136.94, 136.28, 136.10, 135.79, 135.63, 132.35, 129.88, 129.65, 128.23, 125.43, 124.58, 123.74, 121.18, 121.02, 119.57, 117.81, 117.02, 116.94, 94.66, 90.80, 90.01, 86.73,82.77, 70.09, 70.03, 69.38, 67.32, 53.64, 32.40, 32.13, 32.07, 31.99, 30.11, 29.81, 29.71, 28.81, 28.02, 26.27, 26.23, 26.18, 23.20, 23.14, 23.05, 14.63, 14.57; MS *m/z* (FAB): 1879.3 (M^+); UV-*vis* (CH_2Cl_2), λ_{max}: 454, 431, 360, 312, 254 nm.

Electrochemistry

Table S1. Redox potentials at room temperature (in V *vs* Ag/Ag^+).[a]

Comp.	$E_{ap}^{1,ox}$	$E_{ap}^{2,ox}$	$E_{cp}^{1,ox}$	$E_{cp}^{2,ox}$	$E_{cp}^{3,ox}$	$E_{cp}^{1,red}$	$E_{cp}^{2,red}$	$E_{cp}^{3,red}$	$E_{cp}^{4,red}$
C_{60}						-0.72	-1.12	-1.60	-2.05
11	0.26		-0.72			-1.91			
1	0.31		-0.67			-0.84	-1.41	-2.05	
12	0.16	0.62	0.49	0.00		-1.84			
2	0.26	0.57	0.40	0.07	-0.26	-0.86	-1.42	-2.13	-2.66

[a] GCE (glassy carbon) as working electrode, $Ag/AgNO_3$ as reference electrode, Bu_4NClO_4 (0.1 M) as supporting electrolyte, and ODCB/CH_3CN 4/1 (v/v) as solvent. Scan rate 100 mVs^{-1}.

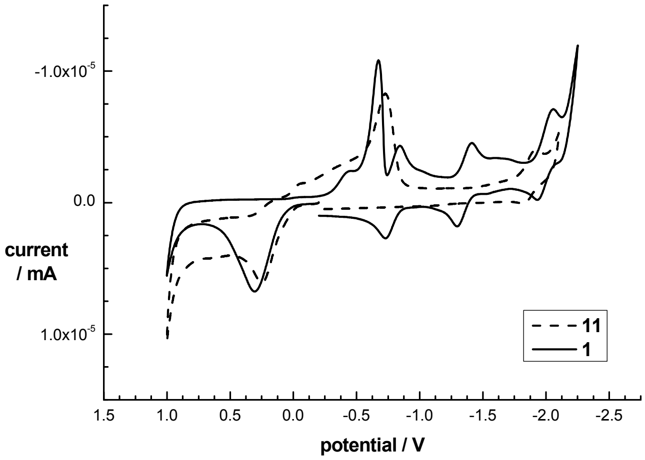

Figure S1. Cyclic voltammograms at 100 mV·s^{-1} of **1** and **9** recorded on a GC electrode (1 mm) in ODCB/CH_3CN 4/1 containing 0.1 M *n*-$Bu_4NClO_4^-$ as supporting electrolyte and a standard $Ag/AgNO_3$ reference electrode.

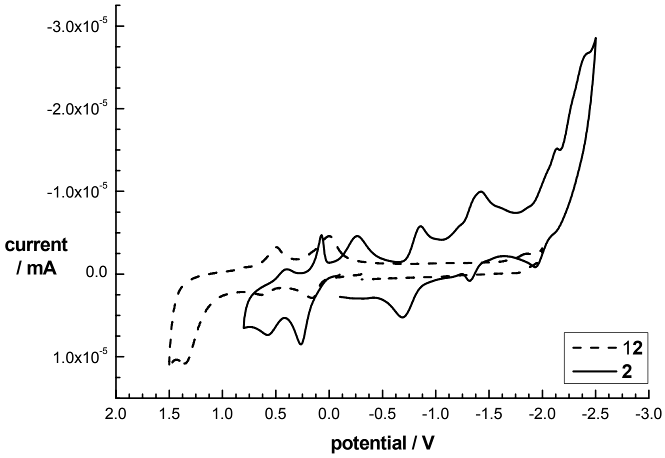

Figure S2. Cyclic voltammograms at 100 mV·s^{-1} of **2** and **12** recorded on a GC electrode (1 mm) in ODCB/CH_3CN 4/1 containing 0.1 M *n*-$Bu_4NClO_4^-$ as supporting electrolyte and a standard Ag/$AgNO_3$ reference electrode.

Photophysical study

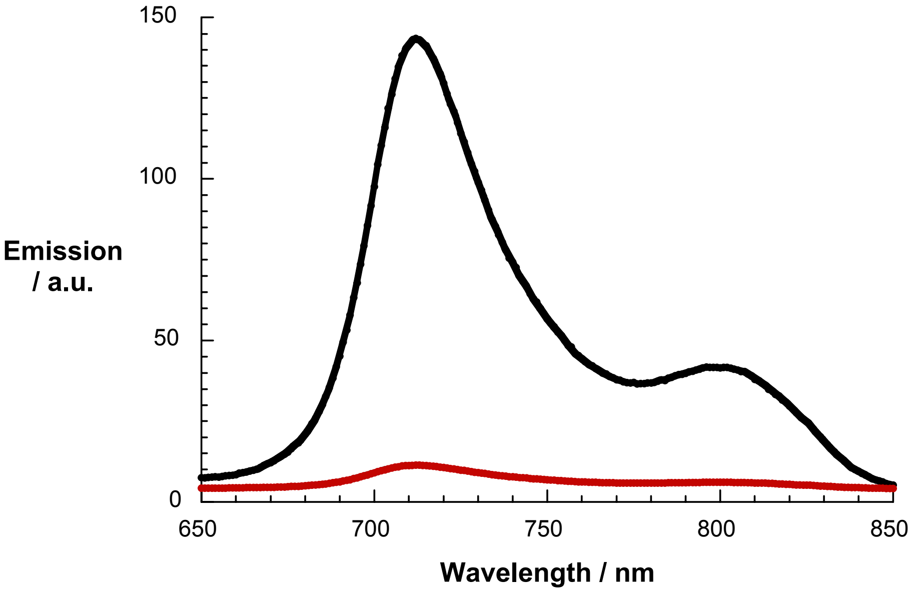

Figure S3. Room temperature fluorescence of the C_{60} reference (black spectrum) and C_{60}-exTTF-TTF in THF (red spectrum) with matching absorption at the 400 nm excitation wavelength (i.e., OD_{410nm} ~ 0.1).

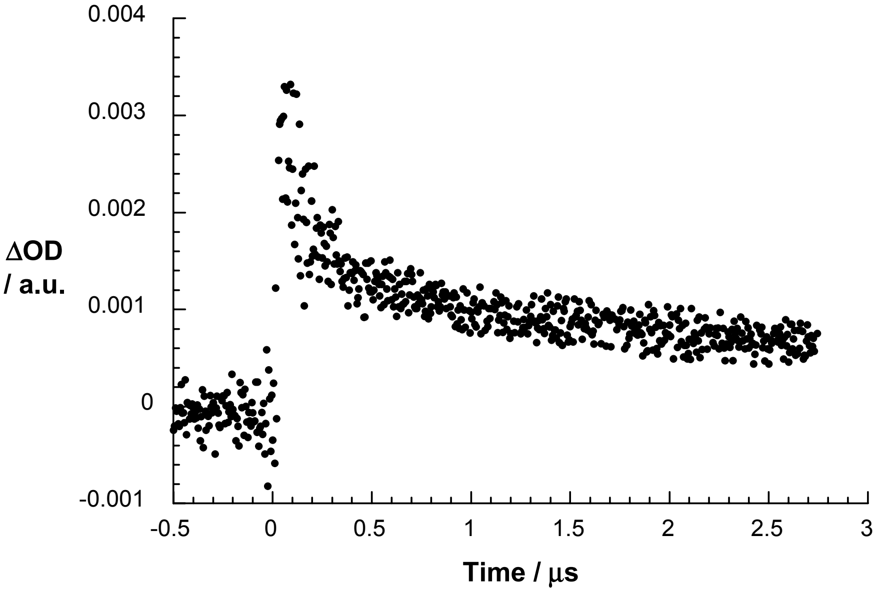

Figure S4. Time-absorption profile recorded upon nanosecond flash photolysis (337 nm) of C_{60}-exTTF-exTTF (~ 10^{-6} M) in deoxygenated THF at 1000 nm, monitoring the two step charge recombination.

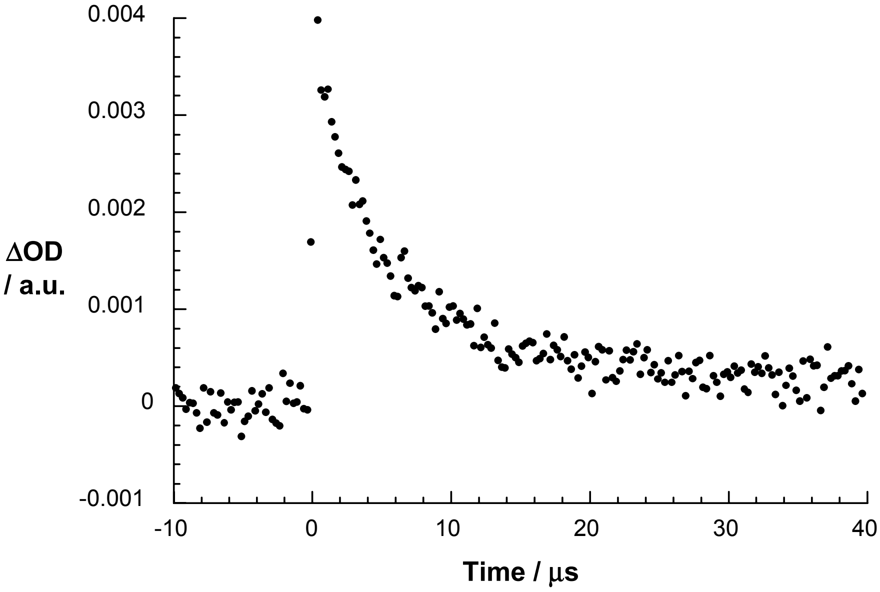

Figure S5. Time-absorption profiles recorded upon nanosecond flash photolysis (337 nm) of C_{60}-exTTF-TTF (~ 10^{-6} M) in deoxygenated THF at 1000 nm, monitoring the single step charge recombination.