Electronic Supplementary Information

Molecular Wire Behavior of Oligovynilfluorenes in exTTF-Fullerene Donor Acceptor Conjugates

Mateusz Wielopolski,[a] José Santos,[b] Beatriz M. Illescas,[b] Alejandro Ortiz,[c] Braulio Insuasty,[c] Thilo Bauer,[d] Timothy Clark,[d] Dirk M. Guldi,*[a] Nazario Martín*[b,e]

[a] *Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials, University of Erlangen, 91058 Erlangen, Germany. Fax: +49-913-185-28307; E-mail: dirk.guldi@chemie.uni-erlangen.de*
[b] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain. Fax: +34-91-394-4103; E-mail: nazmar@quim.ucm.es*
[c] *Departamento de Química, Facultad de Ciencias Naturales y Exactas, Universidad del Valle, 25360 Cali, Colombia.*
[d] *Computer-Chemie-Centrum and Cluster of Excellence Engineering of Advanced Materials, University of Erlangen, Nägelsbachstr. 25, 91052 Erlangen, Germany. Fax: +49-9131-85-26565; E-mail: clark@chemie.uni-erlangen.de*
[e] *Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Campus UAM, Cantoblanco, E-28049, Madrid, Spain.*

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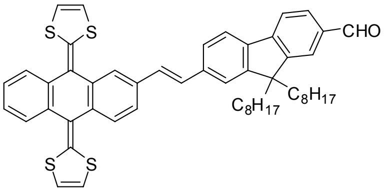
General Information: All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 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.

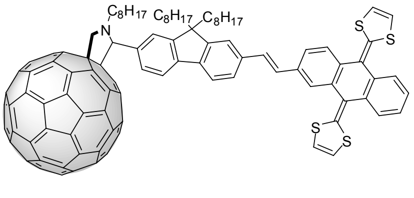
Experimental Part

(E)-7-(2-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)vinyl)-9,9-dioctyl-9H-fluorene-2-carbaldehyde (2)



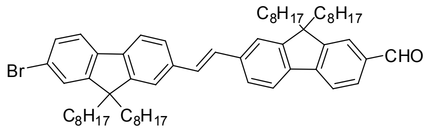
A solution of vinyl-exTTF **1** (208 mg, 0.51 mmol), 7-bromo-9,9-dioctyl-9H-fluorene-2-carbaldehyde **4** (195 mg, 0.39 mmol), Pd(OAc)$_2$ (9 mg, 0.04 mmol) y tri-*o*-tolylphosphine (25 mg, 0.08 mmol) in a mixture of dry DMF (5 mL) and triethylamine (1 mL) is degassed with argon for 30 min. The reaction mixture is kept at 90 ºC for 24 h and then diluted with CH_2Cl_2 (25 mL), washed with H_2O (3 x 20 mL), and dried (Na_2SO_4). After filtration, the solvent is removed under reduced pressure and the resulting residue is purified by column chromatography over silica employing CH_2Cl_2/hexane 6/4 as the eluent mixture. Compound **2** is obtained as an orange solid (58 mg, 18%). FTIR (KBr): 3104, 3001, 2921, 2852, 1690, 1547 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1H), 7.92-7.30 (m, 15H), 6.34 (s, 4H), 2.07 (t, *J* = 8.1 Hz, 4H), 1.09 (m, 20 H), 0.87 (m, 6H), 0.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 153.2, 152.2, 147.7, 139.6, 138.6, 136.3, 136.2, 135.7, 135.6, 135.3, 129.3, 126.5, 125.8, 125.4, 124.8, 123.4, 123.3, 122.6, 122.4, 121.7, 121.4, 120.3, 117.7, 117.5, 55.7, 40.7, 32.2, 30.4, 29.6, 24.2, 23.0, 15.5; MS (ESI) m/z: 823 (M+H$^+$); UV-vis (CH_2Cl_2) λ_{max}: 443, 401, 360 nm.

exTTF-OFV-C_{60} (3)



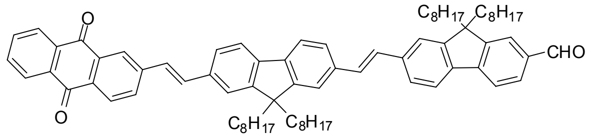
A solution of C_{60} (210 mg, 0.29 mmol), **2** (60 mg, 0.07 mmol) and N-octylglycine (68 mg, 0.365 mmol) in chlorobenzene (60 mL) is refluxed for 5 h under argon. Then, the solvent is removed under reduced pressure and the resulting residue is purified by silica gel column chromatography, employing CS_2 as eluent. Compound **3** was obtained as a brown solid (42 mg, 34%). FTIR (KBr): 2923, 2853, 1506, 1460, 757, 644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.21 (m, 15H), 6.32 (m, 4H), 5.15 (s, 1H), 5.14 (d, *J* = 9.3 Hz, 1H), 4.18 (d, *J* = 9.3 Hz, 1H), 3.27 (m, 1H), 2.65 (m, 1H), 0.78-2.19 (m, 49H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 154.2, 153.5, 151.0, 147.3, 146.8, 146.5, 146.3, 145.9, 145.7, 145.5, 145.3, 144.6, 144.4, 144.1, 143.2, 143.0, 142.6, 142.3, 142.1, 141.7, 141.6, 140.3, 139.9, 139.4, 137.9, 137.2, 136.9, 136.7, 135.9, 135.7, 134.0, 133.8, 133.7, 133.4, 131.8, 131.2, 129.7, 128.9, 128.1, 127.0, 126.8, 125.6, 125.0, 123.7, 118.4, 110.7, 110.2, 69.2, 69.1, 68.9, 66.9, 32.3, 31.5, 29.7, 28.7, 27.5, 25.9, 23.2, 23.0, 14.5, 14.3; MS (ESI) m/z: 1668.53 (M+H$^+$); UV-vis (CH$_2$Cl$_2$) λ_{max}: 441, 400, 359 nm.

(E)-7-(2-(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)vinyl)-9,9-dioctyl-9H-fluorene-2-carbaldehyde (6)



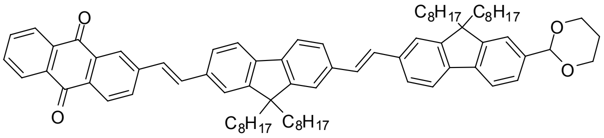
A solution of 7-bromo-9,9-dioctyl-9*H*-fluorene-2-carbaldehyde **4** (435 mg, 0.88 mmol), 2-bromo-9,9-dioctyl-7-vinyl-9*H*-fluorene **5** (434 mg, 0.88 mmol), K$_2$CO$_3$ (133 mg, 0.97 mmol), TBAB (311 mg, 0.97 mmol) and Pd(OAc)$_2$ (12 mg, 0.05 mmol) in dry DMF (3 mL) is degassed with argon for 25 min. The reaction mixture is kept at 110 ºC for 12 h, then diluted with CH$_2$Cl$_2$ (25 mL) and washed with water (3 x 20 mL), dried (Na$_2$SO$_4$), and filtrated. The solvent is removed under reduced pressure and the residue thus obtained is purified by silica gel column chromatography with CH$_2$Cl$_2$/hexane 3/7 as eluent. Compound **6** is obtained as a yellow solid (646 mg, 81%). m.p.: 72 ºC; FTIR (KBr): 3052, 3021, 2915, 2923, 1675, 1585, 1521, 1412, 1383 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 10.08 (s, 1H), 7.89-7.77 (m, 4H), 7.72-7.46 (m, 8H), 7.32-7.28 (m, 2H), 2.09-1.96 (m, 8H), 1.27-1.06 (m, 40H), 0.85-0.79 (m, 12H), 0.65-0.59 (m, 8H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 189.4, 151.4, 140.8, 130.6, 128.7, 125.8, 123.1, 119.6, 55.0, 40.5, 38.6, 31.8, 20.1, 29.3, 23.7, 22.6, 14.1; MS (MALDI-TOF) *m/z* = 910.515 (M$^+$); UV-vis (CHCl$_3$) λ_{max}: 407, 386, 368, 330, 257 nm.

Compound 7:



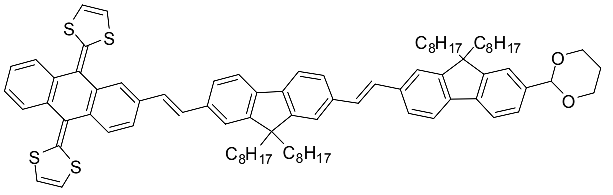
A solution of 2-vinylanthracene-9,10-dione (149 mg, 0.64 mmol), **6** (638 mg, 0.70 mmol), K$_2$CO$_3$ (97 mg, 0.701 mmol), TBAB (226 mg, 0.70 mmol) and Pd(OAc)$_2$ (5 mg, 0.02 mmol) in dry DMF (2 mL) is degassed with argon during 25 min. The reaction mixture is kept at 110 ºC for 12 h, then diluted with CH$_2$Cl$_2$ (25 mL), washed with water (2 x 20 mL) and dried (Na$_2$SO$_4$). After filtration, the solvent was removed under reduced pressure and the residue thus obtained was purified by silica gel column chromatography employing hexane/CH$_2$Cl$_2$ 1/1. Compound **7** was obtained as an orange solid (454 mg, 67%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 10.08 (s, 1H), 8.49 (d, J_2 = 1.8 Hz, 1H), 8.38-8.32 (m, 3H), 7.94 (dd, J_1 = 8.3 Hz, J_2 = 1.8 Hz, 1H), 7.90-7.78 (m, 7H), 7.75-7.72 (m, 2H), 7.62-750 (m, 7H), 7.34-7.32 (m, 2H), 2.08 (t, J = 7.7 Hz, 8H), 1.23-1.07 (m, 40H), 0.84-0.78 (m, 12H), 0.71-0.60 (m, 8H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 183.7, 183.0, 152.2, 152.1, 152.0, 151.1, 144.0, 142.3, 141.8, 141.0, 140.6, 138.1, 137.4, 136.9, 135.6, 134.6, 134.3, 134.2, 134.0, 132.3, 131.8, 129.4, 129.3, 128.9, 128.4, 127.6, 126.8, 126.2, 126.0, 125.7, 125.4, 125.1, 121.7, 121.1, 120.9, 120.6, 120.5, 119.9, 102.5, 67.9, 55.6, 55.5, 41.0, 40.9, 32.2, 30.5, 30.1, 29.7, 24.2, 24.1, 23.0, 14.5; MS (MALDI-TOF) m/z: 1064.605 (M^+); UV-vis (CH_2Cl_2) λ_{max}: 443, 386 nm.

Compound 8:



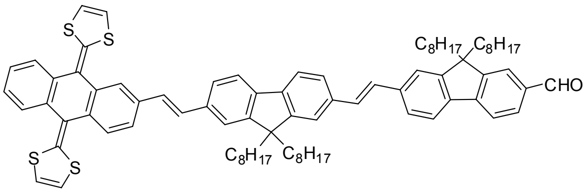
To a solution of **7** (314 mg, 0.29 mmol) and propane-1,3-diol (3.2 mL, 0.44 mmol) in dried toluene (20 mL), a catalytic amount of *p*-toluenesulfonic acid is added under argon. The mixture is refluxed for 48 h using a Dean-Stark trap. Then, the solvent is removed under reduced pressure and the residue purified by alumina column chromatography (hexane/CH_2Cl_2 1/2). Compound **8** is obtained as an orange solid (240 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, J_2 = 1.9 Hz, 1H), 8.37-8.29 (m, 3H), 7.91(dd, J_1 = 8.3 Hz, J_2 = 1.9 Hz, 1H), 7.85-7.72 (m, 9H), 7.63-7.47 (m, 7H), 7.35-7.33 (m, 2H), 5.60 (s, 1H), 4.36-4.33 (m, 2H), 4.10-4.05 (m, 2H), 2.40-2.26 (m, 1H), 2.10-2.07 (m, 8H), 1.52 (m, 1H), 1.26-1.07 (m, 40H), 0.84-0.81(m, 12H), 0.71-0.61 (m, 8H); UV-vis (CH_2Cl_2) λ_{max}: 444, 390, 333, 279 nm.

Compound 9:



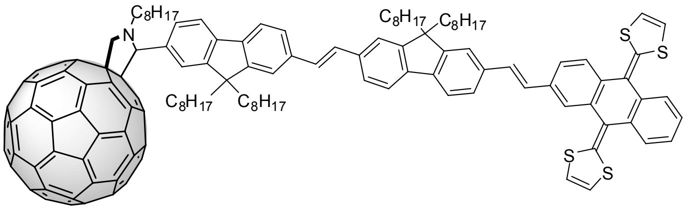
To a solution of dimethyl 1,3-dithiol-2-ylphosphonate (271 mg, 1.28 mmol) in anhydrous THF (60 mL) at -78 ºC and under argon atmosphere, LDA (1.7 M in hexane; 0.88 mL, 1.50 mmol) was added and the mixture is stirred for 30 min. Then, a solution of compound **8** (240 mg, 0.21 mmol) in dried THF (15 mL) is added at -78 ºC. The solution is stirred at -78 ºC for 1 h and at room temperature overnight. After removing the solvent under reduced pressure, water (100 mL) is added and the mixture is extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers are washed with water (2 x 75 mL), and brine (75 mL), dried (Na_2SO_4), filtrated and the solvent evaporated. The resulting residue is purified by flash chromatography over silica using hexane/CH_2Cl_2 2/3 as eluent. Compound **9** is obtained as an orange solid (169 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, J = 1.5 Hz, 1H), 7.75-7.68 (m, 8H), 7.57-7.46 (m, 10H), 7.34-7.30, (m, 4H), 6.33 (s, 2H), 6.32 (m, 1H), 6.31 (s, 1H), 5.61 (s, 1H), 4.37-4.32 (m, 2H), 4.10-4.01 (m, 2H), 2.38-2.24 (m, 1H), 2.10-2.00 (m, 8H), 1.52 (m, 1H), 1.26-1.08 (m, 40H), 0.86-0.80 (m, 12H), 0.73-0.65 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.1, 152.0, 151.9, 151.3, 141.8, 141.2, 141.0, 140.9, 138.5, 138.0, 137.0, 136.9, 136.7, 136.2, 136.1, 135.7, 135.0, 129.8, 129.7, 129.3, 129.2, 129.0, 128.9, 128.1, 126.4, 126.3, 126.2, 126.1, 126.0, 125.7, 125.4, 124.7, 123.2, 122.7, 122.5, 121.2, 121.1, 121.0, 120.9, 120.5, 120.4, 120.3, 119.9, 117.7, 117.6, 117.5, 102.5, 67.9, 55.5, 55.4, 41.0, 40.9, 32.2, 30.6, 30.5, 30.1, 29.7, 24.2, 24.1, 23.0, 14.6, 14.5; MS (MALDI-TOF) m/z: 1294.545 (M^+); UV-vis (CH_2Cl_2) λ_{max}: 406 nm.

Compound 10:



Compound **9** (101 mg, 0.078 mmol) is dissolved in AcOEt (30 mL) and HCl 1M (20 mL) is added. The mixture is stirred for 3 h, the organic layer is extracted, washed with water (2 x 50 mL), dried (Na_2SO_4) and filtrated. The solvent is removed under reduced pressure and pure compound **10** is obtained (96 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 7.93-7.85 (m, 4H), 7.76-7.69 (m, 6H), 7.62-7.53 (m, 8H), 7.34-7.30 (m, 5H), 6.33 (s, 2H), 6.32 (s, 1H), 6.31 (s, 1H), 2.09-2.06 (m, 8H), 1.23-1.09 (m, 40H), 0.85-0.80 (m, 12H), 0.72-0.63 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.8, 153.2, 152.1, 152.0, 151.9, 147.8, 141.3, 141.0, 139.5, 138.8, 138.5, 136.9, 136.6, 136.2, 136.1, 135.7, 135.6, 135.5, 135.0, 133.4, 131.3, 131.1, 130.2, 129.8, 129.3, 128.5. 128.2, 126.4, 126.3, 125.8, 125.4, 124.9, 124.7, 124.4, 123.4, 123.2, 122.7, 122.5, 121.7, 121.2, 120.4, 120.3, 117.7, 117.5, 55.7, 55.5, 41.0, 40.8, 32.4, 32.2, 32.1, 31.9, 31.8, 30.6, 30.5, 30.4, 30.1, 29.7, 29.6, 24.2, 23.0, 14.6, 14.5; MS (MALDI-TOF) m/z: 1236.471 (M^+); UV-vis (CH_2Cl_2) λ_{max}: 411 nm.

exTTF-OFV$_2$-C$_{60}$ (11):



A solution of C_{60} (670 mg, 0.93 mmol), compound **10** (288 mg, 0.23 mmol) and N-octylglycine (214 mg, 1.17 mmol) in chlorobenzene (190 mL) was heated to reflux for 2 h under argon atmosphere. The solvent was then evaporated and the residue thus obtained was purified by flash chromatography over florisil, employing CS_2 as the eluent. Compound **11** was obtained as a brown solid (193 mg, 40%). FTIR (KBr): 3021, 2924, 2853, 1509, 1462, 1004, 755, 643 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (m, 1H), 7.92 (d, J = 1,5 Hz, 1H), 7.75-7.67 (m, 7H), 7.55-7.50 (m, 8H), 7.46 (dd, J_1 = 8,2 Hz, J_2 = 1,7 Hz, 1H), 7.34-7.31 (m, 2H), 7.28 (bs, 1H), 7.25-7.24 (m, 2H), 6.34 (s, 2H), 6.33 (s, 1H), 6.32 (s, 1H), 5.16-5.12 (m, 2H), 4.18 (d, J = 9.4 Hz, 1H), 3.27 (m, 1H), 2.67-2.59 (m, 1H), 2.08-2.02 (m, 8H), 1.48-1.36 (m, 8H), 1.27-1.09 (m, 44H), 0.97-0.68 (m, 23H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 154.7, 154.2, 152.0, 151.9, 147.7, 146.7, 146.6, 146.5, 146.3, 146.0, 145.9, 145.7, 145.6, 145.5, 144.8, 143.5, 143.4, 143.0, 142.6, 142.5, 141.1, 141.0, 140.5, 136.8, 136.7, 136.2, 136.1, 136.0, 135.7, 135.0, 126.4, 125.4, 122.7, 122.5, 117.8, 117.7, 117.5, 69.39, 55.5, 55.4, 41.0, 32.4, 32.3, 32.2, 30.8, 30.5, 30.0, 29.9, 29.7, 24.2, 23.2, 23.1, 23.0, 14.6, 14.5; MS (MALDI-TOF) m/z: 2081.192 (M^+); UV-vis (CH_2Cl_2) λ_{max}: 430, 407, 370, 330, 267 nm.

Electrochemistry

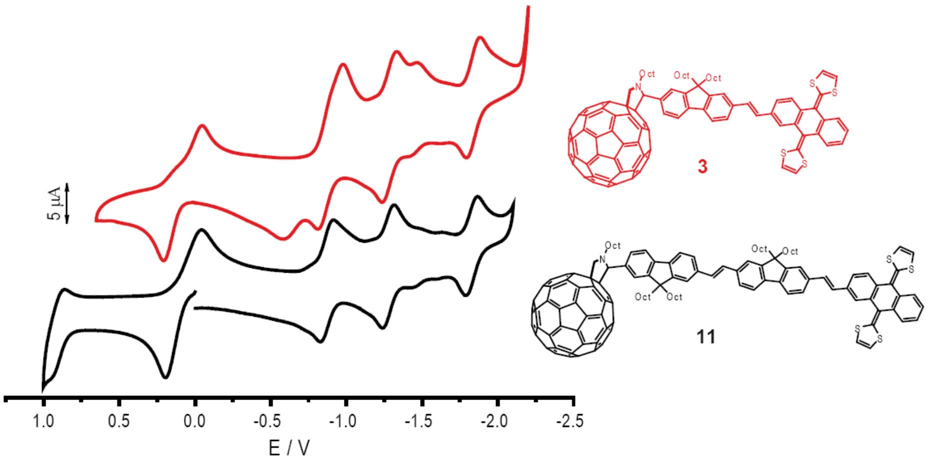


Figure S1. Cyclic voltammetry of compounds **3** and **11** in ODCB/CH_3CN 4:1 at 100 mV·s^{-1}.

Chemical structure of 3b and 11b

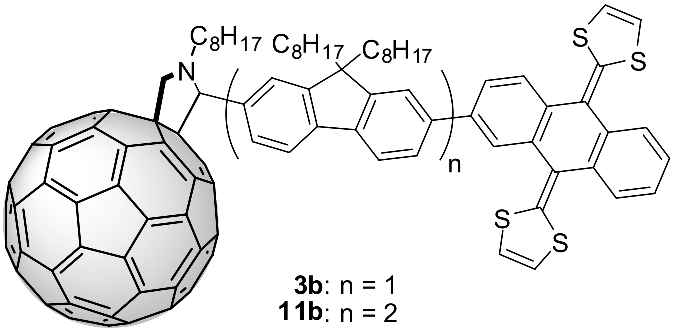


Figure S2. Chemical structure of the hypothetical model compounds as created for the molecular modeling studies **3b** and **11b**.