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Supporting Information

for

Controlling Short- and Long-range Electron Transfer Processes in Molecular Dyads and Triads

By

L. Sánchez,[a] I. Pérez,[a] N. Martín,[a]* D.M. Guldi[b]*

S1 Synthesis

General remarks.

All reagents and solvents were used as received or purified using standard procedures. Flash chromatography was performed using Kieselgel Merck Type 9385 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. Melting points were determined with a Gallenkamp apparatus.

^{1}H-NMR and ^{13}C-NMR spectroscopy were performed on Varian XL-300, Brucker AC-200, Brucker Avance-300 or Brucker AMX-500 equipments as indicated, at 298 K. Coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q =

quartet, p = pentet, dd = double doublet, m = multiplet, br = broad. FT-IR spectra were recorded on a Nicolet-Magna-IR Spectrometer 5550 or on a Shimazdu-8300 instruments. UV-Vis spectra were recorded on a Varian Cary 50-B spectrophotometer. Mass Spectroscopy (MS) was performed on a HP 5989A spectrometer (positive ion EI mode) and on a Brucker Reflex III apparatus endowed with a laser operating at λ = 337 nm and using ditranol as matrix (MALDI-TOF). Elemental analyses were performed by the Microanalytical Service of UCM.

Cyclic Voltammetry was performed using an Autolab PGStat 30.

Picosecond laser flash photolysis experiments were carried out with 355-nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (pulse width 18 ps, 2-3 mJ / pulse). Nanosecond laser studies were performed with laser pulses from a Molectron UV-400 nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ / pulse). The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer. Fluorescence lifetimes were measured with a Laser Strope Fluorescence Lifetime Spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufacture's web site, http://www.pti-nj.com. Emission spectra were recorded with a SLM 8100 Spectrofluorometer. The experiments were performed at room temperature. Each spectrum represents an average of at least 5 individual scans, and appropriate corrections were applied whenever necessary.

***tert-butyl{[6-(hexyloxy)-9,10-dioxo-9,10-dihydroanthracen-2-yl]oxy}diphenylsilane* (9).** Diphenyltertbutylsilylchloride 1.65 mmol, 431 mg) and imydazole (6.9 mmol, 471 mg), in this order, were added to a solution of 2-hexyloxy-6-hydroxy-9,10-anthraquinone (1.38 mmol, 450 mg) in DMF (15 mL). The reaction mixture was stirred at room temperature and under argon atmosphere for 16h. After, DMF was removed under vacuum and the resulting mixture washed with water (50 mL) and extracted with ethyl acetate (3 x 25 mL). The organic extracts were dried with $MgSO_4$ and the solvent removed under vacuum. The final product was purified by column chromatography using a mixture of hexane/methylene dichloride (2/1) as eluent. 32 % yield, m.p. 232-235 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.17 (d, ^3J(H,H)=9 Hz, 1H), 8.01 (d, ^3J(H,H)=9 Hz, 1H), 7.73 (m, 6H), 7.43 (m, 6H), 7.19 (dd, $^3J_1$(H,H)=9 Hz, $^4J_1$(H,H)=2.4 Hz, 1H), 6.97 (dd,

$^3J_1$(H,H)=9 Hz, $^4J_1$(H,H)=2.4 Hz, 1H), 4.12 (t, ^3J(H,H)=6.6 Hz, 2H), 1.84 (q, ^3J(H,H)=6.6 Hz, 2H,), 1.47 (m, 2H), 1.38 (m, 3H), 1.11 (s, 9H), 1.09 (m, 2H), 0.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 182.1, 181.8, 163.8, 160.9, 135.6, 135.3, 134.7, 131.6, 130.2, 129.5, 129.4, 128.0, 127.9, 127.5, 127.3, 126.8, 124.6, 120.7, 117.6, 110.3, 68.6, 31.4, 28.8, 26.5, 26.3, 25.5, 22.4, 19.4, 18.9, 13.9; FTIR (KBr) ν = 2929, 2856, 1664, 1647, 1569, 1508, 1458, 1429, 1330, 1238, 1151, 1112, 1082, 1018, 881, 819, 663 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 256 (4.86), 278 (4.57), 331 (4.15) nm; MS (70eV): *m/z* (%) 562 (63) [M^+]; elemental analysis calcd (%) for $C_{36}H_{38}O_4Si$ (562.78): C 76.83, H 6.81; found: C 77.06, H 6.63.

tert-butyl{[9,10-bis-1,3-dithiol-2-ylidene-6-(hexyloxy)-9,10-dihydroanthracen-2-yl]oxy}diphenylsilane (12) To a solution of phosphonate ester **11a** (1.35 mmol, 283 mg) in dry THF (20 mL) at -78 °C and under argon atmosphere was added *n*-BuLi (1.6 M) (1.46 mmol, 1.25 mL) with a syringe. After 30 min at -78 °C, a solution of **9** in dry THF (20 mL), was added with a syringe into the solution of the phosphonate carbanion. The mixture was stirred for 1 h at-78 °C and then allowed to warm to 20 °C allowed to stand overnight. The THF was evaporated under reduced pressure, water (75 mL) added, and the residue extracted with CH_2Cl_2 (3 x 75 mL). The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using a mixture of hexane/CH_2Cl_2 (4/1) as eluent. 56 % yield, m.p. 239-242 ^oC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.76 (m, 4H), 7.52-7.40 (m, 9H), 7.17 (d, $^3J(H,H)=2.4$ Hz, 1H), 7.01 (d, $^3J(H,H)=2.4$ Hz, 1H), 6.75 (m, 2H), 6.26 (s, 1H), 6.13 (m, 2H), 4.00 (t, $^3J(H,H)=6.6$ Hz, 2H,), 1.80 (q, $^3J(H,H)=6.6$ Hz, 2H), 1.45-1.26 (m, 5H), 1.11 (s, 9H), 0.91 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 157.0, 153.4, 135.8, 135.5, 132.7, 129.8, 129.7, 127.8, 125.9, 125.8, 117.4, 117.0, 116.7, 116.0, 111.9, 110.8, 68.1, 31.5, 29.2, 26.4, 25.7, 22.6, 19.4, 14.0; FTIR (KBr) ν: 2929, 2856, 1664, 1647, 1569, 1508, 1458, 1429, 1330, 1238, 1151, 1112, 1082, 1018, 881, 819, 663 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 243 (4.42), 365 (4.01), 428 (4.32) nm; MS (70eV) *m/z* (%): 735 (100) [M^+]; elemental analysis calcd (%) for $C_{42}H_{42}O_2S_4Si$ (735.11): C 68.62, H 5.76, S 17.44; found: C 68.83, H 5.86, S 17.22.

***9,10-bis-1,3-dithiol-2-ylidene-6-(hexyloxy)-9,10-dihydro-anthracen-2-ol* (13).** To a solution of **12** in dry THF (30 mL) and under argon atmosphere Bu_4NF was added and the resulting mixture stirred for 16 h. After that, the solvent was removed under vacuum and the final product purified by column chromatography on silica gel using chloroform as eluent. 99 % yield, m.p.> 300 °C (dec); ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 7.66 (m, 1H), 7.50 (d, ^3J(H,H)=8.4 Hz, 1H), 7.41 (d, ^3J(H,H)=8.4 Hz, 1H), 7.08 (d, ^4J(H,H)=2.4 Hz, 1H), 7.01 (d, ^4J(H,H)=2.4 Hz, 1H), 6.87 (dd, $^3J_1$(H,H)=8.4, $^4J_2$(H,H)=2.4 Hz, 1H), 6.69 (m, 4H), 4.00 (t, ^3J(H,H)=7.5 Hz, 2H), 1.72 (q, ^3J(H,H)=6.6 Hz, 2H), 1.41-1.29 (m, 6H), 0.86 (t, ^3J(H,H)=6.9 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ 156.9, 155.7, 136.7, 136.6, 134.8, 133.9, 129.5, 127.8, 126.5, 126.3, 121.3, 118.4, 118.3, 118.2, 112.1, 111.7, 110.9, 68.0, 31.5, 28.9, 25.5, 22.4, 14.2; FTIR (KBr) ν: 3413, 2925, 2854, 1604, 1560, 1544, 1508, 1500, 1465, 1425, 1284, 1217, 1099, 794, 636 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) 242 (4.61), 364 (4.12), 421 (4.31) nm; MS (70eV): *m/z* (%) 496 (100) [M$^+$]; elemental analysis calcd (%) for $C_{26}H_{24}O_2S_4$ (496.71): C 62.87, H 6.81, S 25.82; found: C 62.83, H 6.96, S 25.62.

Synthesis of aldehydes 17, 19a,b and 23. General Procedure. DMAP (0.28 mmol), and DCC (0.58 mmol) were added to a suspension of the corresponding alcohol (**13**, **15a** , **15b**, **20**) (0.52 mmol) in CH$_2$Cl$_2$ (5 mL), and the mixture was stirred at room temperature for 20.min. A solution of 4-carboxybenzaldehyde (stoichiometric amounts) in CH_2Cl_2 (5 mL) was added, and the mixture stirred for a further 20 h. at room temperature. The solvent was removed under reduced pressure, and the solid residue was purified by flash column chromatography on silica gel by using CH_2Cl_2 as eluent.

***9,10-bis-(1,3-dithiol-2-ylidene)-6-(hexyloxy)-9,10-dihydroan-thracen-2-yl 4-formylbenzoate* (17).** 62 % yield, m.p.> 300 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.16 (s, 1H), 8.40 (d, ^3J(H,H)=7.8 Hz, 2H), 8.04 (d, ^3J(H,H)=7.8 Hz, 2H), 7.72 (m, 2H), 7.69 (m, 1H), 7.41 (m, 1H), 7.14 (m, 1H), 7.14 (dd, $^3J_1$(H,H)=8.4 Hz, $^4J_2$(H,H)=2.4 Hz, 1H), 6.84 (dd, $^3J_1$(H,H)=8.4 Hz, $^4J_2$(H,H)=2.4 Hz, 1H), 6.45 (d, ^3J(H,H)=8.4 Hz, 4H), 4.03 (t, ^3J(H,H)=7.5 Hz, 2H), 1.75 (q, ^3J(H,H)=6.6 Hz, 2H), 1.43-1.32 (m, 6H), 0.89 (t, ^3J(H,H)=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 191.5, 157.2, 148.2, 139.5, 137.1, 136.7, 136.1, 134.7, 134.5, 133.4, 130.8, 129.6, 128.0, 126.7, 126.0, 125.0, 118.3, 118.0, 117.1, 112.2, 110.8, 68.2, 31.6, 29.2, 25.7, 22.6, 14.0; FTIR (KBr) ν: 2925, 2854, 1728, 1705, 1602, 1546, 1515, 1463, 1411, 1388, 1263, 1199, 1105, 1074, 661 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 241 (4.38), 362 (4.15), 432 (4.25) nm MS (70eV): *m/z* (%) 628 (100) [M^+]; elemental analysis calcd (%) for $C_{34}H_{28}O_4S_4$ (628.83): C 64.94, H 4.49, S 20.39; found: C 64.92, H 4.19, S 20.41.

2,6-Bis(4-formylphenylcarbonyloxy)-9,10-bis(1,3-dithiol-2-yliden)-9,10-dihydroanthracene (19a). 37% yield; m.p.> 300 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.16 (s, 2H), 8.40 (d, ^3J(H,H)=8.4 Hz, 4H), 8.05 (d, ^3J(H,H)=8.4 Hz, 4H), 7.76 (d, ^3J(H,H)=8.4 Hz, 2H), 7.62 (d, ^4J(H,H)=2.2 Hz, 2H,), 7.17 (dd, $^3J_1$ (H,H) =8.4 Hz, $^4J_2$ (H,H) =2.2 Hz, 2H), 6.35 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 191.5, 164.9, 148.3, 137.5, 136.9, 135.1, 134.7, 134.5, 130.8, 129.6, 127.7, 118.7, 117.7; FTIR (KBr) ν: 1733, 1701, 1604, 1546, 1508, 1463, 1411, 1388, 1259, 1186, 1155, 1110, 1070, 1014, 900, 835, 815, 752 cm^{-1}, UV/Vis (CH_2Cl_2): λ_{max} (log ε) 256 (4.84), 368 (4.22), 434 (4.40) nm; MS (70eV): *m/z* (%) 676 (100) [M^+]; elemental analysis calcd (%) for $C_{36}H_{20}O_6S_4$ (676.79): C 63.89, H 2.98, S 18.95; found: C 63.93, H 2.99, S 18.76.

2,6-Bis(4-formylphenylcarbonyloxy)-9,10-bis[4,5-bis(methylthio)-(1,3-dithiol-2-yliden)]-9,10-dihydroanthracene (19b). 39% yield; m.p.> 300 °C (dec); ^{1}H NMR (500 MHz, [D_6]DMSO, 25 °C): δ = 10.16 (s, 2H), 8.36 (d, ^3J(H,H)=8.5 Hz, 4H), 8.12 (d, ^3J(H,H)=8.5 Hz, 4H), 7.65 (d, ^3J(H,H)=8.5 Hz, 2H), 7.53 (d, ^4J(H,H)=2.5 Hz, 2H,), 7.40 (dd, $^3J_1$ (H,H)

=8.5 Hz, ${}^4J_2$ (H,H) =2.5 Hz, 2H), 2.41 (s, 12H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 193.0, 163.7, 148.7, 139.5, 135.0, 133.5, 132.4, 131.4, 130.6, 129.7, 126.4, 125.3, 124.7, 121.5, 120.1, 118.8, 18.5, 18.4; FTIR (KBr) ν: 1733, 1705, 1600, 1533, 1496, 1460, 1411, 1382, 1253, 1188, 1151, 1103, 1068, 1014, 972, 894, 833, 812, 752, 682 cm^{-1}, UV/Vis (CH_2Cl_2): λ_{max} (log ε) 256 (4.50), 375 (4.18), 442 (4.38) nm; MS (70eV): *m/z* (%) 860 (100) [M$^+$]; elemental analysis calcd (%) for $C_{40}H_{28}O_6S_8$ (859.96): C 55.79, H 3.28, S 29.78; found: C 55.54, H 3.39, S 29.76.

[9,10-Bis(1,3-dithiol-2-yliden)-9,10-dihydro-2-anthryl]-methyl 4-formylbenzoate (22). 67% yield, m.p.> 300 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.11 (s, 1H), 8.27 (d, ${}^3J$(H,H)=8.4 Hz, 2H), 8.21 (d, J(H,H)=8.0 Hz, 1H), 7.95 (d, ${}^3J$(H,H)=8.4 Hz, 2H), 7.80 (d, ${}^4J$(H,H)=1.4 Hz, 1H), 7.70 (m, 2H), 7.36 (dd, ${}^3J_1$ (H,H)=8.0 Hz; ${}^4J_2$ (H,H)=1.4 Hz, 1H), 7.30 (m, 2H), 6.30 (m, 4H), 5.45 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 191.6, 167.3, 143.4, 139.2, 135.8, 135.5, 135.3, 135.2, 135.1, 133.0, 130.4, 130.2, 129.5, 126.0, 125.8, 125.2, 125.0, 124.9, 124.8, 117.3, 117.2, 117.1, 116.9, 67.1; FTIR (KBr) ν: 1701, 1608, 1544, 1508, 1450, 1419, 1380, 1265, 1201, 1101, 1014, 800, 756 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 242 (4.56), 366 (4.06), 432

(4.27) nm; MS (70eV) *m/z* (%) 542 (100) [M^+]; elemental analysis calcd (%) for $C_{29}H_{18}O_3S_4$ (542.70): C 64.18, H 3.34, S 23.63; found: C 64.09, H 3.18, S 23.87.

Synthesis of 24a and 24b. General procedure.

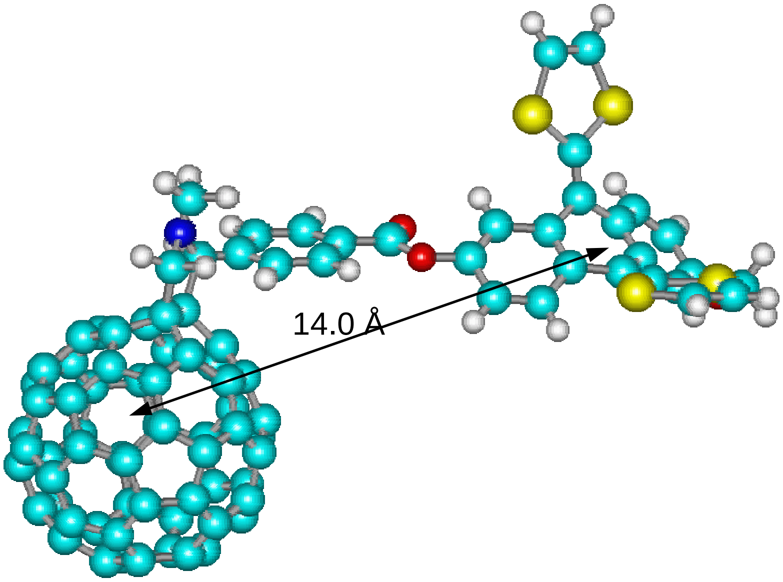
A solution of triphenylphosphonium salt (**21**) (0.06 mmol, 43 mg) and Bu^tOK (0.06 mmol, 10 mg) in toluene was refluxed under argon atmosphere for 15 min. After that, a solution of bisaldehyde (**19a** or **19b**) (0.06 mmol) was added. The resulting mixture was refluxed under argon atmosphere for 16 h. The solvent was removed under vacuum and the final compound was purified by column chromatography using methylene chloride as eluent.

9,10-bis-1,3-dithiol-2-ylidene-6-[(4-formylbenzoyl)oxy]-9,10-dihydroanthracen-2-yl 4-[(E)-2-(9,10-bis-1,3-dithiol-2-ylidene-9,10-dihydroanthracen-2-yl)vinyl]benzoate (24a). 43 % yield, m.p.> 300 °C (dec); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.17 (s, 1H), 8.40 (d, $^3J(H,H)=9$ Hz, 2H), 8.23 (d, $^3J(H,H)=9$ Hz, 2H), 8.05 (d, $^3J(H,H)=9$ Hz, 2H), 7.91 (s, 1H), 7.78-7.58 (m, 8H), 7.48 (dd, $^3J_1(H,H)=6$ Hz, $^4J_2(H,H)=1.2$ Hz, 1H), 7.32-7.24 (m, 5H), 7.17 (dd, $^3J_1(H,H)=6$ Hz, $^4J_2(H,H)=1.2$ Hz, 1H), 6.34 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 193.0, 167.3, 163.8, 148.2, 147.7, 143.4, 139.6, 139.2, 138.3, 136.1, 135.8, 135.5, 135.3, 135.2, 135.1, 133.5, 133.0, 132.5, 130.6, 130.4, 130.2, 129.7, 126.0, 125.8, 125.2, 125.0, 124.9, 124.8, 119.5, 118.9, 118.4, 118.2, 114.6; FTIR (KBr): ν: 2927, 2854, 1733, 1718, 1701, 1683, 1652, 1602, 1558, 1541, 1508, 1488, 1257, 1176, 1112, 1068, 1014, 800, 704 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 242 (4.49), 339 (4.10), 439 (4.29) nm; MS (70eV): *m/z* (%) 1053 (57) [M^+]; elemental analysis calcd (%) for $C_{57}H_{32}O_5S_8$ (1053.38): C 64.99, H 3.06, S 24.35; found: C 64.62, H 3.19, S 24.41.

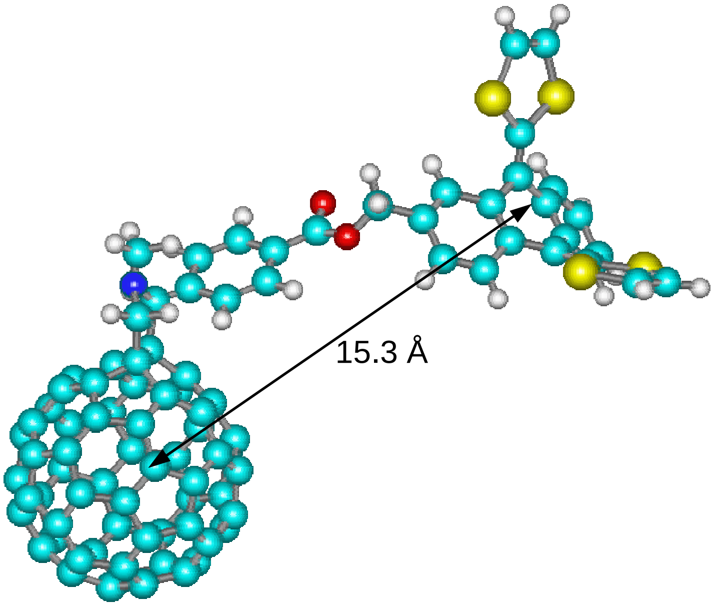
***9,10-bis[4-5-bis(methylthio)-1,3-dithiol-2-ylidene]-6-[(4-formylbenzoyl)oxy]-9,10-dihydroanthracen-2-yl 4-[(E)-2-(9,10-bis-1,3-dithiol-2-ylidene-9,10-dihydroanthracen-2-yl)vinyl]benzoate (24b*).** 38 % yield, m.p.> 300 °C (dec); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 10.18 (s, 1H), 8.41 (d, ^3J(H,H)=8.5 Hz, 2H), 8.23 (d, ^3J(H,H)=8.5 Hz, 2H), 8.07 (d, ^3J(H,H)=8.5 Hz, 2H), 7.92 (s, 1H), 7.74-7.61 (m, 8H), 7.45 (dd, $^3J_1$(H,H)=6 Hz, $^4J_2$(H,H)=1.2 Hz, 1H), 7.34-7.20 (m, 5H), 7.17 (dd, $^3J_1$(H,H)=6 Hz, $^4J_2$(H,H)=1.2 Hz, 1H), 6.32 (m, 4H), 2.42 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 191.5, 164.7, 163.9, 149.1, 148.6, 142.7, 139.7, 136.2, 136.0, 135.9, 135.5, 135.2, 134.4, 134.3, 132.6, 132.2, 131.5, 130.9, 130.7, 129.6, 127.9, 127.3, 126.5, 126.4, 126.0, 125.5, 125.4, 124.9, 124.7, 123.2, 122.1, 122.0, 119.5, 119.1, 118.7, 118.5, 117.3, 117.0, 19.2, 19.1; FTIR (KBr): ν: 2922, 2852, 2731, 1733, 1717, 1701, 1682, 1655, 1604, 1560, 1541, 1508, 1255, 1066, 752, 669 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) 241 (4.46), 346 (4.17), 426 (4.31) nm; MS (70eV): *m/z* (%) 1237 (63) [M^+]; elemental analysis calcd (%) for $C_{61}H_{40}O_5S_{12}$ (1235.95): C 59.20, H 3.26, S 31.08; found: C 58.92, H 3.09, S 31.41.

S2 HYPERCHEM 5.1

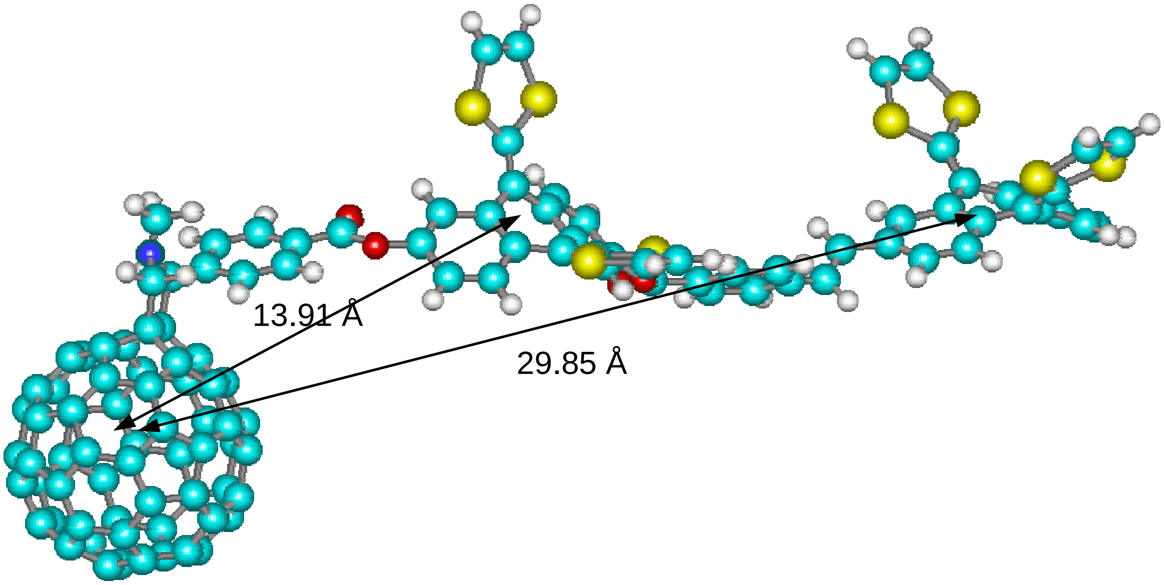
1.- *Dyad C_{60}-exTTF (18).*



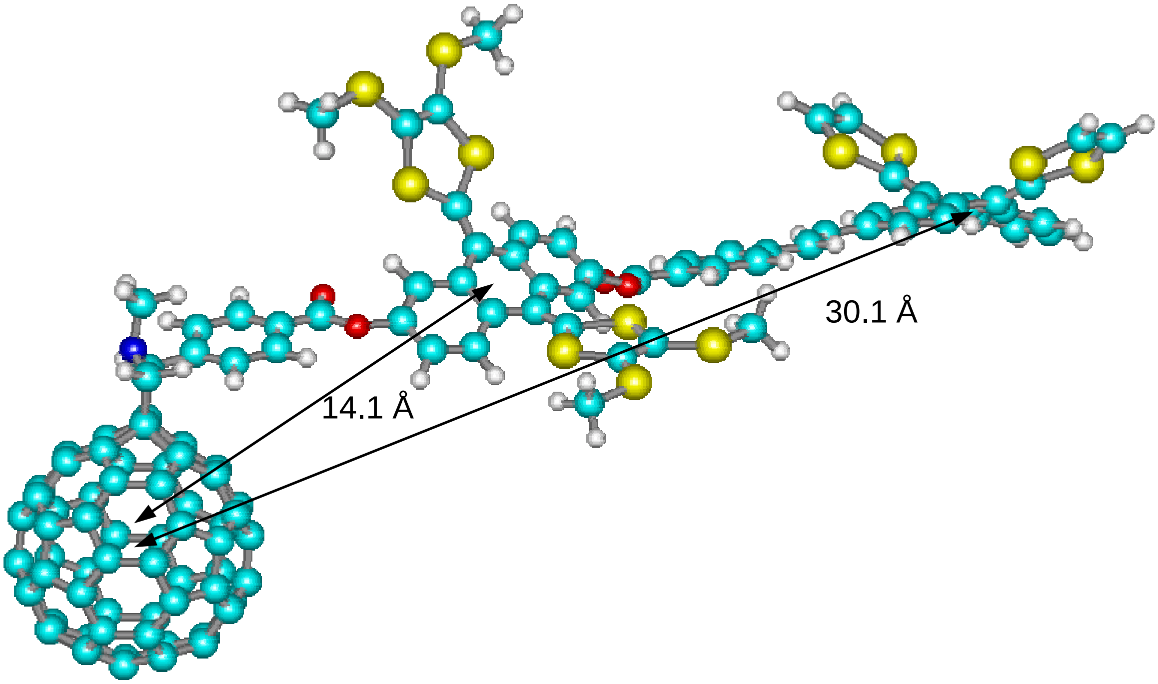
2.- *Dyad C_{60}-exTTF (23).*



3.- *Triad C_{60}-exTTF$_1$-exTTF$_1$* (25).



4.- *Triad C_{60}-exTTF$_2$-exTTF$_1$*(26).



S3 Thermodynamics

The driving forces ($-\Delta G_{CR}^{\circ}$ [eV]) for the intramolecular charge-recombination (CR) processes were calculated by applying equation S1:

$$-\Delta G_{\mathrm{CR}}^{\circ} = E_{1/2}(\mathrm{D}^{\bullet +}/\mathrm{D}) - E_{1/2}(\mathrm{A}/\mathrm{A}^{\bullet -}) + \Delta G_{\mathrm{S}} \qquad \text{(S1)}$$

where $E^{\circ}_{1/2}(\mathrm{D}^{\bullet +}/\mathrm{D})$ is the first one-electron oxidation potential of the exTTF donor moiety, while $E^{\circ}_{1/2}(\mathrm{A}/\mathrm{A}^{\bullet -})$ refers to the first one-electron reduction potential of the C_{60} electron acceptor. In the next step we elucidate the role of the solvent (ΔG_S) on the relative energy of the charge-separated state by referring to the “Dielectric Continuum Model”:

$$\Delta G_{\mathrm{S}} = \frac{e^2}{4\pi\varepsilon_0}\left[\left(\frac{1}{2R_+} + \frac{1}{2R_-} - \frac{1}{R_{\mathrm{D-A}}}\right)\frac{1}{\varepsilon_{\mathrm{S}}} - \left(\frac{1}{2R_+} + \frac{1}{2R_-}\right)\frac{1}{\varepsilon_{\mathrm{R}}}\right] \qquad \text{(S2)}$$

Furthermore, the driving forces ($-\Delta G_{CS}^{\circ}$ [eV]) for the intramolecular charge-separation (CS) processes were determined by:

$$-\Delta G_{\mathrm{CS}}^{\circ} = \Delta E_{0\text{-}0} - \left(-\Delta G_{\mathrm{CR}}\right) \qquad \text{(S3)}$$

Hereby, $\Delta E_{0\text{-}0}$ is the energy of the 0-0 transition energy gap between the lowest excited state and the ground state (1.76 eV). The accordingly calculated $-\Delta G_{CS}^{\circ}$ and $-\Delta G_{CR}^{\circ}$ values are given in Table S1.

Table S1: Center-to-Center Separation ($r_{D\text{-}A}$) and Thermodynamic Parameters (ΔG_S, $-\Delta G_{CS}^\circ$, $-\Delta G_{CR}^\circ$) for Different Donor-Acceptor Ensembles.

	$r_{D\text{-}A}$ [Å]	Solvent	ΔG_S [eV]	$-\Delta G_{CS}^\circ$ [eV]	$-\Delta G_{CR}^\circ$ [eV]
4a	9.5	Toluene	-1.25		
		CH_2Cl_2	-0.20	0.44	1.32
		PhCN	+0.04	0.68	1.08
23	14.0	Toluene	-1.17		
		THF	-0.21	0.47	1.29
		CH_2Cl_2	-0.13	0.55	1.21
		PhCN	+0.10	0.78	0.98
18	15.3	Toluene	-1.18		
		THF	-0.21	0.44	1.32
		CH_2Cl_2	-0.14	0.51	1.25
		PhCN	+0.09	0.74	1.02
25	13.91	Toluene	-1.18		
		THF	-0.21	0.38	1.38
		CH_2Cl_2	-0.14	0.45	1.31
		PhCN	+0.09	0.68	1.08
		DMF	+0.14	0.73	1.03
26	14.1	Toluene	-1.18		
		THF	-0.21	0.27	1.49
		CH_2Cl_2	-0.14	0.34	1.42
		PhCN	+0.09	0.57	1.19
		DMF	+0.14	0.62	1.14