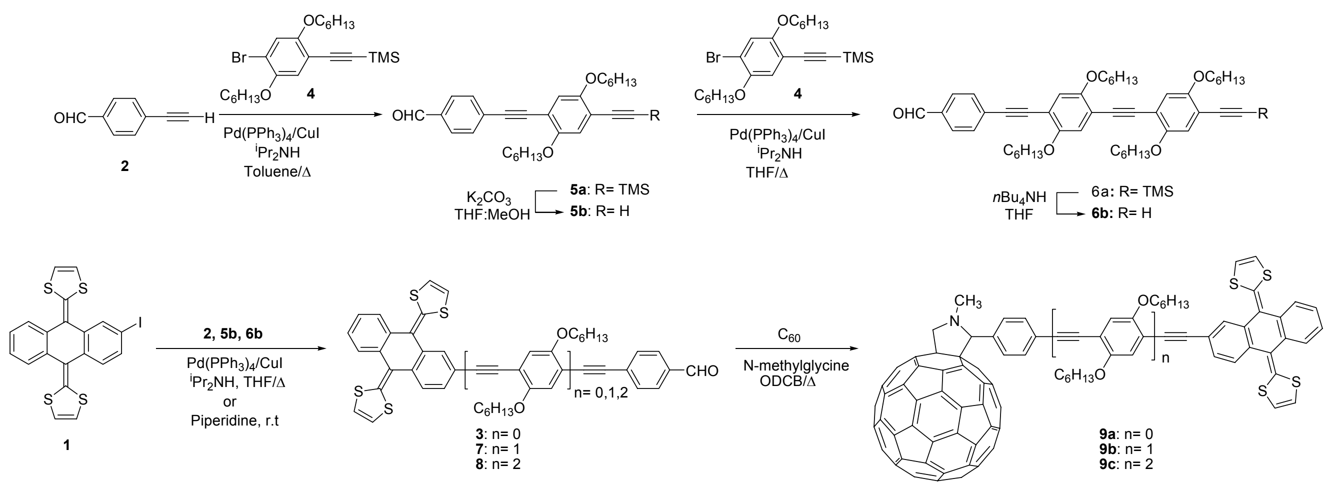
Some selected spectroscopical data for **9a-c**:

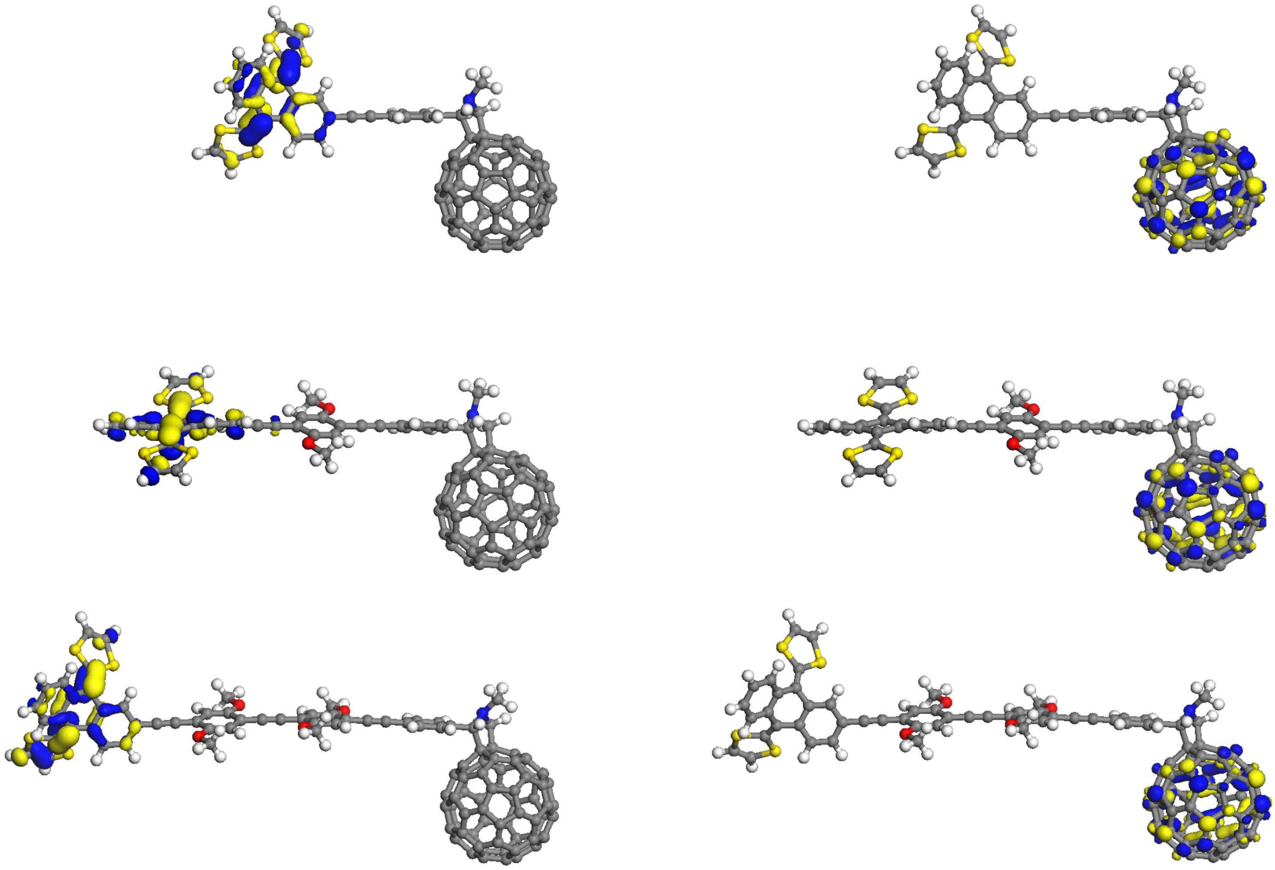
9a: ^{1}H- NMR (300 MHz, $CDCl_3$), δ: 7.87 (bs, 2H), 7.76 (bs, 1H), 7.69-7.63 (m, 5H), 7.42-7.29 (m, 3H), 6.38 (d, *J* = 6.8 Hz, 4H), 5.09 (s, 1H), 5.05 (s, 1H), 4.38 (d, *J*= 9.33 Hz, 1H), 2.94 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ: 156.53, 154.28, 153.63, 153.38, 147.84, 147.81, 147.15, 146.93, 146.89, 146.82, 146.78, 146.74, 146.70, 146.65, 146.57, 146.50, 146.29, 146.19 146.17, 146.02, 145.96, 145.91, 145.86, 145.79, 145.73, 145.25, 144.94, 143.72, 143.60, 143.26, 143.19, 143.16, 142.86, 142.80, 142.71, 142.67, 142.61, 142.48, 142.46, 142.25, 142.16, 140.82, 140.78, 140.61, 140.24, 138.07, 138.04, 137.57, 137.47, 137.15, 136.48, 136.32, 136.05, 135.89, 135.69, 132.67, 130.28, 129.90, 129.80, 129.27, 128.41, 126.89, 126.86, 125.62, 125.58, 125.51, 124.52, 122.26, 121.78, 121.29, 118.94, 118.12, 118.02, 92.15, 90.88, 83.81, 77.65, 70.62, 69.47, 40.67, 30.86. FTIR (KBr), ν: 527, 1259, 1375, 1460, 2923, 2850, 3434 cm^{-1}. MS m/z (EI), (% I): 1255 (M, 100), 1254 (M^+). UV-*vis* (CH_2Cl_2), λ_{max}: 232, 255, 313, 376, 431, 444 nm.

9b: ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 8.4 (d, *J* = 1.5 Hz, 1H), 8.35-8.29 (m, 3H), 7.90 (dd, J_1 = 8.1 Hz, J_2 = 1.65, 2H), 7.87-7.81 (m, 3H), 7.64-7.61 (d, *J* = 7.96, 2H), 7.05 (s, 1H), 7.03 (s, 1H), 6.79 (s, 4H), 5.03 (d, *J* =9.19 Hz, 1H), 4.98 (s, 1H), 4.30 (d, *J* = 9.19 Hz, 1H), 4.07-4.02 (m, 4H), 2.86 (s, 3H), 1.90-1.83 (m, 4H), 1.6-1.5 (m, 4H), 1.38-1.35 (m, 8H), 0.92-0.87 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ: 193.17, 183.01, 182.90, 155.68, 154.35, 154.04, 147.77, 146.76, 146.66, 146.36, 145.70, 145.13, 144.75, 143.56, 143.04, 142.51, 142.38, 142.08, 140.59, 140.32, 140.04, 136.79, 134.57, 133.99, 133.90, 132.65, 132.51, 130.52, 129.88, 127.76, 127.71, 118.75, 117.38, 117.20, 114.47, 113.35, 93.89, 91.54, 75.88, 70.02, 40.46, 39.88, 35.11, 31.95, 30.12, 29.63, 26.15, 23.04, 14.48, 14.43. FTIR (KBr), ν: 527, 669, 758, 1186, 1217, 1222, 2395, 2150, 2175 cm^{-1}. MS m/z (EI), (% I): 1554 (M^+, 56), 1384 (35). UV-*vis* (CH_2Cl_2), λ_{max}: 491, 384, 317, 250 nm.

9c: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.45 (bs, 1H), 8.36-8.30 (m, 3H), 7.91-7.82 (m, 5H), 7.63-7.60 (m, 2H), 7.06 (s, 2H), 7.04 (s, 2H), 7.01 (s, 2H), 7.00 (s, 2H), 5.02 (d, *J* = 9.19 Hz, 1H), 4.99 (s, 1H), 4.30 (d, *J* = 9.19 Hz, 1H), 4.09-4.01 (m, 4H), 2.85 (s, 3H), 1.88-1.80 (m, 4H), 1.59-1.57 (m, 4H), 1.36-1.26 (m, 8H), 0.93-0.84 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 183.03, 182.92, 154.35, 154.10, 153.90, 153.86, 147.81, 146.80, 146.67, 146.43, 146.37, 146.26, 146.12, 145.93, 145.79, 145.72, 145.16, 144.93, 144.67, 143.56, 143.41, 143.12, 142.83, 142.54, 142.48, 142.29, 142.06, 141.90, 140.65, 140.58, 140.36, 140.13, 136.79, 135.84, 134.71, 134.60, 133.99, 133.89, 133.83, 132.88, 132.84, 132.74, 132.62, 132.44, 131.93, 131.30, 130.52, 130.25, 129.85, 129.74, 129.20, 128.99, 128.81, 128.68, 127.78, 127.71, 11751, 117.38, 115.76, 114.90, 113.88, 113.15, 93.87, 92.40, 91.95, 91.67, 83.64, 70.12, 70.09, 69.95, 68.55, 32.02, 31.97, 31.95, 30.11, 29.66, 26.07, 23.06, 14.49, 14.46. FTIR (KBr), ν: 526, 756, 928, 1050, 2232, 2399 cm^{-1}. MS *m/z* (EI), (% I): 1855 (M^+, 33), 1275 (50), 720 (67). UV-*vis* (CH_2Cl_2), λ_{max}: 494, 396, 314, 245 nm.



Scheme S1: Synthetic route towards C_{60}-*o*PPE-*ex*TTF



45 Figure S1: HOMO (left) and LUMO (right) in C_{60}-*o*PPE-*ex*TTF

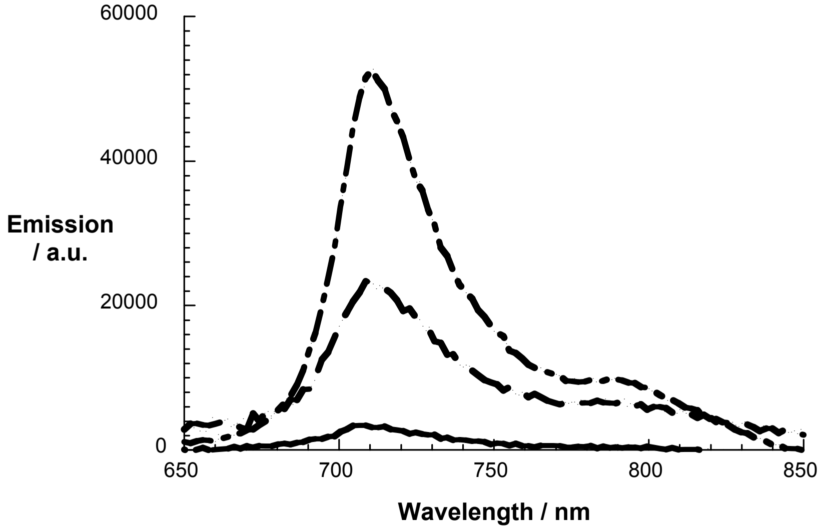


Figure S2: Fluorescence spectra of C_{60}-reference (dotted line), 1-mer (solid line) and 2-mer (dashed line) in THF in room temperature experiments with matching absorption at the 431 nm excitation wavelength – $OD_{431\ nm} = 0.2$.

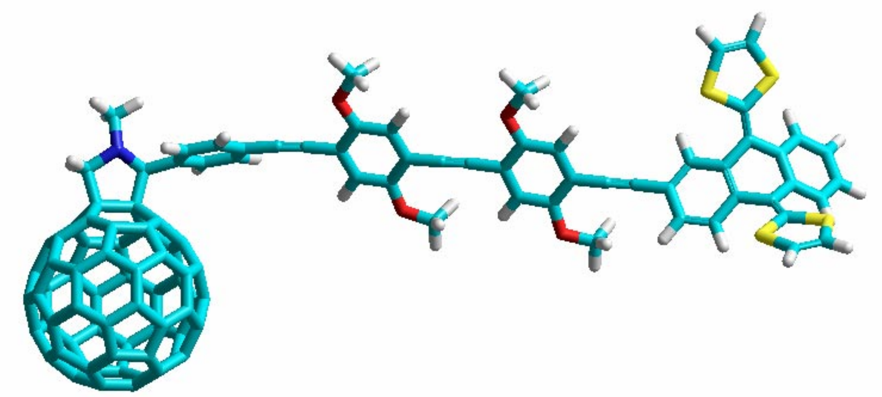


Figure S3: Molecular Geometry of C_{60}-*o*PPE-*ex*TTF (**9c**) at the PM3 level.

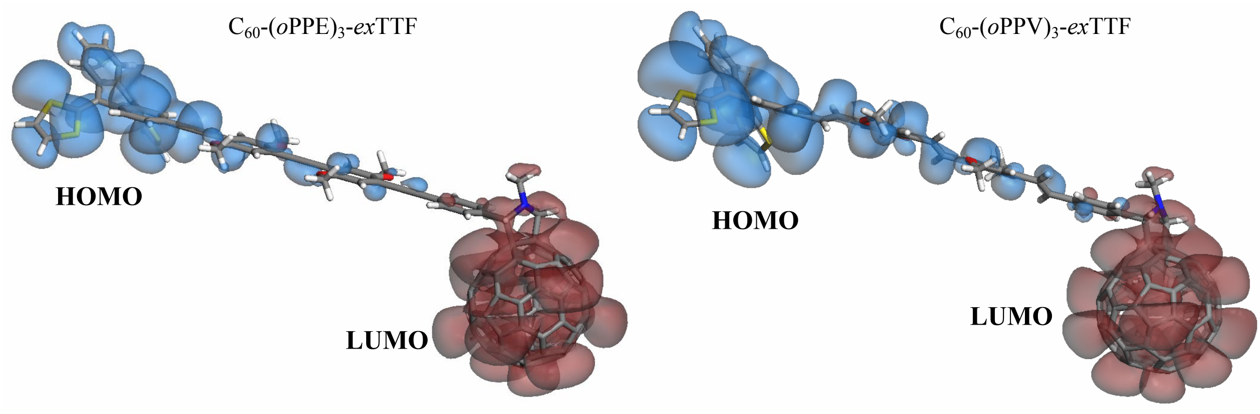


Figure S4: Molecular Orbital Scheme of HOMO and LUMO of C_{60}-*o*PPE-*ex*TTF (**9c**) vs. C_{60}-*o*PPV-*ex*TTF at the AM1* level.

Table S1: HOMO and LUMO energies in C_{60}-*o*PPV-*ex*TTF and C_{60}-*o*PPE-*ex*TTF

compound	**HOMO eV**	**LUMO eV**
C_{60}	-9.088	-2.898
*ex*TTF	-7.450	-0.508
1-mer; *o*PPE	-8.870	-0.162
2-mer; *o*PPE	-8.516	-0.771
3-mer; *o*PPE	-8.369	-0.973
1-mer; C_{60}-oPPE	-9.084	-2.795
2-mer; C_{60}-*o*PPE	-8.666	-2.775
3-mer; $C_6$0-*o*PPE	-8.482	-2.765
1-mer; *o*PPV	-8.431	0.079
2-mer; *o*PPV	-8.111	-0.423
3-mer; *o*PPV	-7.961	-0.594
1-mer; C_{60}-oPPV	-8.895	-2.796
2-mer; C_{60}-oPPV	-8.289	-2.709
3-mer; C_{60}-oPPV	-8.097	-2.685
1-mer; C_{60}-oPPE-*ex*TTF	-7.551	-2.771
2-mer; C_{60}-oPPE-*ex*TTF	-7.502	-2.769
3-mer; C_{60}-oPPE-*ex*TTF	-7.484	-2.769
1-mer; C_{60}-oPPV-*ex*TTF	-7.530	-2.760
2-mer; C_{60}-oPPV-*ex*TTF	-7.471	-2.755
3-mer; C_{60}-oPPV-*ex*TTF	-7.448	-2.750