Supporting Information

Impact of Concentration Self-Quenching on the Charge Generation Yield of Fullerene Based Donor-Bridge-Acceptor Compounds in the Solid State.

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Contents:

SI. Supplementary figures and fitting routine

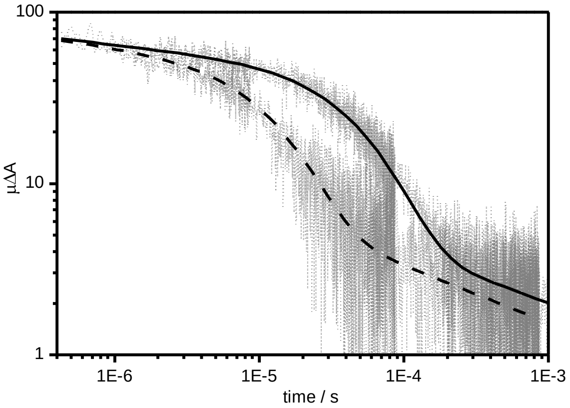


Figure S1. The TAS decays of a 10:90 **1**:PS film in nitrogen (solid line) and oxygen (dashed line). The black lines are fits to Eq. 1.

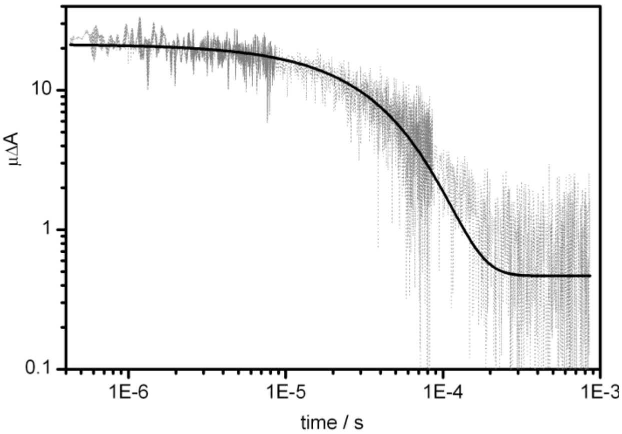


Figure S2. TAS decay of a dilute film of **1** in PS, **1**:PS 2.5:97.5 w:w showing that the charge separation step is effectively shut off at this low dielectric constant.

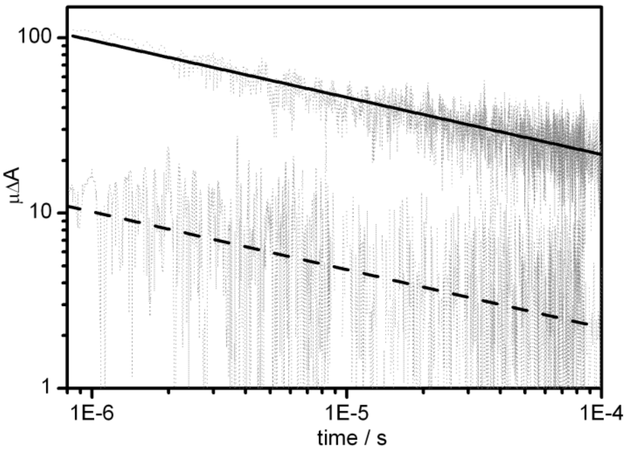


Figure S3. TAS decay of neat **1** film (solid line) and a **2**:**3** blend (1:1 molar ratio, dashed line).

The Fitting procedure

The fitting is based on that in solution the singlet life-time is approximately 1.5 ns and the triplet quantum yield is around 1 so that the inter-system crossing rate, k_{ISC}, is $6.67 \cdot 10^8$ s^{-1}.[1] This property is expected to stay more or less constant when changing the concentration and is a fixed parameter inserted into the fitting scheme. Firstly, the mass-weighted decays were fitted to a sum of a power-law and an exponential decay – corresponding to diffusing charges and triplets, respectively – according to:

S1

Secondly, the resulting parameters were used in a fitting procedure for estimating the quantum yields of triplets and charges. This fitting utilises that the difference in triplet signal between films containing 1 and 2 is due to the additional deactivation pathway introduced in 1 relative to 2, i.e. charge separation. In this scheme the concentration dependent signal associated with triplet formation was first fitted to:

S2

Here I is an instrument dependent factor kept the same for all cases, $\tau_{Solution}$ is the life-time of the reference compound in dilute solution, $k_Q([C_{60}]) = k_{Q1}[C_{60}]^{Q1} + k_{Q2}[C_{60}]^{Q2}$ is the rate of concentration dependent self-quenching of the fullerene singlet, and $k_{CS}([C_{60}]) = k_{CS1}[C_{60}]^{CS1} + k_{CS2}[C_{60}]^{CS2}$ is the concentration dependent (due to increased driving force with increased concentration) effective rate of charge separation. For the case of 2, k_{CS} was set to zero in this fitting procedure. The resulting parameters; k_{Q1}, k_{Q2}, Q1, and Q2 were then kept the same when fitting to the data collected for 1. The used concentration of 1 was mass weighted to correspond to the equivalent mass concentration of 2 units. The parameters from these fits were then used to derive the quantum yields for the three processes:

S3a

S3b

S3c

Additionally, the signal corresponding to triplets (see Eq. S1) were normalized to the derived quantum yield for triplet formation (Eq. S3a) and the signal corresponding to exTTF cation radicals was normalised to the derived quantum yield for charge separation (Eq. S3b). The errors between these two sets of normalised transient absorption signals and their derived quantum yields was minimised simultaneously to the other relations. On top of that, the ratio of the transient absorption signals, weighted with the corresponding absorption coefficient, corresponding to charges and triplets was fitted to the ratio of the quantum yields of charges and triplets, i.e. the expression $[\text{exTTF}^{\bullet +}]_{norm}/[{}^3\text{C60}^*]_{norm}$ – Charge QY/Triplet QY was minimized for all concentrations.

References

(1) Sanchez, L.; Perez, I.; Martin, N.; Guldi, D. M. *Chem. - Eur. J.* 2003, *9*, 2457-2468.

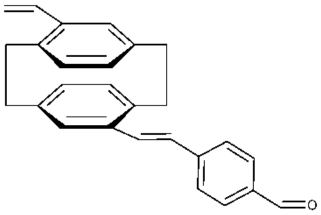
SII. Synthetic details and characterization

All solvents were dried 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 coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) 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, t = triplet, m = multiplet. Mass spectra (FAB-MS) and Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 termo spectrometer and a Bruker REFLEX spectrometer respectively.

Compounds **4**, **5** and iodo-exTTF were prepared according to previously reported synthetic procedures, see: a) A. de la Escosura, M. V. Martinez-Diaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte, T. Torres, *J. Am. Chem. Soc.* **2003**, *125*, 12300. b) M. C. Díaz, B. M. Illescas, C. Seoane, N. Martín, *J. Org. Chem.* **2004**, *69*, 4492 and showed identical spectroscopic properties to those reported therein. 4-Iodobenzaldehyde was purchased from Sigma-Aldrich and used as received.

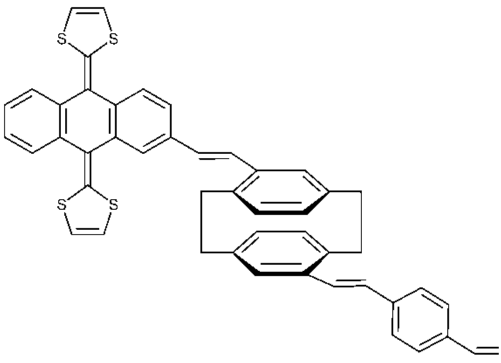
General procedure for palladium catalyzed Heck type C-C cross-coupling. To a dry round bottom flask equipped with a stirrer bar, the corresponding 4-iodobenzaldehyde or iodo-exTTF, 4-vinylparacyclophane or 4,12-divinylparacyclophane, Pd complex (10%), Bu_4NBr (1 equiv.), K_2CO_3 (3 equiv.) and DMF (5 ml) were added. Oxygen was removed by successive vacuum-Ar atmosphere purge cycles and the temperature, being from room temperature to 100 °C. The reaction evolution was monitored by TLC. The resulting mixture was allowed to reach room temperature and the solvent was removed under vacuum, the mixture was then extracted with CH_2Cl_2. The organic extracts were washed with water and dried over $MgSO_4$. The elimination under vacuum of the organic solvent led to a crude which was purified by flash column chromatography on silica-gel, being the eluents described for each compound.

Compound 6.



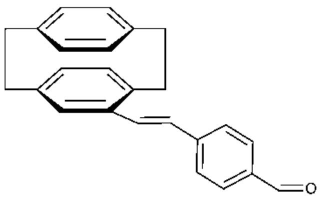
4,12-Divinylparacyclophane (**5**) (390 mg, 1.5 mmol), 4-iodobenzaldehyde (232 mg, 1 mmol), $PdCl_2(CH_3CN)_2$ (26 mg, 0. 1 mmol), Bu_4NBr (322 mg, 1 mmol), K_2CO_3 (415 mg, 3 mmol) and DMF (5 ml) was stirred at 100 °C during 48 h. The crude product was purified by flash column chromatography (silica gel, hexane/CH_2Cl_2 4:1) to afford **6** as a slightly yellow solid (172 mg, 0.47 mmol), 47% yield.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.02 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 16.1 Hz, 1H), 6.92 (d, J = 16.1 Hz, 1H), 6.86 (dd, J = 11.0 Hz, J´ = 12.0 Hz, 1H), 6.77-6.70 (m, 2H), 6.63-6.58 (m, 2H), 6.43-6.35 (m, 2H), 5.55 (dd, J = 17.6 Hz, J´ = 1.4 Hz, 1H), 5.31 (dd, J = 10.7 Hz, J´ = 1.4 Hz, 1H), 3.70-3.40 (m, 2H), 3.10-2.80 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.71, 192.62, 144,01, 144,01, 143,65, 139.77, 139.57, 139.39, 139.25, 138.83, 137.88, 137.80, 137.77, 136.63, 135.21, 135.18, 134.72, 134.64, 133.81, 133.74, 133. 48, 133.35, 130.35, 130.27, 130.18, 129.84, 129.66, 129.48, 129.29, 128.76, 128.67, 127.84, 126.87, 114.59, 114.49, 34.58, 34.26, 34.01, 33.32, 33.02, 32.97, 32.72; FAB-MS m/z: 365.3 $[M+H]^+$.

Compound 7.



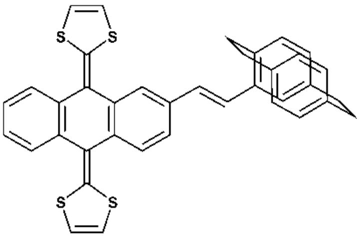
Compound **6** (146 mg, 0.4 mmol), iodo-exTTF (203 mg, 0.4 mmol), $PdCl_2(CH_3CN)_2$ (10.4 mg, 0.04 mmol), Bu_4NBr (129 mg, 0.4 mmol), K_2CO_3 (166 mg, 1.2 mmol) and DMF (5 ml) was stirred at 100 °C during 48 h. The crude product was purified by flash column chromatography (silica gel, hexane/CH_2Cl_2 1:1) to afford **7** as an orange solid (84 mg, 0.113 mmol), 40% yield.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.02 (s, 1H), 8.00-7.90 (m, 3H, Ar), 7.80-7.70 (m, 4H, Ar), 7.50-7.30 (m, 6H, Ar and vinylic), 7.00-6.90 (m, 2H, vinylic) 6.80-6.70 (m, 2H, Ar), 6.65-6.60 (m, 2H, Ar), 6.50-6.30 (m, 6H, Ar and vinylic); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 192.03, 137.56, 137.46, 137.21, 136.89, 136.20, 136.00, 135.57, 133.47, 129.20, 129.61, 129.51, 129.00, 128.84, 128.39, 126.53, 125.47, 125.40, 125.32, 125.06, 121.99, 121.52, 120.29, 117.75, 117.69, 117.56, 91.77, 88.45; FAB-MS m/z: 743.7 $[M+H]^+$.

Compound 8.



4-Vinylparacyclophane (**8**) (117 mg, 0.5 mmol), 4-iodobenzaldehyde (139 mg, 0.6 mmol), $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol), Bu_4NBr (161 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol) and DMF (5 ml) was stirred at 100 °C during 48 h. The crude product was purified by flash column chromatography (silica gel, hexane/CH_2Cl_2 4:1) to afford **8** as a slightly yellow solid (118 mg, 0.35 mmol), 70% yield.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.03 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.71 (d, J= 8.0 Hz, 1H), 7.38 (d, J = 16.1 Hz, 1H), 6.91 (d, J = 16.1 Hz, 1H),), 6.77-6.70 (m, 2H), 6.63-6.58 (m, 2H), 6.43-6.35 (m, 2H), 3.70-3.40 (m, 2H), 3.10-2.80 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.06, 144.39, 139.81, 139.56, 139.44, 137.07, 135.61, 135.53, 133.53, 133.44, 133.11, 130.75, 130.61, 130.43, 128.63, 128.11, 127.27, 35.86, 35,63, 35.43, 34.36; FAB-MS m/z: 339.4 $[M+H]^+$.

Compound 3.

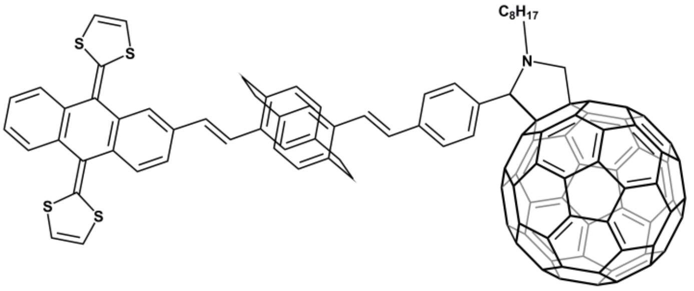


4-Vinylparacyclophane (**8**) (94 mg, 0.4 mmol), iodo-exTTF (203 mg, 0.4 mmol), $PdCl_2(CH_3CN)_2$ (10.4 mg, 0.04 mmol), Bu_4NBr (129 mg, 0.4 mmol), K_2CO_3 (166 mg, 1.2 mmol) and DMF (5 ml) was stirred at 100 °C during 48 h. The crude product was purified by flash column chromatography (silica gel, hexane/CH_2Cl_2 2:1) to afford **3** as an orange solid (88 mg, 0.144

mmol), 36% yield.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.00-7.90 (m, 1H, Ar), 7.80-7.70 (m, 2H, Ar), 7.50-7.30 (m, 6H, Ar and vinylic), 7.00-6.90 (m, 2H, vinylic), 6.80-6.70 (m, 2H, Ar), 6.65-6.60 (m, 2H, Ar), 6.50-6.30 (m, 6H, Ar and vinylic), 3.60-3.40 (m, 1H), 3.10-2.80 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.86, 137.84, 136.25, 136.03, 135.74, 135.65, 135.36, 135.03, 133.43, 132.13, 127.47, 126.46, 126.41, 125.73, 125.39, 125.32, 124.79, 123.07, 122.51, 117.71, 117.66, 35.89, 35.65, 35.32, 34.50; FAB-MS m/z: 613.5 $[M+H]^+$.

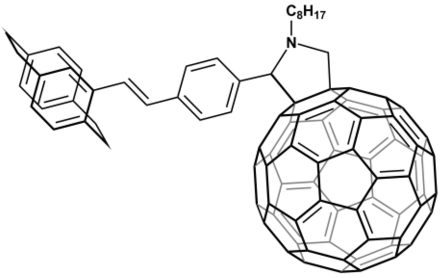
General procedure for 1,3-dipolar cycloaddition reactions. The corresponding aldehyde (1 equiv.), [60]fullerene (1 equiv.) and N-octylglycine (3 equiv) were dissolved in chlorobenzene and the mixture was refluxed for 5-7 hours. The reaction was allowed to reach room temperature and the solvent was removed under vacuum. The crude was purified by flash column chromatography. The black solid thus obtained was further purified by repeated (3x) precipitation and centrifugation in methanol to yield the corresponding hybrids as black solids.

Compound 1.



Yield, 42%.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.00-7.90 (m, 3H, Ar), 7.80-7.70 (m, 4H, Ar), 7.50-7.30 (m, 6H, Ar and vinylic), 7.00-6.90 (m, 2H, vinylic) 6.80-6.70 (m, 2H, Ar), 6.65-6.60 (m, 2H, Ar), 6.50-6.30 (m, 6H, Ar and vinylic), 5.20-5.10 (m, 2H, pyrrolidine), 4.15-4.10 (m, 1H, pyrrolidine), 3.70-3.40 (m, 2H, pCp), 3.10-2.80 (m, 6H, pCp), 2.60-2.50 (m, 2H), 2.10-1.30 (m, 12H), 1.00-0.90 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.03, 154.78, 154.08, 147.73, 147.29, 146.73, 146.70, 146.64, 146.56, 146.37, 146.20, 145.99, 145.95, 145.75, 145.69, 145.57, 145.15, 145.05, 144.84, 143.59, 143.42, 143.11, 142.99, 142.72, 142.56, 142.47, 142.42, 142.10, 139.90, 138.66, 136.28, 136.12, 135.75, 135.66, 134.05 133.99, 130.68, 130.01, 127.61, 127.10, 126.47, 126.42, 125.75, 125.40, 124.78, 123.10, 122.53, 117.70, 117.52, 82.87, 69.44, 53.62, 34.93, 33.86, 33.72, 32.38, 30.11, 29.78, 28.81, 28.02, 23.15, 14.60; MALDI-TOF m/z: 1588.3 $[M+H]^+$.

Compound 2.



Yield, 66%.^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.90-7.80 (m, 2H, Ar), 7.65-7.60 (m, 2H, Ar), 7.22 (d, J= 16.0 Hz, 1H, vinylic), 6.88 (d, J= 16.0 Hz, 1H, vinylic), 6.75-6.45 (m, 7H, Ar), 5.15-5.10 (m, 2H, pyrrolidine), 4.15-4.10 (m, 1H, pyrrolidine), 3.65-3.55 (m, 1H, pCp), 3.40-2.90 (m, 7H, pCp), 2.65-2.55 (m, 2H), 2.10-1.30 (m, 12H), 1.00-0.90 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.05,154.76, 154.06, 154.01, 147.72, 146.93, 146.72, 146.69, 146.63, 146.58, 146.55, 146.51, 146.36, 146.34, 145.98, 145.95, 145.92, 145.74, 145.68, 145.64, 145.15, 145.04, 144.83, 143.58, 143.41, 143.10, 142.98, 142.77, 142.71, 142.55, 142.53, 142.44, 142.41, 140.60, 140.56, 140.35, 139.76, 139.68, 138.80, 138.30 137.77, 137.11, 137.00, 136.26, 136.12, 135.37, 133.44, 133.38, 132.31, 132.21, 130.68, 130.42, 130.29, 129.18, 127.54, 127.50, 127.09, 82.83, 69.42, 67.30, 53.63, 35.89, 35.67, 35.35, 34.36, 32.4, 30.13, 29.79, 28.82, 28.02, 23.16, 14.64; MALDI-TOF m/z: 1184.3 $[M+H]^+$.