Supporting Information

Cooperativity Between π,π and H-bonding Interactions – A Supramolecular Complex Formed by C_{60} and exTTF

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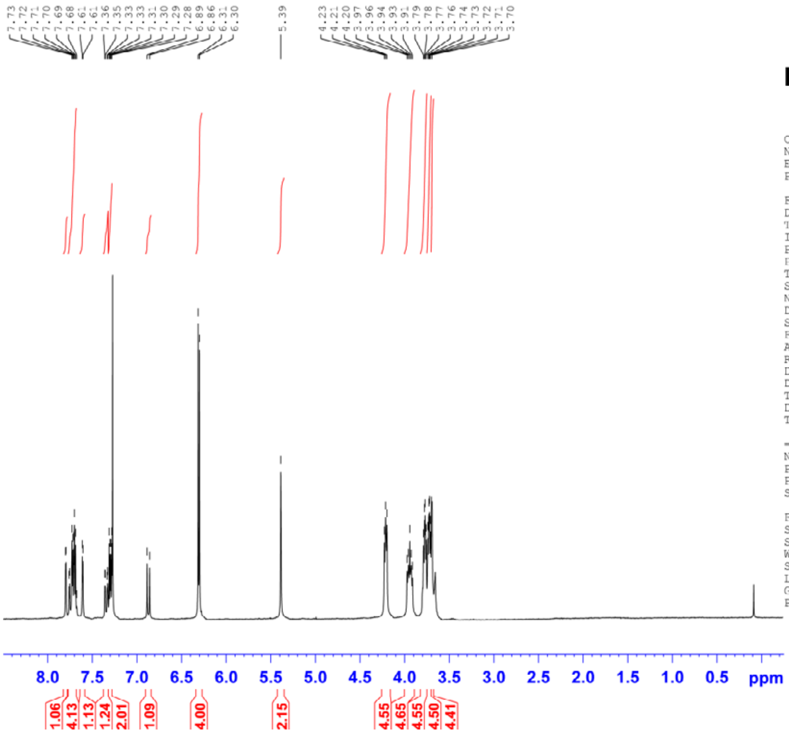
General Information: All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, kieselgel 60, 230-240 mesh or Scharlau 60, 230-240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

Synthesis of exTTF crown-ether (1): To a solution of (9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methanol[1] (187 mg, 0.46 mmol), 4-dimethylaminopyridine (61.4 mg, 0.503 mmol), and N,N'-dicyclohexylcarbodiimide (18.8 mg, 0.09 mmol) in CH_2Cl_2 (10 mL), a solution of 4'-carboxybenzo-18-crown-6 (179 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The resulting solution was allowed to stir at room temperature for 2 h, then concentrated under reduced pressure and purified by flash chromatography on silica gel (chloroform/methanol 98:2), to afford 270 mg (79 % yield) of the title compound. Mp 191-193 ºC; FTIR (KBr) 3068, 2924, 1701, 1653, 1506, 1269, 1113 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.80 (d, *J* = 1.5 Hz, 1H), 7.76-7.68 (m, 4H), 7.61(d, *J* = 1.9 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.31-7.28 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.31 (s, 2H), 6.30 (s, 2H), 5.39 (s, 2H), 4.23-4.20 (m, 4H), 3.97-3.91 (m, 4H), 3.79-3.70 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 166.61, 148.61, 136.51, 136.33, 136.11, 135.68, 135.66, 135.64, 134.25, 126.43, 125.99, 125.51, 125.34, 124.97, 124.56, 123.13, 122.22, 117.63, 117.60, 117.56, 114.76, 112.34, 71.24, 71.15, 71.09, 71.02, 70.97, 69.79, 69.68, 69.42, 69.14, 66.80; ESI-MS 749.4 [M + H$^+$]; HR-FAB: calculated for C$_{38}$H$_{36}$S$_4$O$_8$: 748.1293, found 748.1270; UV/Vis (CH$_2$Cl$_2$) λ_{max} = 430, 413, 364, 298, 263, 238 nm.



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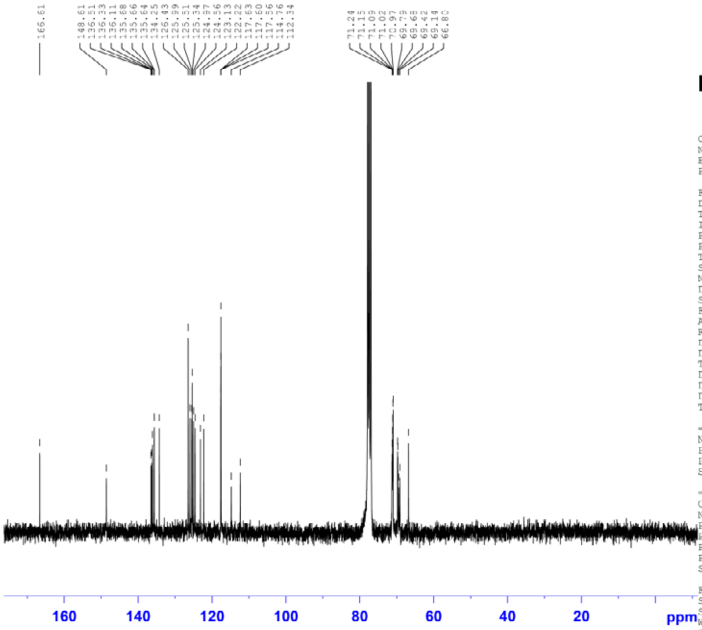

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UV/Vis Titrations: Complex **3** binding constant was evaluated by titrating a fixed concentration solution of exTTF **1** ($2{\cdot}10^{-5}$ M^{-1}) with variable amounts of C_{60} **2** (from 0 to $9.09{\cdot}10^{-5}$ M^{-1}) either in chlorobenzene and chloroform. The resulting solutions were measured by UV/Vis spectroscopy at room temperature. Some spectra were corrected by background substraction. ΔAbs of **1** at 431 nm was plotted versus total concentration of C_{60}. The resulting curve was fitted using Microcal Origin 7.5 software. The binding constant was evaluated using the equation:[2]

$$\Delta Abs = \Delta Abs_{max}(1 + K_{assoc}[\mathbf{2}] + K_{assoc}[\mathbf{1}]_0) - ((1 + K_{assoc}[\mathbf{2}] + K_{assoc}[\mathbf{1}]_0)^2 - 4\,K_{assoc}[\mathbf{2}][\mathbf{1}]_0)^{½})/(2K_{assoc}[\mathbf{1}]_0)$$

The Job plot for **1** in chlorobenzene corroborates a 1:1 complex (see Figure S1).

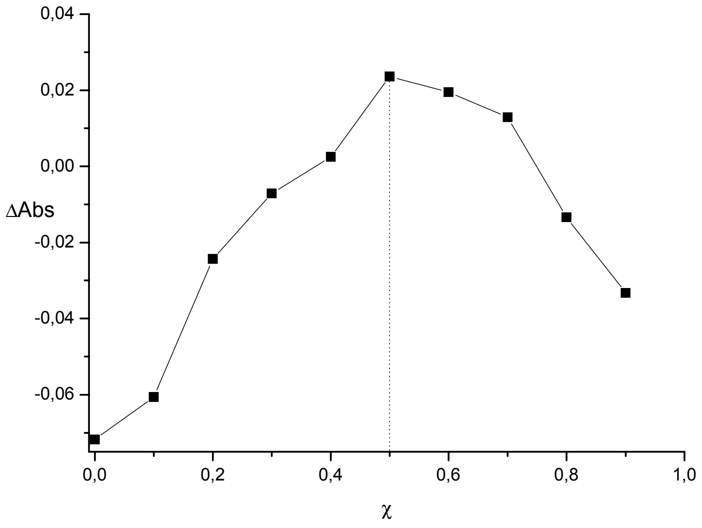

Fig. S 1. Job plot of **1** in chlorobenzene.

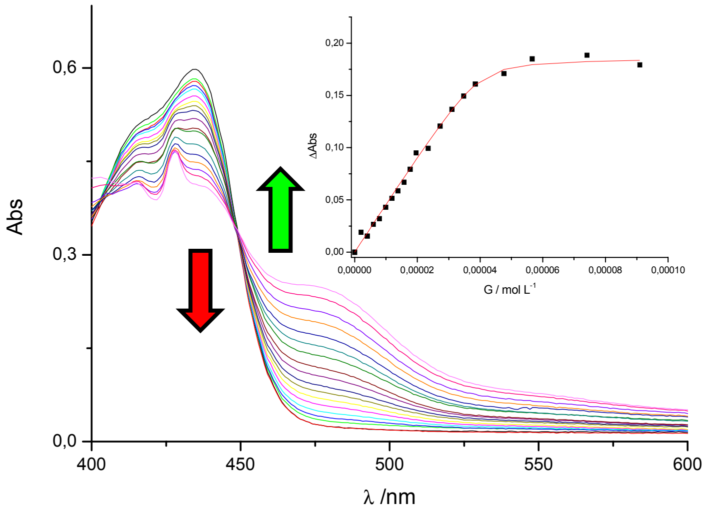

Fig. S 2. Spectral changes of **1** when threading with several amounts of **2** in chlorobenzene.

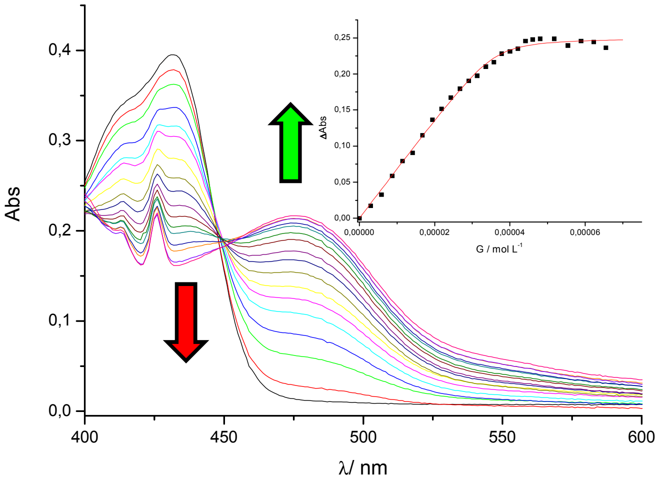

Fig. S 3. Changes of **1** when threading with several amounts of **2** in chloroform.

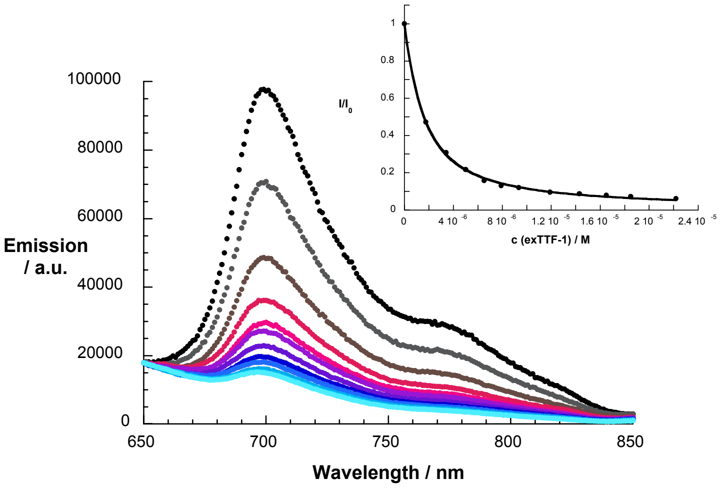

Fig. S 4. C_{60} fluorescence evolution upon addition of increasing amounts of exTTF

^{1}H NMR experiments:

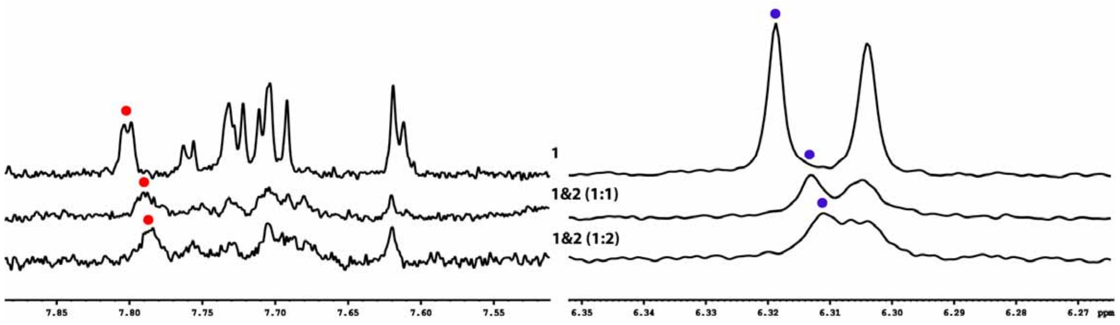

Fig. S 5. Partial ^{1}H NMR spectra (300 MHz, 298 K, $CDCl_3$) of **1** upon addition of **2** depicting the shielding of the aromatic protons (left). The shielding of the 1,3-dithiole signals is also shown (right).

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[1] S. González, N. Martín, D. M. Guldi, *J. Org. Chem.*, 2003, **68**, 779-791.

[2] a) Z.-Q. Wu, X.-B. Shao, C. Li, J.-L. Hou, K. Wang, X.-K. Jiang, Z.-T. Li, *J. Am. Chem. Soc.*, 2005, **127**, 17460-17468. b) E. M. Pérez, L. Sánchez, G. Fernández, N. Martín, *J. Am. Chem. Soc.*, 2006, **128**, 7172-7173.