Supporting Information

exTTF-capped Gold Nanoparticles as Multivalent Receptors for C_{60}.

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Supporting Figures:

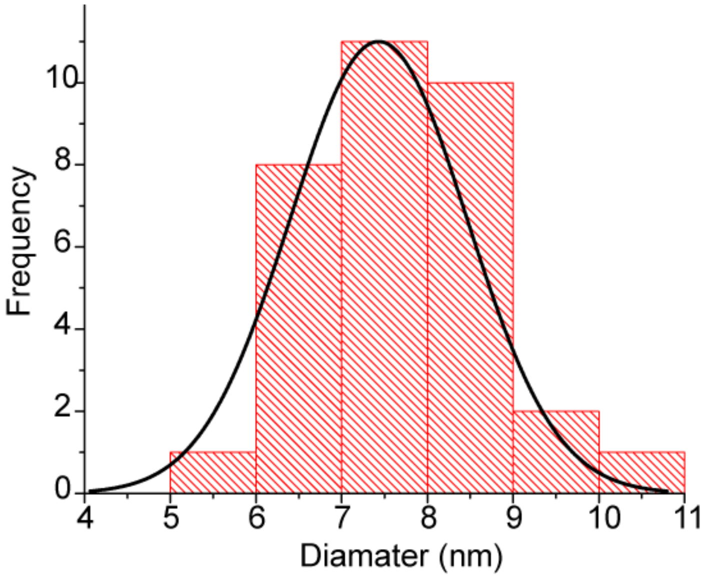


Figure S1. Statistical analysis of the diameter of the exTTFAuNPs.

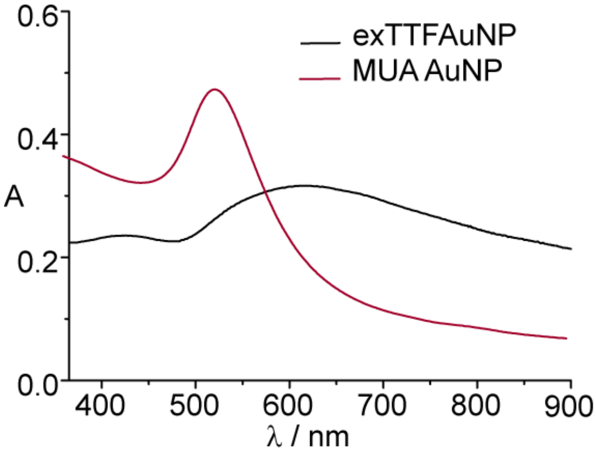


Figure S2. UV-vis spectra of exTTFAuNP and MUAAuNP in o-DCB at room temperature.

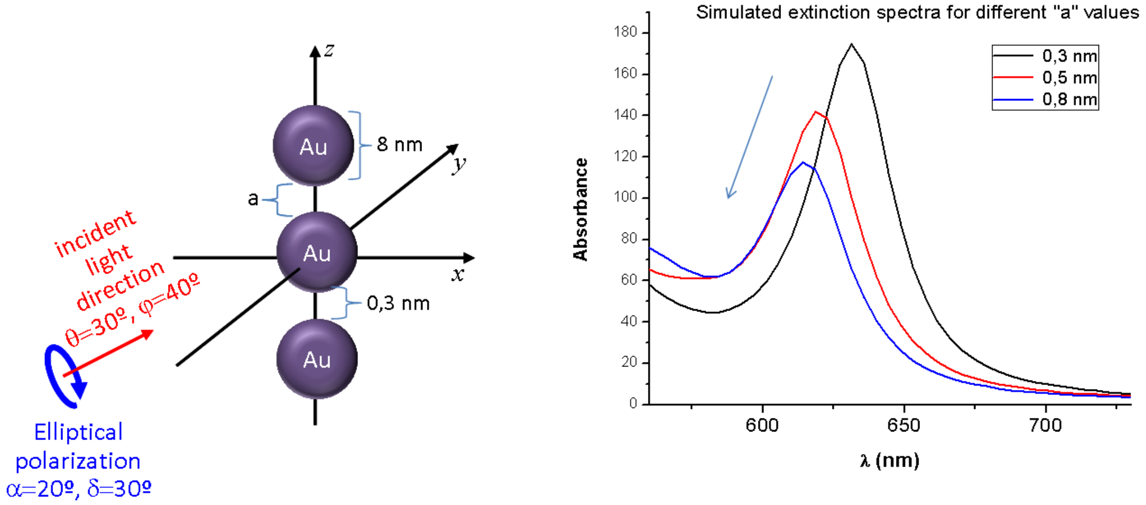


Figure S3. Model for the computational simulation of the impact of the dissagregation process on their UV-vis spectra, and results of the simulation. For three dimensional ensembles the extinction band of coupled free electron oscilation will be broader as in case of Figure 1 (main text).

It can also be observed that the decrease in intensity of the band is more significant than its blue shift. In case of three dimensional ensembles , in which the coupled electron resonating band is very broad, during a partial disaggregation process, the decrease in intensity of the band should be more noticeable than the hypsochromic shift, as experimentally observed.

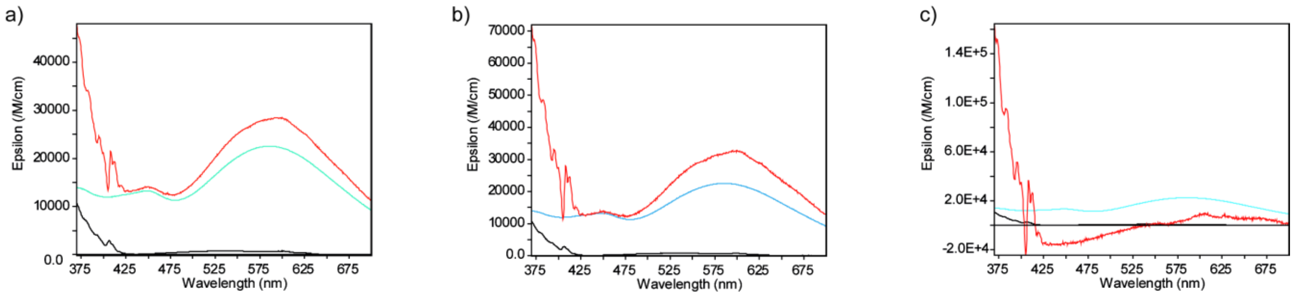


Figure S4. Simulated spectra (specfit) for the exTTFAuNP•C_{60} associate (red) for a) 2:1 binding model; b) 3:1 binding model; and c) 6:1 binding model. The spectra of exTTFAuNP (blue) and C_{60} (black) are determined experimentally and introduced as data for the fit. As indication of satisfactory fitting, we examined both the binding isotherms at key wavelengths (see main text, Figure 1) and the sensibleness of the simulated spectra. Note that in a) and b) the trends during the titration experiment (decrease in absorption of the bands at λ = 450 and 590 nm) are not reproduced, while the 6:1 model in c) produces a chemically meaningless strong negative absorption for the exTTFAuNP•C_{60} associate.

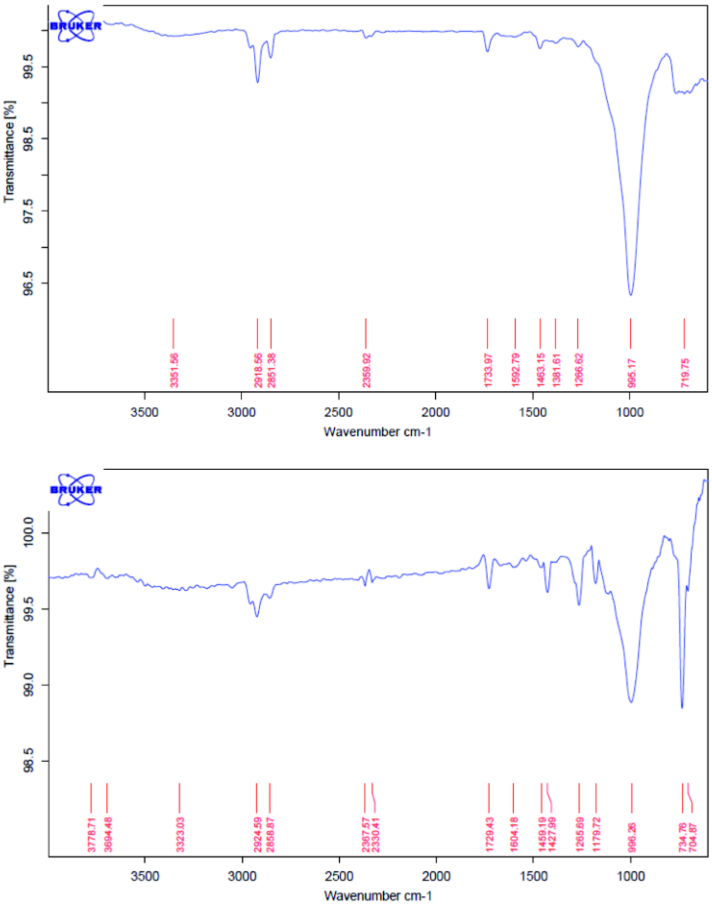


Figure S5. Fourier Transform Infrared (FTIR) spectra of exTTFAuNPs (top) and exTTFAuNP•C_{60} (bottom).

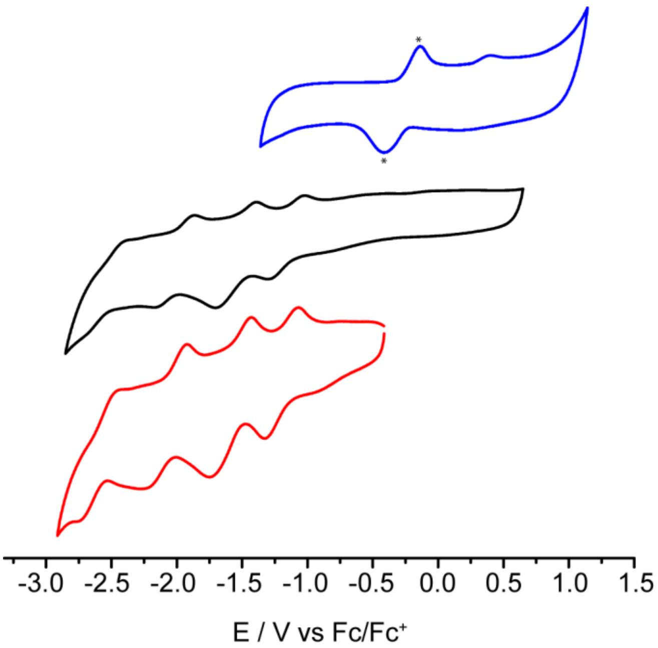


Figure S6. Cyclic voltammogramms of exTTFAuNPs (blue), exTTFAuNP•C_{60} (black) and C_{60}

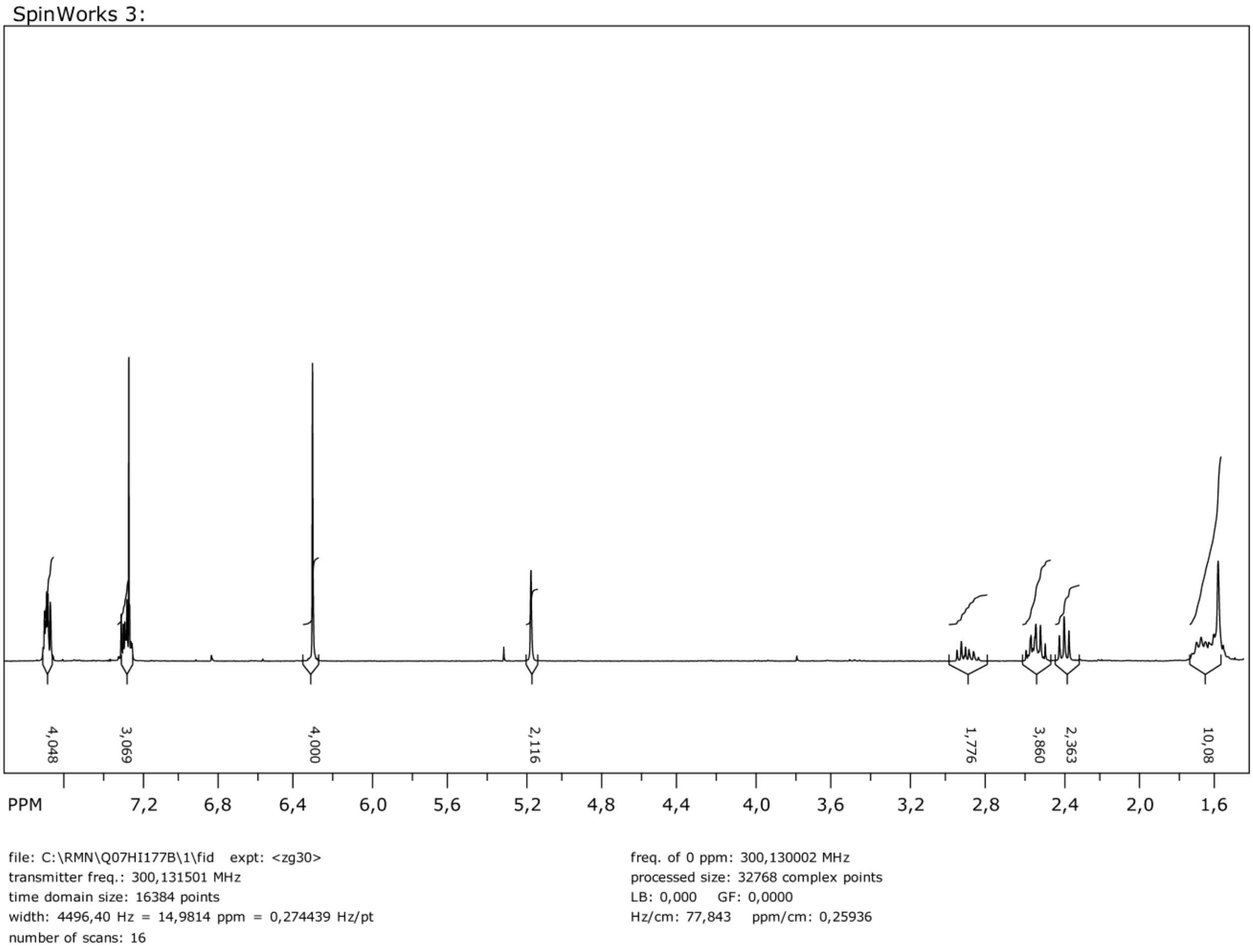
(red). The electrochemical data are summarized in Table 1 in the main text. For experimental conditions, see the main text.

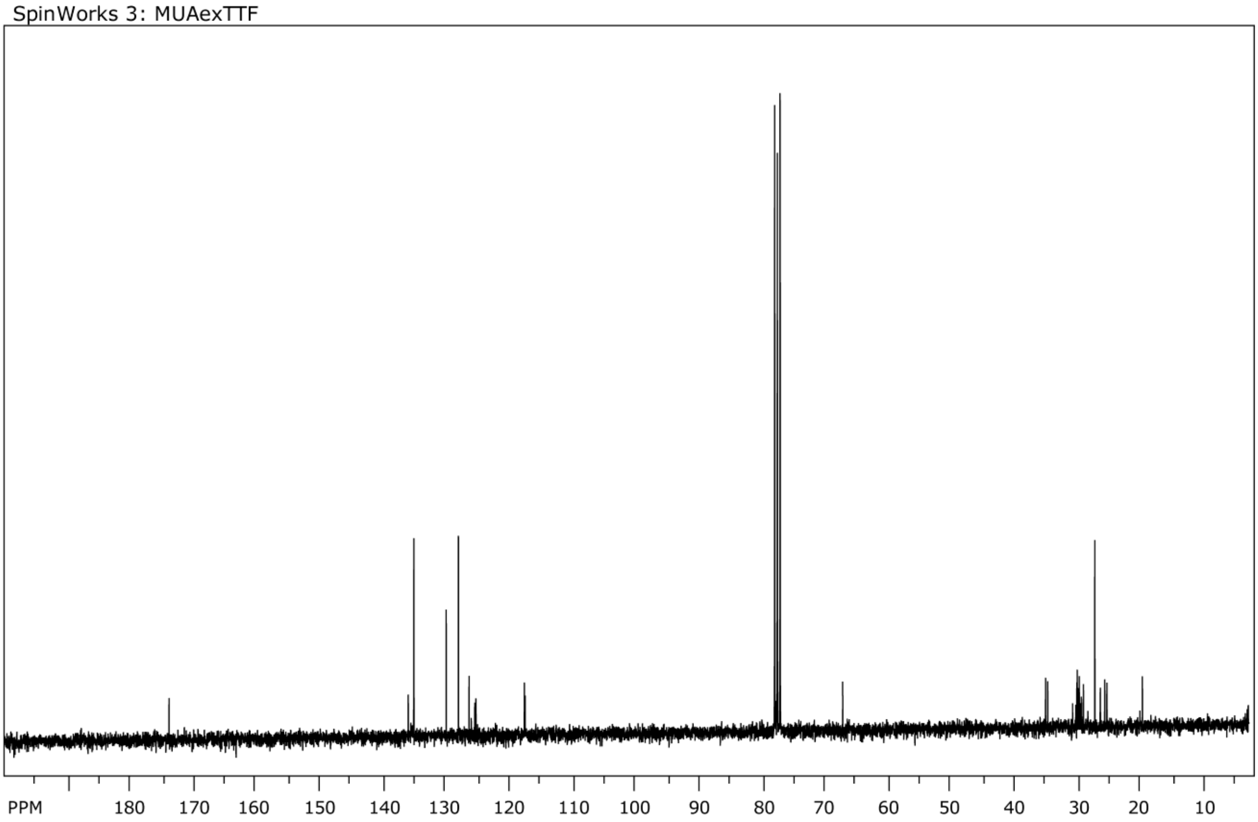
Synthesis and characterization

General. 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 chromatographies (TLC) were performed using aluminium-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, unless otherwise stated, 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, b = broad. Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) spectrometry was carried out on a Bruker REFLEX spectrometer.

Synthesis of exTTF-MUA: 100 mg of exTTF-CH_2OH (0.24 mmol), 64 mg of MUA (0.29 mmol) and 58 mg of 4-dimethylaminopyridine (0.48 mmol) were dissolved in 30 mL of dry CH_2Cl_2 under argon atmosphere. Then 69 mg of *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (0.36 mmol) were added in small portions. The reaction mixture was stirred at room temperature for 3 h, then diluted with 30 mL CH_2Cl_2, and washed successively with 1 M HCl (aq.), and 1 M $NaHCO_3$ (aq.). The combined organic layers were collected and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2) to afford exTTF-MUA in 76% yield.

^{1}H NMR ($CDCl_3$) δ 7.74- 7.66 (4H, m, Ar-$\underline{H}$), 7.33- 7.24 (3H, m, Ar-$\underline{H}$), 6.29 (4H, bs,S-C$\underline{H}$-C$\underline{H}$-S), 4.75 (2H, s, C$\underline{H}_2$-O), 2.96- 2.83 (4H, m, C$\underline{H}_2$-C$\underline{H}_2$-COOR), 2.60- 2.48 (4H, m,alkyl), 2.39 (2H, t, J = 7.5 Hz, C$\underline{H}_2$-SH), 1.72- 1.54 (10 H, m, alkyl) ppm. ^{13}C NMR ($CDCl_3$) δ 174.1, 136.1, 135.7, 135.4, 135.2, 134.2, 130.1, 128.1, 126.8, 126.4, 126.1, 125.5, 125.3, 125.1, 117.7, 117.6, 117.5, 34.8, 34.4, 29.8, 29.7, 29.6, 29.4, 28.8, 27.0, 26.1, 25.4, 25.0, 19.4 ppm. MS *m/z*: calcd. for $C_{32}H_{34}O_2S_5$ [M^+] 610.1 found (MALDI-TOF) 609.9.





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width: 18832,39 Hz = 249,5149 ppm = 0,287359 Hz/pt
number of scans: 512

freq. of 0 ppm: 75,467719 MHz
processed size: 32768 complex points
LB: 0,000 GF: 0,0000
Hz/cm: 597,380 ppm/cm: 7,91483

Synthesis of exTTF-capped gold nanoparticles: 220 mg of sodium citrate dihydrate (0.748 mol) were dissolved in 200 mL of milliQ water, and the solution heated to reflux. When the solution is boiling vividly, 10 µL of $AuCl_3$•HCl (30%) were added. After a few seconds, the solution turns deep red colour, and the solution is kept at reflux for 40-60 min, and then allowed to cool to room temperature. To this aqueous solution, a solution of 26 mg of exTTF-MUA (42 mmol) in 50 mL of chlorobenzene were added. The corresponding biphasic mixture was stirred vigorously for approximately 1h or until complete decoloration of the aqueous phase. The golden-green organic phase was separated and distributed in centrifuge tubes which were topped up with CH_2Cl_2 and subjected to centrifugation (6000 rpm, 10 min) to precipitate the nanoparticles. The yellow supernatant was decanted and further washes with CH_2Cl_2 (3x) and CH_3OH (3x) were carried out to remove excess exTTF-MUA and other organic impurities. The exTTFAuNPs were obtained as a black powder and used as such.