Supporting Information

Voltammetric studies on the inter-relationship of the redox chemistry of TTF, TTF•+, TTF^{2+} and HTTF^{+} in acidic media

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Table S1 Diffusion coefficients (D) of TTF, TTF[+•], TTF[2+] in acetonitrile (0.1 M Bu$_4$NPF$_6$).

Technique	Equation used for determination of D[a]	$D_{TTF} \times 10^5$ cm^2 s^{-1}	$D_{TTF^{+•}} \times 10^5$ cm^2 s^{-1}	$D_{TTF^{2+}} \times 10^5$ cm^2 s^{-1}
Linear sweep voltammetry	$I_p = 0.4463\ nFAC\left(\dfrac{nFvD}{RT}\right)^{0.5}$	2.20	1.95	1.65
RDE voltammetry	$I_{lim} = 0.620\ n\ F\ A\ D^{2/3}\ \omega^{1/2}\ v^{-1/6}\ C$	2.10	1.90	1.60
Microelectrode voltammetry	$I_{lim} = 4n\ F\ r_e\ D\ C$	2.10	1.90	1.60

[a] I_p = oxidation peak potential, I_{lim} = limiting current, v = scan rate

w = angular rotation rate, v = kinematic viscosity (4.54 $\times$ 10^{-3} cm^2 s^{-1}),[22] r_e = electrode radius,

C = concentration, n = number of electrons transfered (1.0). Other symbols have there usual
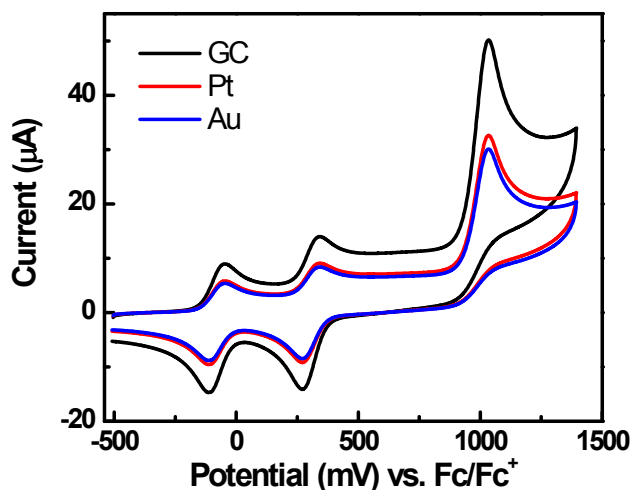
meaning or are defined in the text.

Figure S1 Cyclic voltammograms obtained for 1.0 mM TTF in CH_3CN (0.1 M Bu_4NPF_6) in the presence of 10 mM ethereal HBF_4 (0.1 M Bu_4NPF_6) at GC, Au and Pt electrodes with a scan rate of 100 mV s^{-1}.
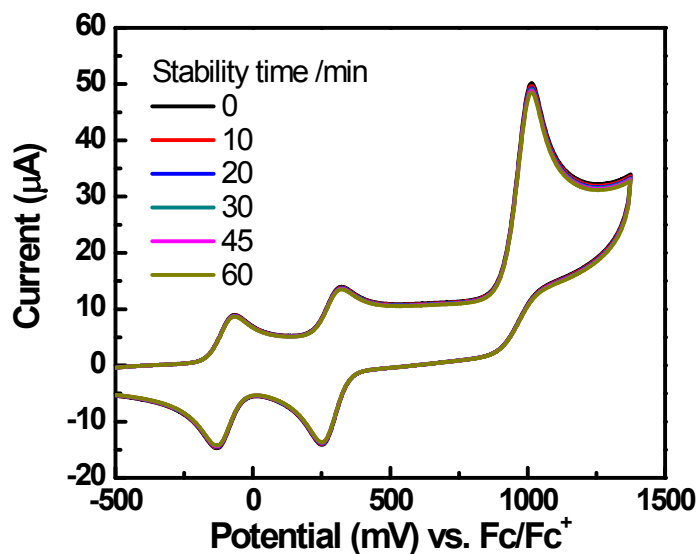

Figure S2 Cyclic voltammograms obtained as a function of time for 1.0 mM TTF in CH_3CN (0.1 M Bu_4NPF_6) at a 3 mm diameter GC electrode (scan rate of 100 mV s^{-1}) in the presence of 10 mM ethereal HBF_4.
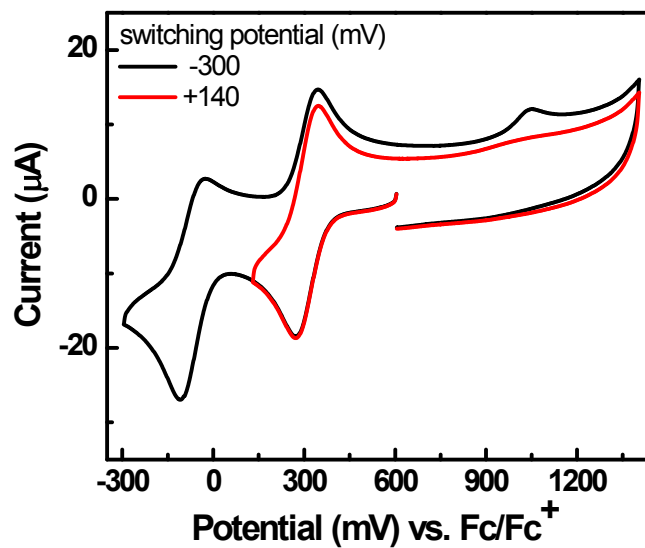
Figure S3 Cyclic voltammograms obtained at scan rate 100 mV s^{-1} in acetonitrile (0.1 M Bu$_4$NPF$_6$) for 1 mM TTF^{2+} in the presence of 66 mM ethereal HBF$_4$ with a 3 mm GC electrode at designated switching potential values.
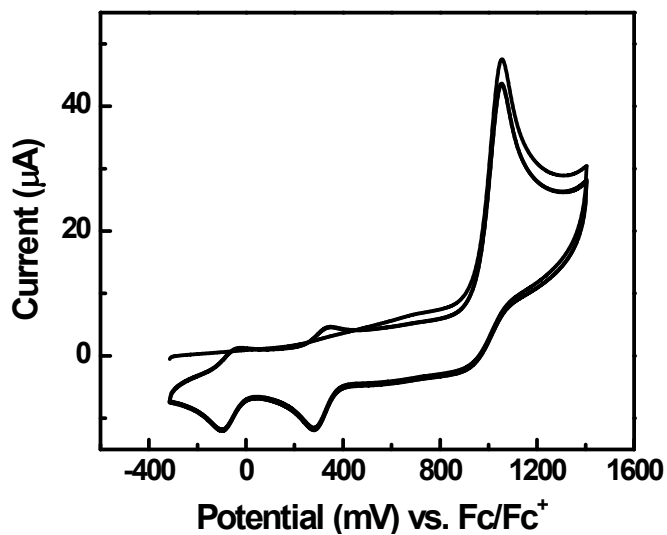

Figure S4 A cyclic voltammogram (2 cycles of potential) for HTTF$^+$ obtained after back reduction electrolysis of 0.91 mM TTF^{2+} in acetonitrile (0.1 M Bu$_4$NPF$_6$) in the presence of 66 mM ethereal HBF$_4$ with a 3 mm GC electrode at a scan rate of 100 mV s^{-1}.
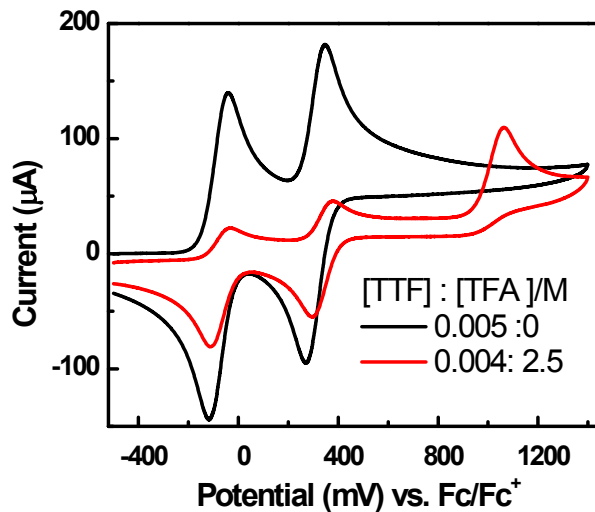
Figure S5 Cyclic voltammograms of TTF obtained at scan rate 100 mV s^{-1} in acetonitrile (0.1 M Bu$_4$NPF$_6$) for TTF in with a 3 mm GC electrode at designated TTF and TFA concentrations.
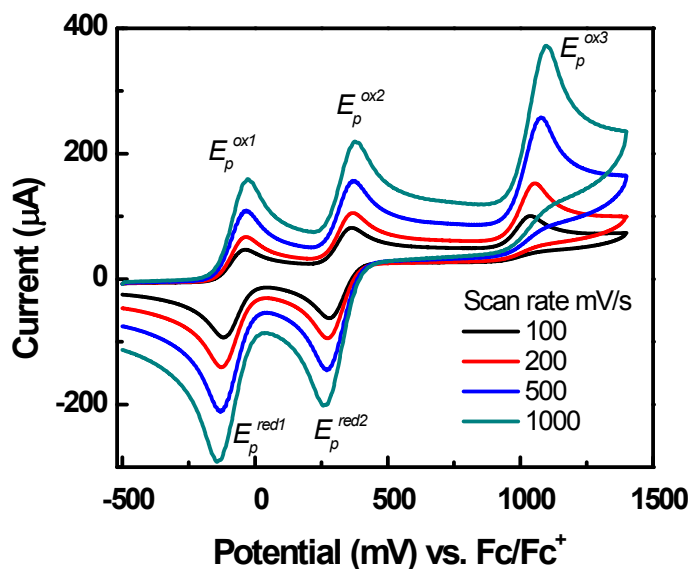

Figure S6 Cyclic voltammograms for 4.35 mM TTF in the presence of 1.5 M TFA obtained at a scan rate of 100 mV s^{-1} in acetonitrile (0.1 M Bu$_4$NPF$_6$) with a 3 mm diameter GC electrode.
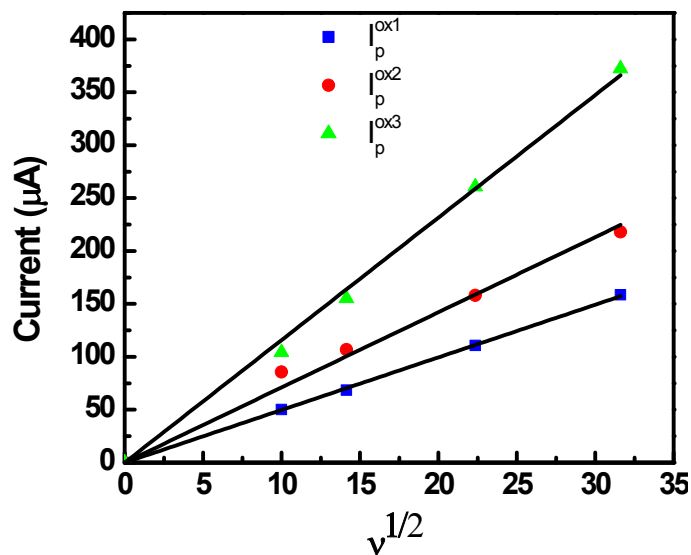
Figure S7 Dependence of peak currents, for the first (I_p^{ox1}), second (I_p^{ox2}) and third (I_p^{ox3}) consecutive processes versus the square root of scan rate for 4.35 mM TTF in the presence of 1.5 M TFA in acetonitrile (0.1 M Bu$_4$NPF$_6$) .
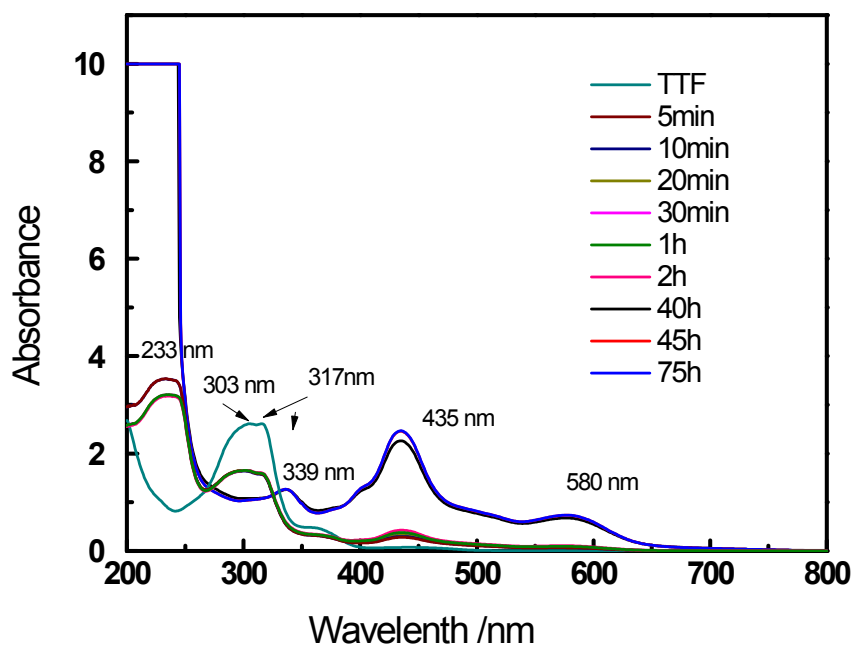

Figure S8 UV-vis spectra of obtained as a function of time after addition of 500 mM TFA to 0.25 mM TTF in CH$_3$CN (0.1 M Bu$_4$NPF$_6$).