

Supporting Information

A systematic study of the variation of tetrathiafulvalene (TTF), TTF^{•+} and TTF²⁺ reaction pathways with water in the presence and absence of light

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Table S1 Cyclic voltammetric parameters (vs. Fc/Fc⁺) obtained for the oxidation of 1 mM TTF with a 3 mm diameter GC electrode using a scan rate of 100 mV s⁻¹ in acetonitrile (0.1 M Bu₄NPF₆) in the absence and presence of 10 % water.

Water% (v/v)	TTF ^{0/+}				TTF ^{+2/+}			
	E_p^{ox1}	E_p^{red1}	E_{m1}	ΔE_{p1}	E_p^{ox2}	E_p^{red2}	E_{m2}	ΔE_{p2}
	mV	mV	mV	mV	mV	mV	mV	mV
0	-34	-114	-74	80	350	272	311	78
10	-50	-137	-94	87	325	245	285	80

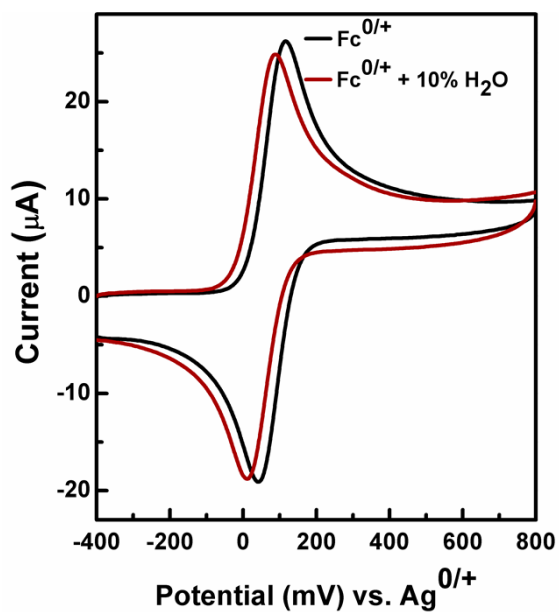


Figure S1 Cyclic voltammograms for the oxidation of 1 mM Ferrocene (Fc) in acetonitrile (0.1 M Bu₄NPF₆) obtained with a 3 mm diameter GC electrode using a scan rate of 100 mV s⁻¹ in the absence and presence of 10% water.

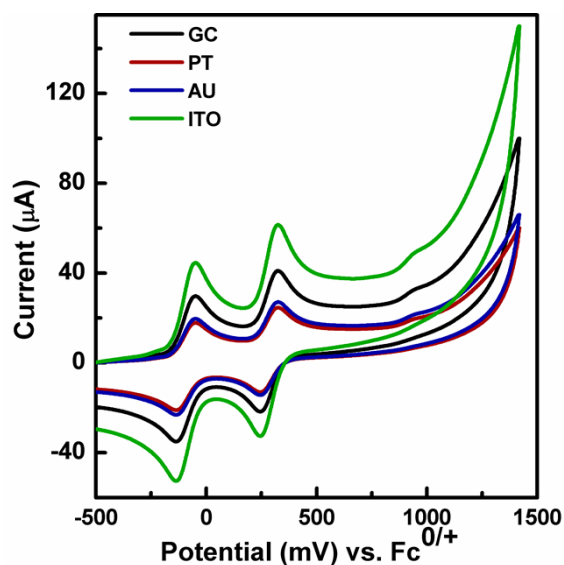


Figure S2 Cyclic voltammograms for the oxidation of 1mM TTF in acetonitrile/water (90:10%) (0.1 M Bu_4NPF_6) obtained with GC, Au, Pt and ITO electrodes using a scan rate of 100 mV s^{-1} .

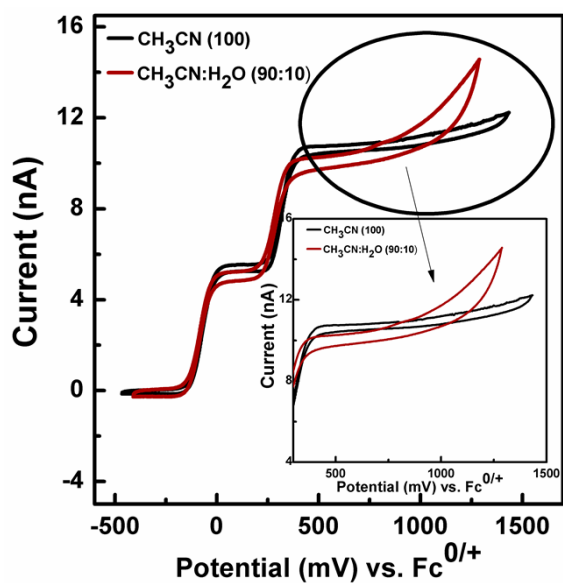


Figure S3 Steady-state voltammograms obtained with a $12 \mu\text{m}$ diameter carbon fiber microdisc electrode using a scan rate of 20 mV s^{-1} for the oxidation of 1 mM TTF in acetonitrile (0.1 M Bu_4NPF_6) in the absence and in the presence of 10% water.

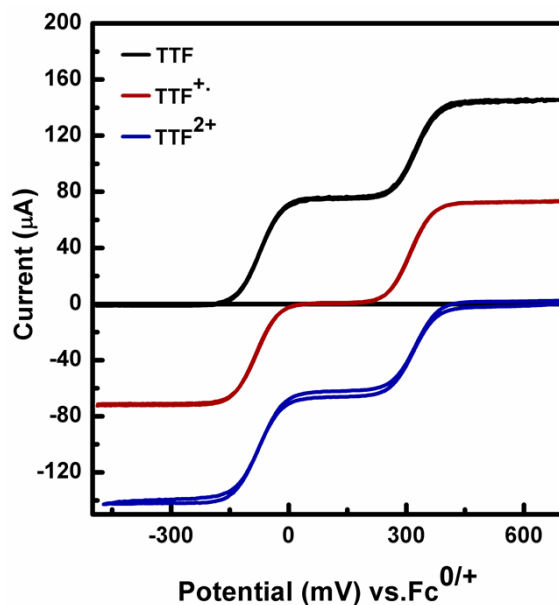


Figure S4 RDE voltammograms obtain with a 3 mm diameter GC electrode using a rotation rate of 1000 rpm and scan rate of 20 mV s^{-1} for 1 mM TTF, and TTF^{+} and TTF^{2+} generated by bulk electrolysis at 120 and 620 mV vs. $\text{Fc}^{0/+}$ respectively in acetonitrile (0.1 M Bu_4NPF_6) inside a dry box. During this bulk electrolysis experiment, the initially pale-yellow TTF solution changed to dark red TTF^{+} , which upon further oxidation at 620 mV generates a light-yellow TTF^{2+} solution; thus the oxidation of TTF to TTF^{2+} occurs in two steps. The position of zero current in the steady state RDE voltammogram confirms that complete oxidation of TTF to TTF^{2+} is achieved in the absence of oxygen and water under dry box conditions.

Table S2 Cyclic voltammetric parameters (vs. Fc/Fc⁺) obtained for the oxidation and reduction of 1mM TTF^{+/2+} at a 3 mm diameter GC electrode in acetonitrile and mixed acetonitrile/water (90:10%, v/v) solvent media (0.1 M Bu₄NPF₆) in the dark and after irradiation with white light ($\lambda = 275-750$ nm).

Water % (v/v)	TTF ^{0/+}				TTF ^{+/2+}				HTTF ⁺
	E_p^{ox1}	E_p^{red1}	E_{m1}	ΔE_{p1}	E_p^{ox2}	E_p^{red2}	E_{m2}	ΔE_{p2}	E_p^{ox3}
	mV	mV	mV	mV	mV	mV	mV	mV	mV
0	-33	-110	-71	77	350	272	311	78	-
10 (dark)	-57	-134	-95	77	324	246	285	78	-
10 (white light)	-57	-134	-95	77	318	246	282	72	1024

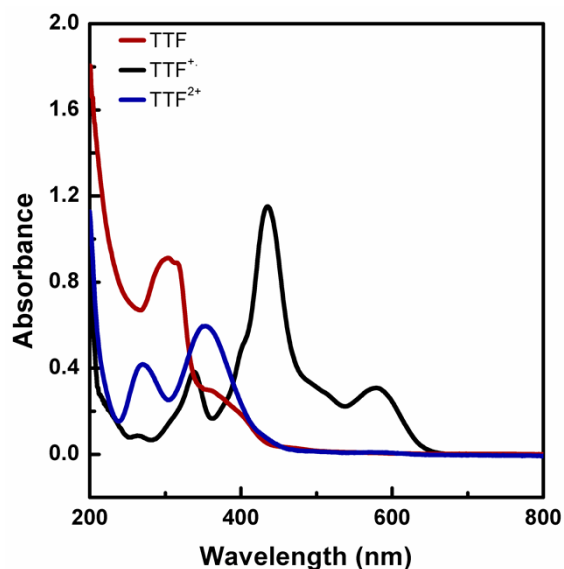


Figure S5 UV-visible spectra of 1 mM TTF, TTF⁺ and TTF²⁺ in acetonitrile (0.1 M Bu₄NPF₆).

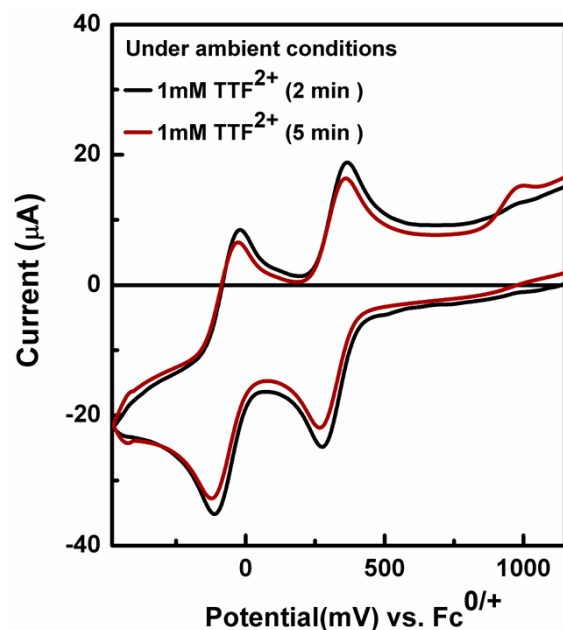


Figure S6 Voltammograms obtained at a 3 mm diameter GC electrode at a scan rate of 100 mV s⁻¹ for 1mM TTF²⁺ generated by bulk electrolysis in acetonitrile (0.1 M Bu₄NPF₆) under dry box conditions followed by 2 min and 5 min exposure to ambient conditions (outside dry box).

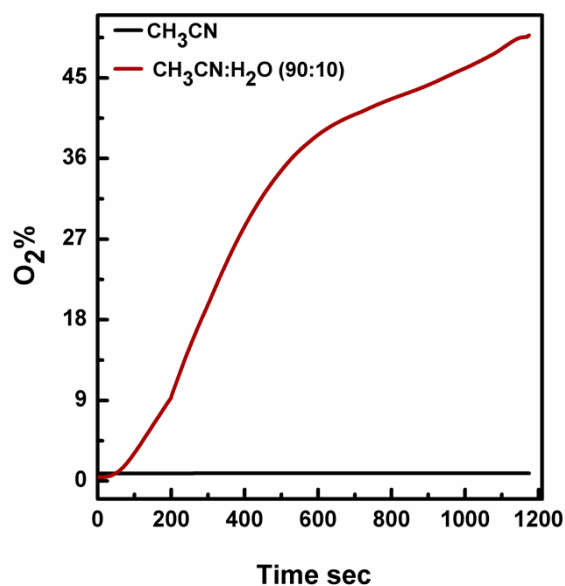


Figure S7 Oxygen percentages as a function of time for 1 mM TTF²⁺ in acetonitrile (0.1 M Bu₄NPF₆) with or without added water under nitrogen atmosphere with exposure to white light.