Supplementary Information (SI) for Energy Advances.

Supporting Information for

Electrochemical and Spectroscopic Characterisation of Organic Molecules with High Positive Redox Potentials for Energy Storage in Aqueous Flow Cells

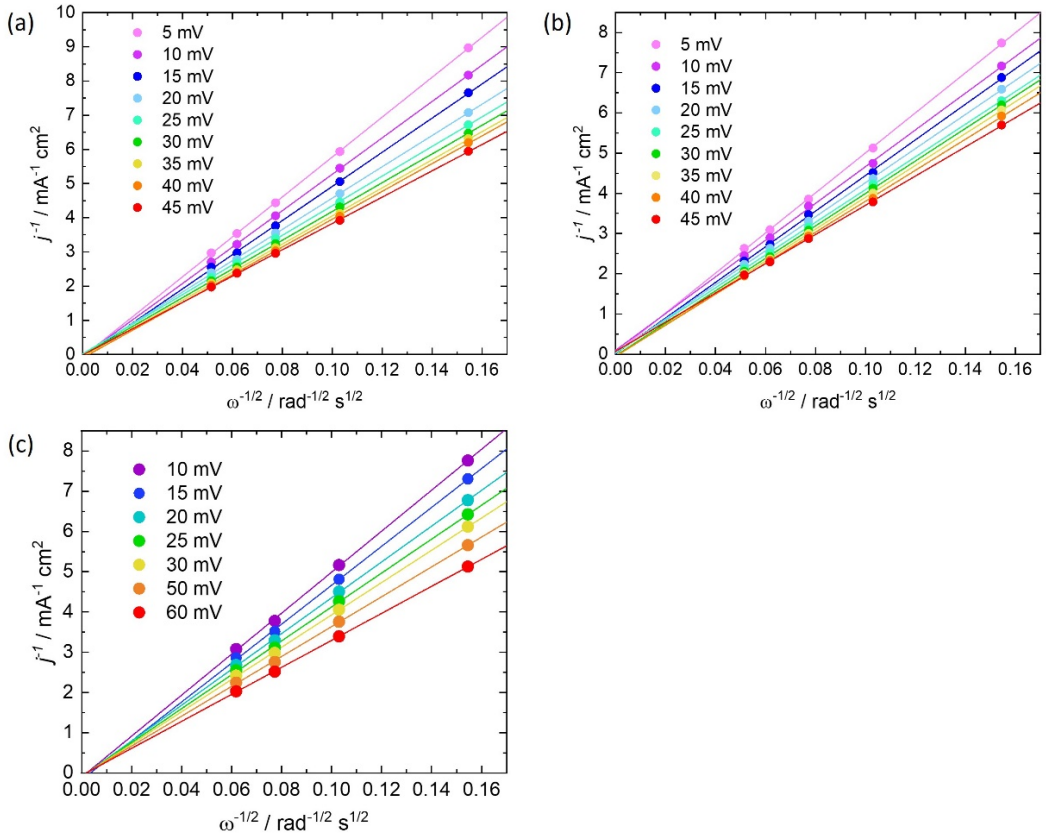

Figure S1: Koutechy-Levich analysis of (a-b) 1 mM ABTS / 1 M $HClO_4$ and (c) CPZ in 1 M H_2SO_4

Intercepts in Figure S1 are all <0.1 mA^{-1} cm^2, hence a minimum kinetic current density of 10 mA cm^{-2}.

	E_0 vs SHE / V	Supporting Electrolyte	z	c / M	E_V / Wh dm^{-3}	k / cm s^{-1}	D /10^{-6} cm^2 s^{-1}	$(D/D(Fe^{2+}))^{2/3}$	k_m /10^{-4} cm s^{-1}	$k_{composite}$ / 10^{-4} cm s^{-1}	P / W cm^{-2}	Ref.
4,4'-BPTS	0.92	1 M H_2SO_4	2	1.1	54.25	1.12E-04	1.84	0.4246	5.96	0.943	0.0184	*1*
BQDS	0.85	1 M H_2SO_4	2	0.65	29.62	1.55E-04	3.80	0.6886	9.66	1.336	0.0351	*2*
DHBS	0.71	1 M H_2SO_4	2	0.8	30.45	5.52E-04	4.28	0.7454	10.5	3.613	0.0396	*3*
DHDMBS	0.82	1 M H_2SO_4	2	2	87.91	1.30E-04	4.12	0.7267	10.2	1.153	0.0365	*4*
$Fe_2(SO_4)_3$	0.77	$[Fe_2(SO_4)_3]$	1	1.4	28.89	1.60E-03	3.76	0.6838	9.59	5.997	0.0624	*5*
$FeCl_3$	0.77	[FeCl3]	1	0.8	16.51	1.60E-03	6.65	1	14.0	7.475	0.0444	*6, 7*
VO^{2+}/VO_2^+	1.00	1 M H_2SO_4	1	**1**	26.80	6.80E-05	2.80	0.5618	7.88	0.626E	0.00604	*8*
MB (1 M)	0.52	1 M H_2SO_4	2	**1**	27.87	8.65E-03	2.69	0.5473	7.68	7.052	0.0708	*9*
MB	0.52	1 M H_2SO_4	2	1.2	33.45	8.65E-03	2.69	0.5473	7.68	7.052	0.0849	*9*
ABTS'	0.78	1 M $HClO_4$	1	**1**	20.91		3.34	0.6314	8.86	8.859	0.0667	
ABTS''	1.08	1 M $HClO_4$	1	**1**	28.95		3.29	0.6249	8.77	8.767	0.0914	
CPZ	0.802	1 M H_2SO_4	1	**1**	21.49		4.50	0.7709	10.8	10.82	0.0837	
TMB	0.829	1 M H_2SO_4	2	**1**	44.44	9.43E-03	4.77	0.8010	11.2	10.04	0.1606	
NHPI	1.34	1 M H_2SO_4	1	**1**	35.91	1.96E-02	6.67	1.0024	14.1	13.12	0.1697	
VIO	1.158	1 M H_2SO_4	1	**1**	31.04	2.83E-02	5.75	0.9073	12.7	12.18	0.1361	

Table S1: Experimentally determined electrochemical parameters and hypothetical figures of merit for FB positive electrolyte.

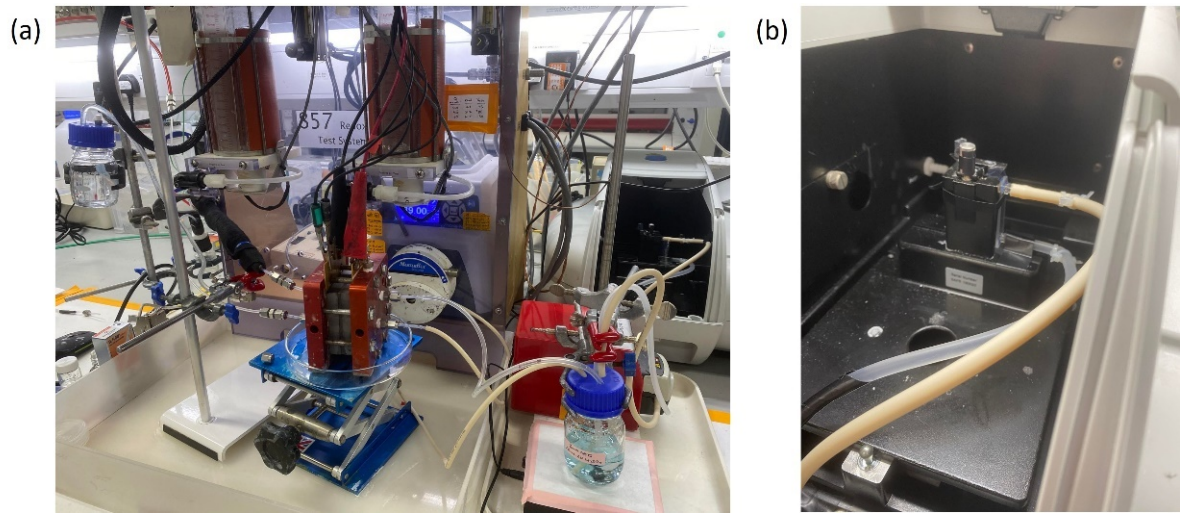

Figure S2: (a) Photograph of RFC experimental setup and (b) closer view of the in-operando *UV-Vis flow-through cuvette in the photospectrometer (lid closed when running).*

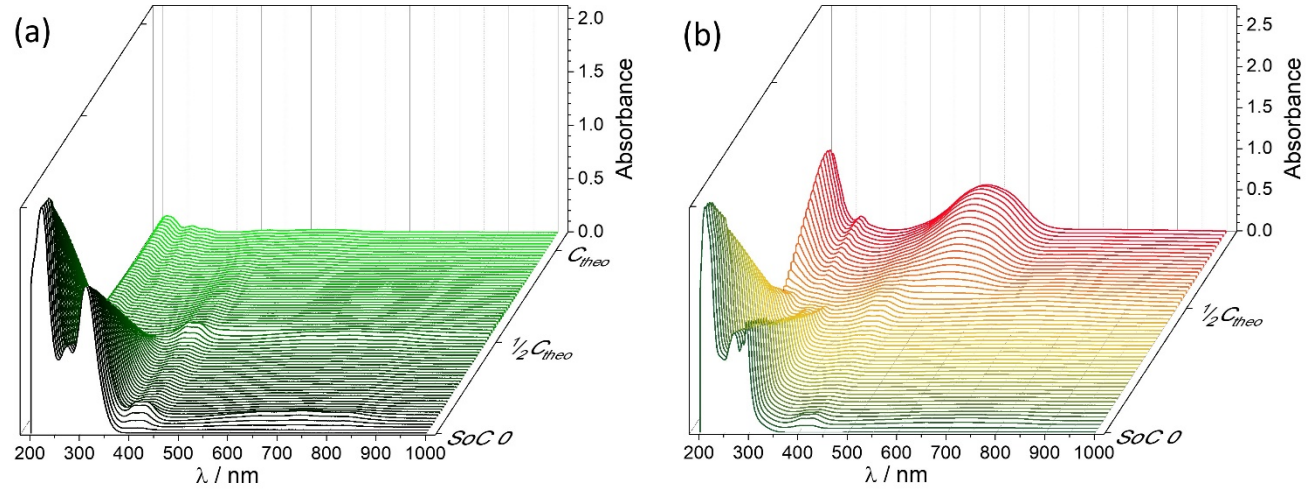

Figure S3: Waterfall plots of UV-Vis absorption spectra (1 scan min^{-1}) during charging process of 5 mM ABTS in (a) 1 M $HClO_4$ and (b) 6 M H_2SO_4

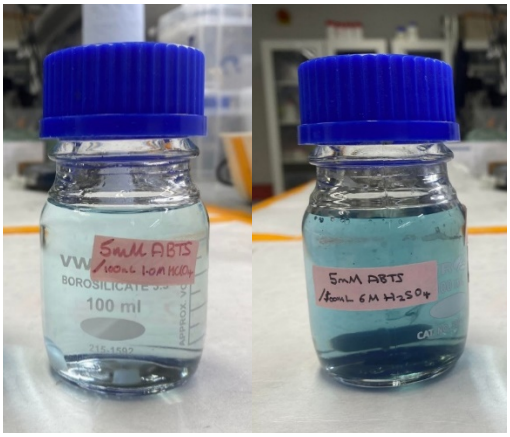

Figure S4: 100 mL electrolyte samples of ABTS in 1 M HClO4 (left) and 6 M H_2SO_4 (right). The 6 M H_2SO_4 sample shows a dark blue precipitate.

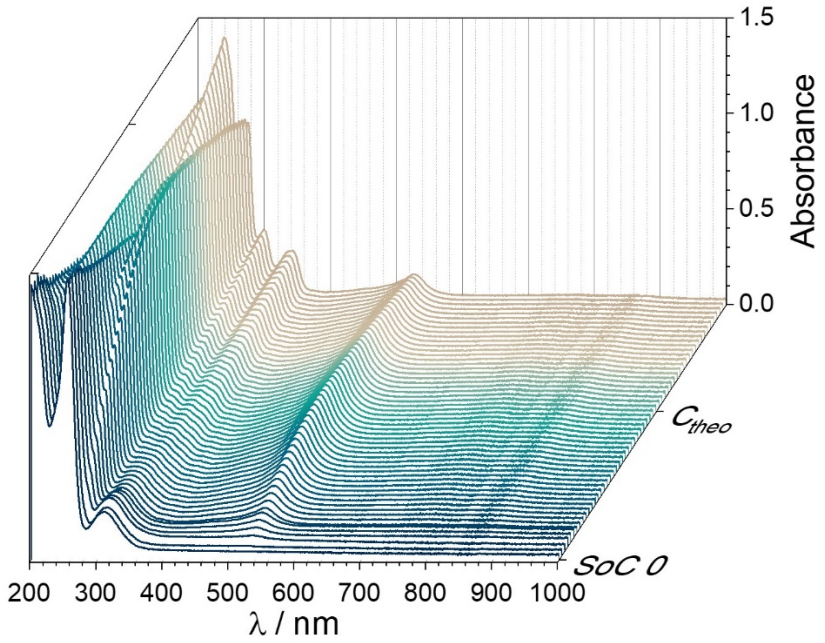

Figure S5: Waterfall plot of UV-Vis absorption spectra (1 scan min^{-1}) during charging process of 5 mM CPZ

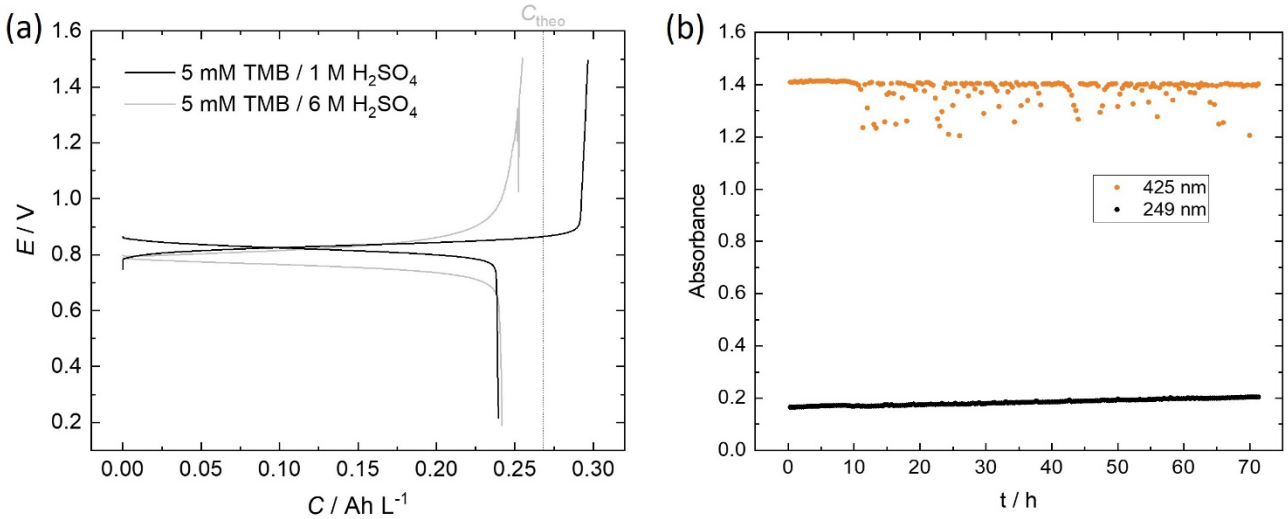

Figure S6: (a) E vs C cycle profiles of 5 mM TMB in 1 M H_2SO_4 at SoC 1 with a 5 min open-circuit potential (OCP) and in 6 M H_2SO_4 at SoC 1 with a 72 h OCP and (b) magnitude of absorbance at both 249 and 425 nm during a 72 h OCP at SoC 1 during a cycle of 5 mM TMB in 6 M H_2SO_4.

The solubility of ABTS in 1 M $HClO_4$ was not determined due to the requirement to saturate a relatively strong perchlorate solution with a dehydrating agent. The saturation point of CPZ was not obvious by the presence of undissolved solid, but formed a gel-like liquid, with a CPZ concentration that appeared to plateau with increasing solid added.

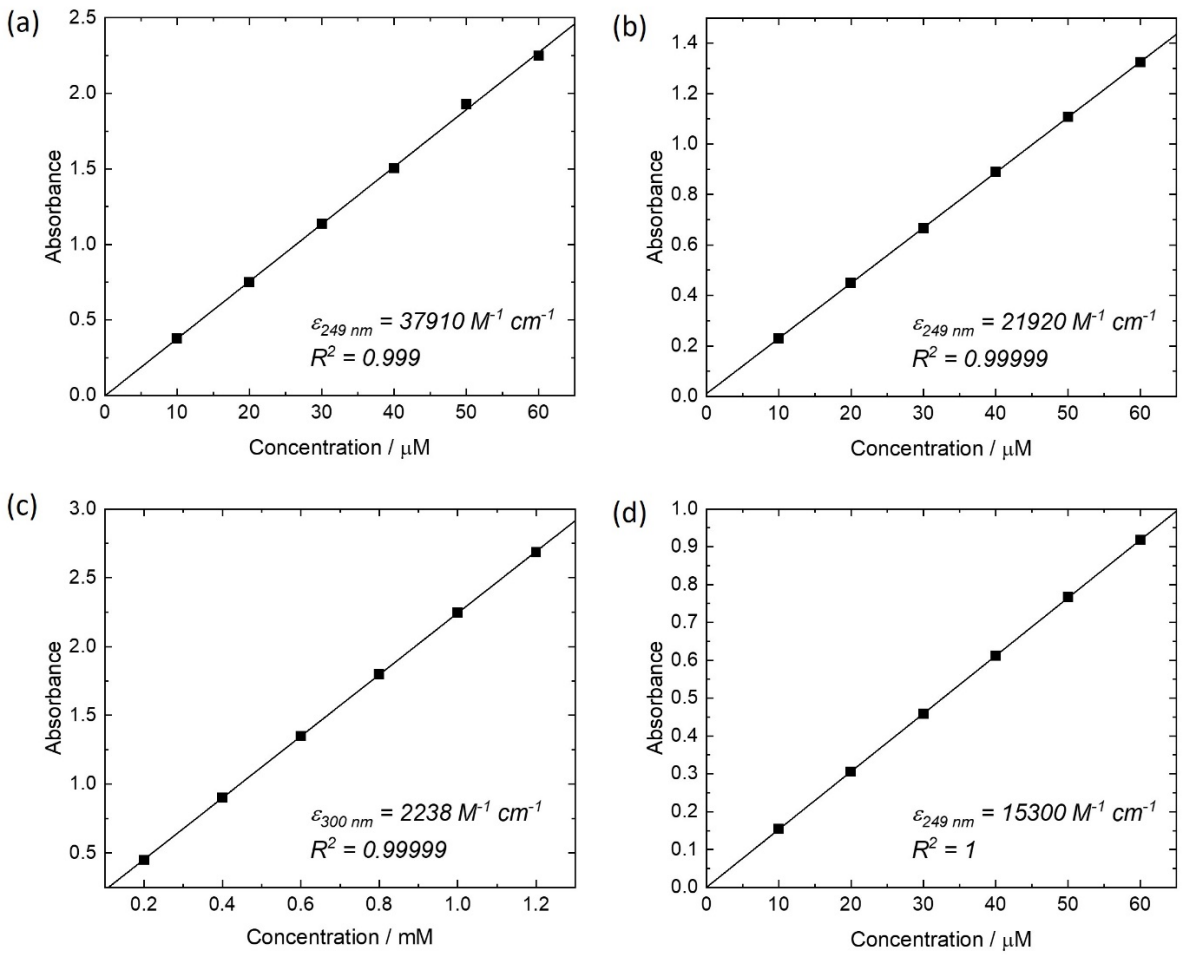

Figure S7: Absorbance in 1 M H_2SO_4 vs concentration for (a) CPZ, (b) TMB, (c) NHPI and (d) VIO.

Table S2: Calculation of the concentration and volumetric energy density of saturated solutions

X	***S.E.***	**Abs**	**Dilution Factor**	***ε / M^{-1} cm^{-1}***	***Max. Apparent Concentration / M***	***n***	***E / V***	***E(V) / Wh L^{-1}***	**λ /nm**
CPZ	1 M H_2SO_4	0.815	40000	37910	0.860	1	0.80	18.437	240
TMB	1 M H_2SO_4	0.905	20000	21920	0.825	2	0.83	36.719	249
	6 M H_2SO_4	0.373	100000	21920	1.702	2	0.83	75.730	
NHPI	1 M H_2SO_4	0.855	20	2238	0.008	1	1.34	0.274	300
VIO	1 M H_2SO_4	0.250	2000	15300	0.033	1	1.16	1.016	249

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