Supporting information

Selection and Characterisation of Weakly Coordinating Solvents for Semiconductor Electrodeposition

Alexander W. Black[a] and Philip N. Bartlett.*[a]

School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.

Table S1: Kamlet and Taft parameters of weakly coordinating solvents, common electrochemical solvents and typical ionic liquids.

Solvent	Abbreviation	Code	π^*	α	β	Ref.
Dichloromethane	DCM		0.82	0.13	0.10	[1]
Trifluorotoluene	TFT		0.64	0	0	[2]
o-dichlorobenzene	oDCB		0.80	0	0.03	[1]
p-fluorotoluene	pFT		0.60	0	0.11	π^* estimated from Eq. 25 in [3]. α, β estimated from [4]
Chlorobenzene	CB		0.71	0.07	0	[1]
1,2-dichloroethane	DCE		0.81	0.10	0	[1]
Water	-	a	1.09	1.17	0.47	[1]
Dimethyl sulphoxide	DMSO	b	1.00	0	0.76	[1]
Dimethylformamide	DMF	c	0.88	0	0.69	[1]
Ethylene glycol	EG	d	0.92	0.90	0.52	[1]
Propylene carbonate	PC	e	0.90	0	0.38	[1]
Acetonitrile	ACN	f	0.75	0.19	0.4	[1]
Tetrahydrofuran	THF	g	0.58	0	0.55	[1]
Dimethoxyethane	DME	h	0.53	0	0.41	[1]
1-butyl-3-methylimidazolium tetrafluoroborate	[bmim][BF_4]	i	1.05	0.63	0.38	[5]
1-butyl-3-methylimidazolium triflate	[bmim][TfO]	j	1.01	0.63	0.46	[5]
1-butyl-2,3-dimethylimidazolium tetrafluoroborate	[bm_2im][BF_4]	k	1.08	0.40	0.36	[5]

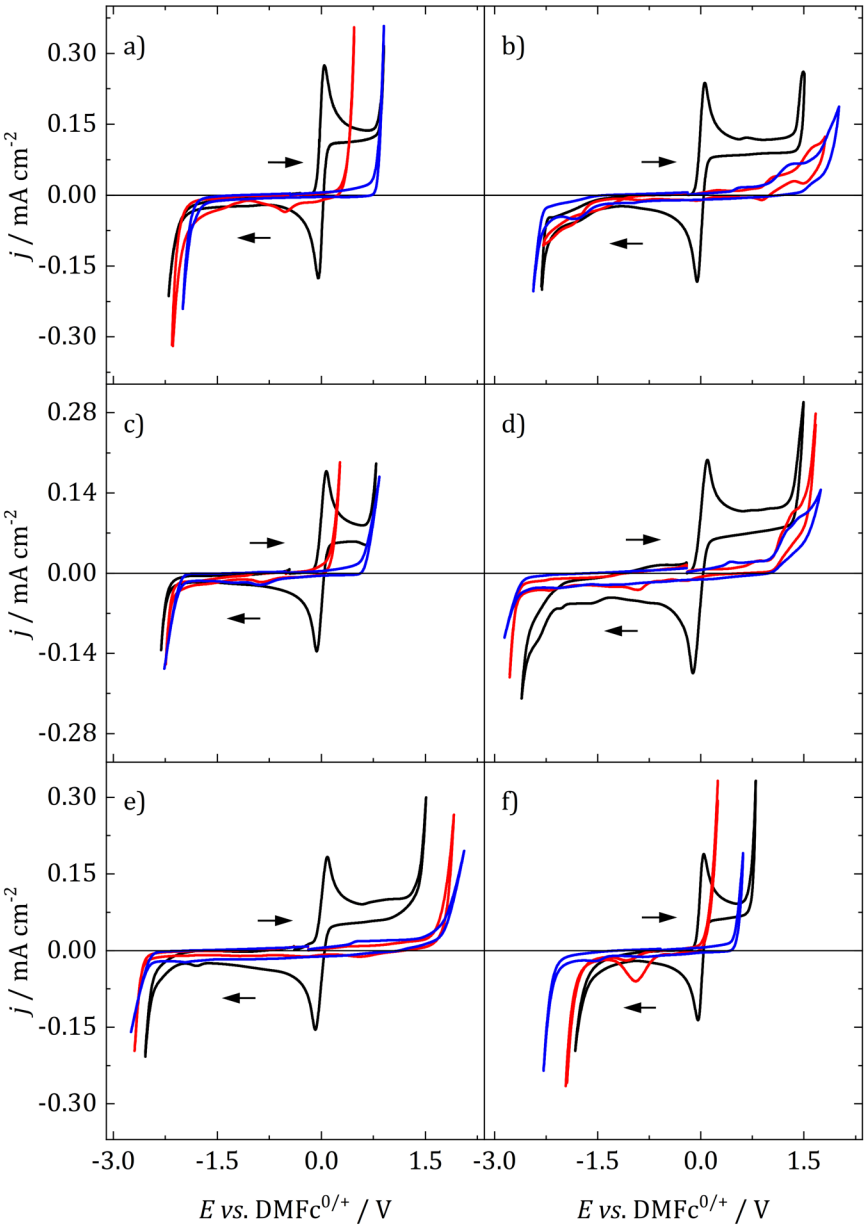

Figure S1: Voltammograms to determine the solvent windows of solvents at various electrode materials with 1 mM DMFc, 100 mM a), c), f): [N^{n}Bu$_4$]Cl and b), d), e): [N^{n}Bu$_4$][BF$_4$]. Scan swept from -0.5 V *vs*. DMFc at 50 mV s^{-1} in the direction indicated by the arrows. CE: Pt mesh, RE: Ag/AgCl. a): DCM, b): TFT, c): oDCB, d): pFT, e): CB, f): DCE. Black: r = 0.25 mm Pt WE, red: r = 0.25 mm Au, blue: r = 1.5 mm glassy carbon.

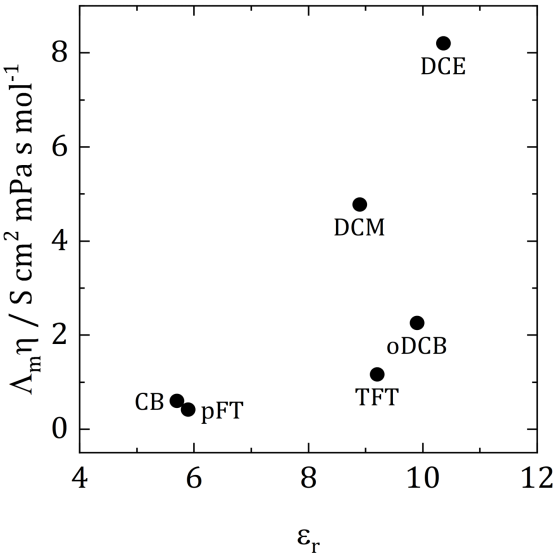

Figure S2: Solvent dependence of $\Lambda_m\eta$ for 100 mM [N^{n}Bu$_4$][BF$_4$] at 25°C, with the solvent dielectric constant.

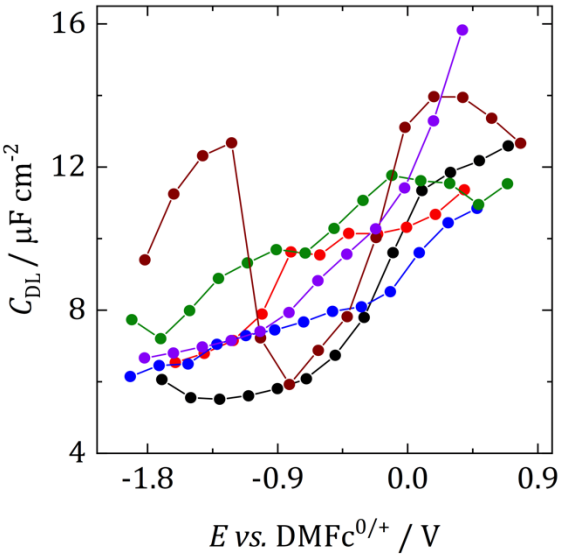

Figure S3: Differential capacitance curves for 100 mM [N^{n}Bu$_4$][BF$_4$] at a r = 0.25 mm Pt electrode, scanning in the cathodic direction. Black: DCM, red: TFT, blue: oDCB, green: pFT, brown: CB, purple: DCE.

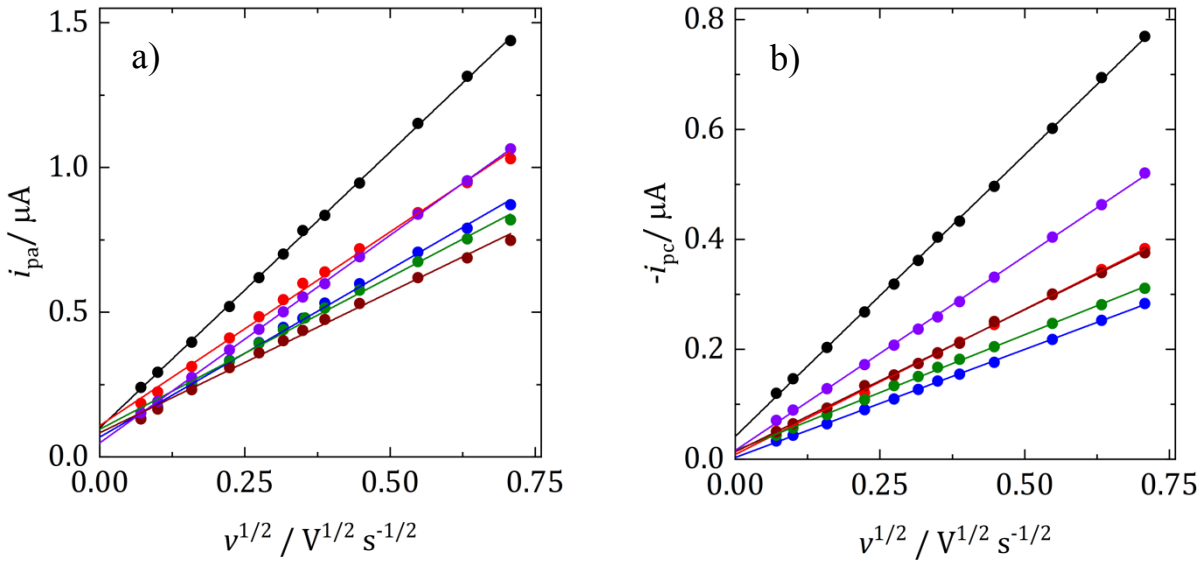

Figure S4: Randles-Sevčik plots for a) 1 mM DMFc and b) 0.5 mM $CcPF_6$ collected at a r = 0.25 mm Pt WE for scan rates between 5-500 mV s^{-1}. Black: DCM, red: TFT, blue: oDCB, green: pFT, brown: CB, purple: DCE.

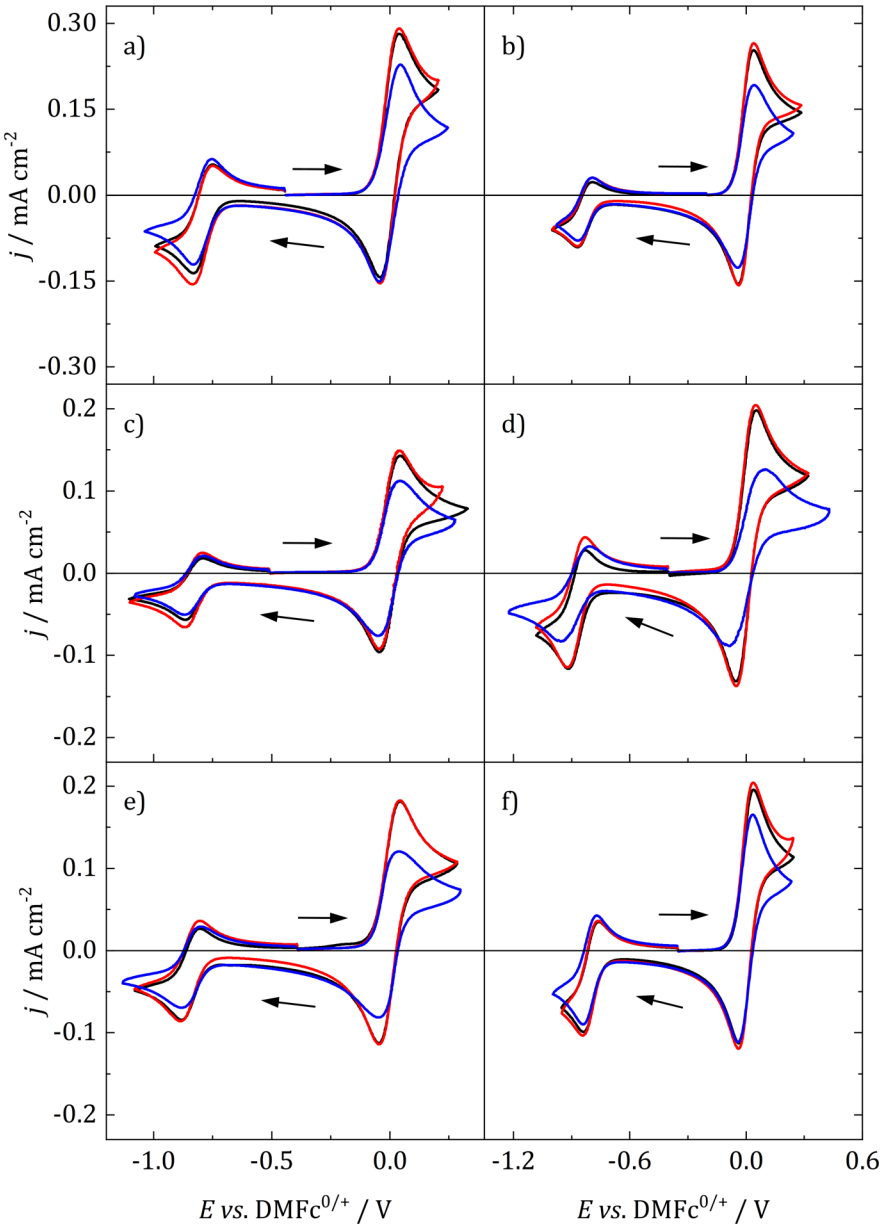

Figure S5: *iR* corrected macrodisc CVs for 1 mM DMFc and 0.5 mM $CcPF_6$ at various electrode materials with 100 mM a), c), f): $[N^nBu_4]Cl$ and b), d), e): $[N^nBu_4][BF_4]$. Scan swept from -0.3 V *vs*. DMFc at 50 mV s^{-1} in the direction indicated by the arrows. CE: Pt mesh, RE: Ag/AgCl. a): DCM, b): TFT, c): oDCB, d): pFT, e): CB, f): DCE. Black: Pt WE, red: Au, blue: glassy carbon.

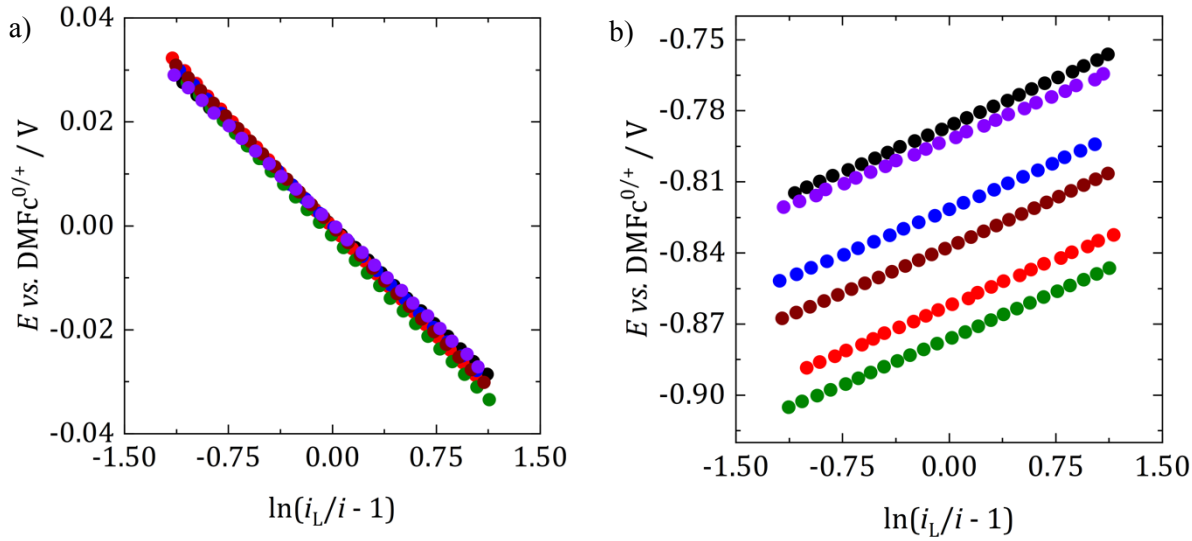

Figure S6: Representative mass transport corrected Tafel plots for a) 1 mM DMFc and b) 0.5 mM $CcPF_6$ at a r = 12.5 µm WE at 25 °C. Black: DCM, red: TFT, blue: oDCB, green: pFT, brown: CB, purple: DCE.

Solvent	D / 10^{-5} cm^2 s^{-1}	
	DMFc	$CcPF_6$
DCM	1.61(3)	1.27(3)
TFT	1.15(2)	0.35(3)
oDCB	0.51(1)	0.21(1)
pFT	1.06(10)	0.29(4)
CB	0.84(3)	0.29(2)
DCE	0.84(2)	0.56(2)

Table S2: Diffusion coefficients obtained from a potential step at a microelectrode at 25°C. Values the average of three repeats and the error the standard deviation.

References

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