Enhancing the solubility of 1,4-diaminoanthraquinones in electrolytes for organic redox flow batteries through molecular modification

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Electronic Supplementary Information (ESI)

Table S1. Maximum solubility of DB-134 in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system (v/v)	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
DB-134	MeCN/toluene 1/0	17750 (637 nm)	0.0194 ± 0.0002
DB-134	MeCN/toluene 3/1	18400 (640 nm)	0.0668 ± 0.0005
DB-134	MeCN/toluene 1/1	17780 (642 nm)	0.128 ± 0.004
DB-134	MeCN/toluene 1/3	17320 (644 nm)	0.1461 ± 0.0008
DB-134	MeCN/toluene 0/1	17800 (646 nm)	0.144 ± 0.002
DB-134	1 mol L^{-1} $TEATf_2N$ in MeCN	17750 (637 nm)	0.0157 ± 0.0005

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

Table S2. Maximum solubility of Et-He-DAAQ in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
Et-He-DAAQ	MeCN/toluene 1/0	17800 (644 nm)	0.01192 ± 0.00002
Et-He-DAAQ	MeCN/toluene 3/1	20400 (647 nm)	0.0484 ± 0.0007
Et-He-DAAQ	MeCN/toluene 1/1	20740 (649 nm)	0.236 ± 0.001
Et-He-DAAQ	MeCN/toluene 1/3	16840 (651 nm)	0.457 ± 0.002
Et-He-DAAQ	MeCN/toluene 0/1	16790 (652 nm)	0.471 ± 0.002
Et-He-DAAQ	1 mol L^{-1} $TEATf_2N$ in MeCN	17800 (644 nm)	0.0064 ± 0.0005

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

Table S3. Maximum solubility of Me_3N-Et-DAAQ in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system (v/v)	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
Me_3N-Et-DAAQ	MeCN/toluene 1/0	13020 (580 nm)	0.046 ± 0.002
Me_3N-Et-DAAQ	MeCN/toluene 3/1	12900 (581 nm)	0.0399 ± 0.0008
Me_3N-Et-DAAQ	MeCN/toluene 1/1	12700 (581 nm)	0.0192 ± 0.0002
Me_3N-Et-DAAQ	MeCN/toluene 1/3	13060 (621 nm)	0.00557 ± 0.00007
Me_3N-Et-DAAQ	MeCN/toluene 0/1	Not determined	insoluble
Me_3N-Et-DAAQ	1 mol L^{-1} $TEATf_2N$ in MeCN	13020 (580 nm)	0.0449 ± 0.0003

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

Table 4. Maximum solubility of Me_3N-Pr-DAAQ in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system (v/v)	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
Me_3N-Pr-DAAQ	MeCN/toluene 1/0	14210 (632 nm)	0.601 ± 0.007
Me_3N-Pr-DAAQ	MeCN/toluene 3/1	14040 (633 nm)	0.520 ± 0.004
Me_3N-Pr-DAAQ	MeCN/toluene 1/1	14000 (634 nm)	0.32 ± 0.01
Me_3N-Pr-DAAQ	MeCN/toluene 1/3	14800 (634 nm)	0.028 ± 0.004
Me_3N-Pr-DAAQ	MeCN/toluene 0/1	Not determined	insoluble
Me_3N-Pr-DAAQ	1 mol L^{-1} $TEATf_2N$ in MeCN	14210 (632 nm)	0.346 ± 0.008

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

Table 5. Maximum solubility of Et-DEG-DAAQ in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system (v/v)	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
Et-DEG-DAAQ	MeCN/toluene 1/0	15300 (636 nm)	1.7 ± 0.1
Et-DEG-DAAQ	MeCN/toluene 3/1	14400 (638 nm)	1.7 ± 0.1
Et-DEG-DAAQ	MeCN/toluene 1/1	13900 (640 nm)	1.50 ± 0.02
Et-DEG-DAAQ	MeCN/toluene 1/3	16650 (641 nm)	1.3 ± 0.1
Et-DEG-DAAQ	MeCN/toluene 0/1	14120 (642 nm)	0.97 ± 0.03
Et-DEG-DAAQ	1 mol L^{-1} $TEATf_2N$ in MeCN	15300 (636 nm)	1.29 ± 0.04

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

Table 6. Maximum solubility of Me-TEG-DAAQ in different solvent mixtures of acetonitrile and toluene, as measured by UV-VIS absorption spectroscopy.

DAAQ	Solvent system (v/v)	Molar absorption coefficient ε (L mol^{-1} cm^{-1})[a]	Maximum solubility (mol L^{-1})[b]
Me-TEG-DAAQ	MeCN/toluene 1/0	15840 (636 nm)	Miscible
Me-TEG-DAAQ	MeCN/toluene 3/1	15160 (638 nm)	Miscible
Me-TEG-DAAQ	MeCN/toluene 1/1	13900 (640 nm)	Miscible
Me-TEG-DAAQ	MeCN/toluene 1/3	14580 (641 nm)	Miscible
Me-TEG-DAAQ	MeCN/toluene 0/1	14120 (642 nm)	Miscible
Me-TEG-DAAQ	1 mol L^{-1} $TEATf_2N$ in MeCN	15840 (636 nm)	Miscible

[a] determined at the wavelength of maximum absorption, indicated between brackets

[b] values are averages of three separate measurements

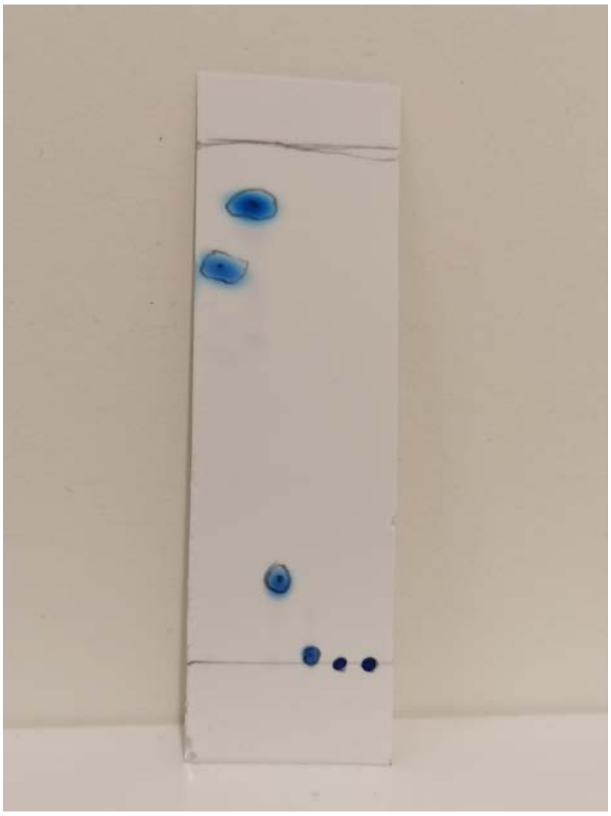

Figure S1. TLC experiment of from left to right: DB-134 (R_f = 0.74), Et-He-DAAQ (R_f = 0.87), Et-DEG-DAAQ (R_f = 0.16), Me-TEG-DAAQ (R_f = 0.02), Me_3N-Et-DAAQ (R_f = 0), and Me_3N-Pr-DAAQ (R_f = 0) on a silica plate, eluted with ethyl acetate/heptane 1/1 .

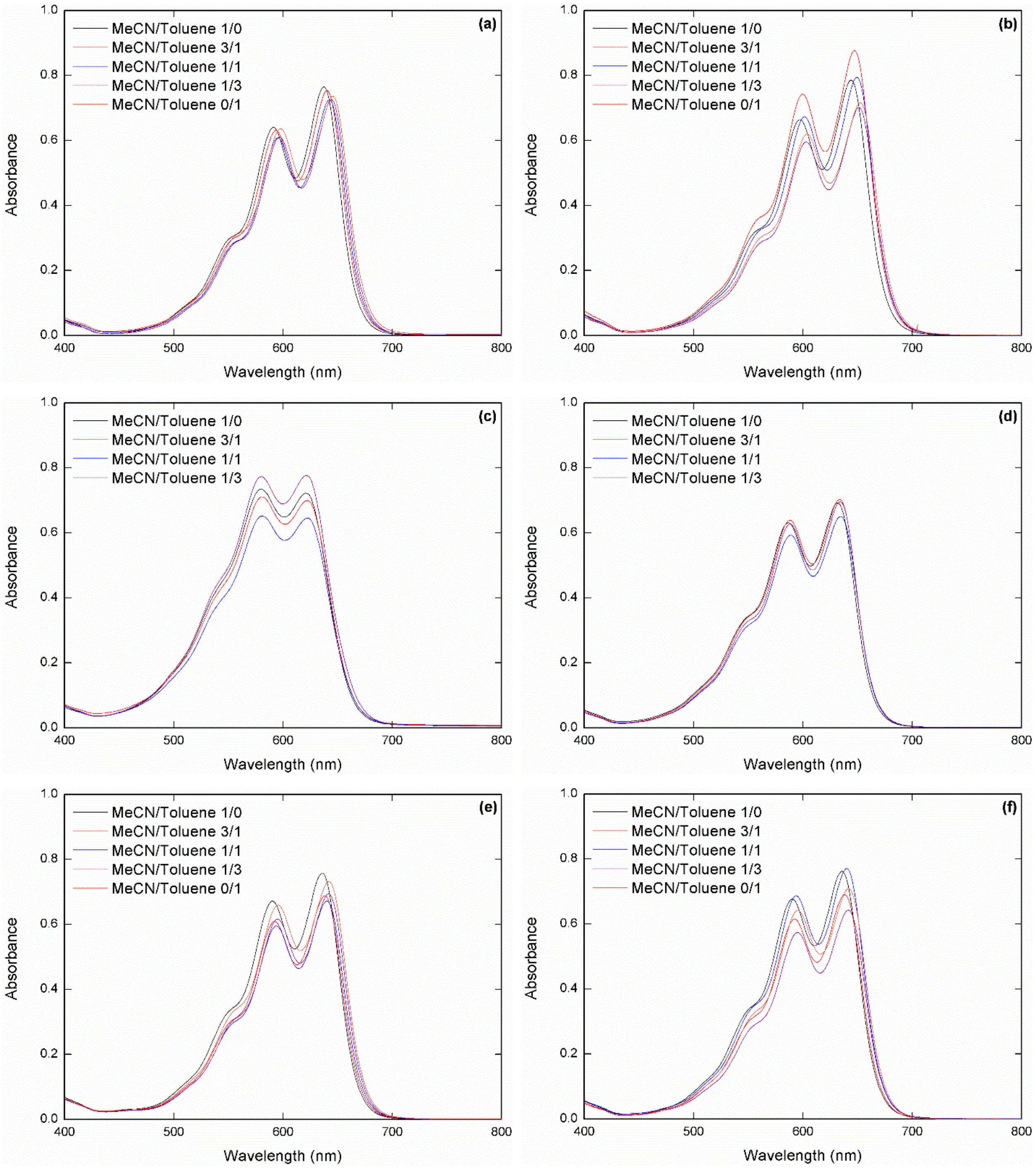

Figure S2. Optical absorption spectra of (a) DB-134, (b) Et-He-DAAQ, (c) Me$_3$N-Et-DAAQ, (d) Me$_3$N-Pr-DAAQ, (e) Et-DEG-DAAQ, and (f) Me-TEG-DAAQ (40–50 µmol L^{-1}) in several MeCN/toluene solvent mixtures.

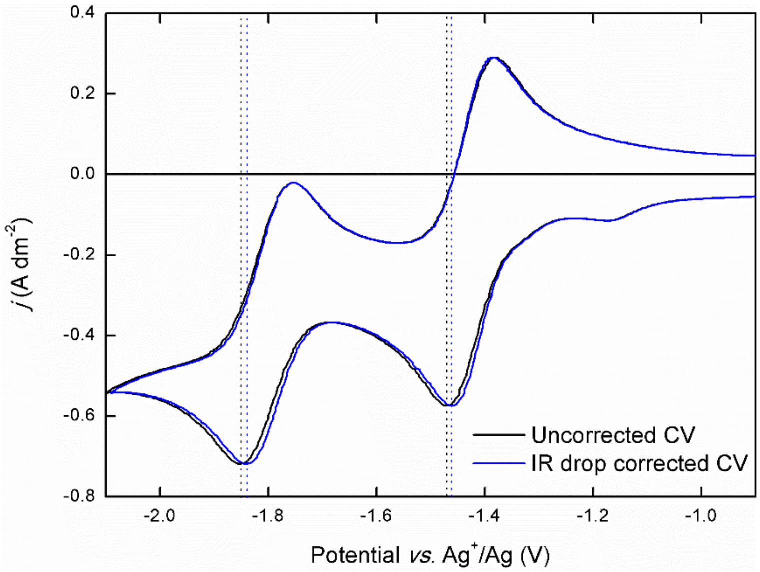

Figure S3. Cyclic voltammograms of 0.01 mol L^{-1} DB-134 in 0.1 mol L^{-1} TEATf$_2$N in acetonitrile, recorded on a platinum disc working electrode (∅ = 0.5 mm) with a scan rate of 50 mV s^{-1}. The black curve was uncorrected for IR drop and the blue curve was corrected (R = 800 Ω). The dotted lines are an aid to visualize the corrected potential shift. The reference electrode was a silver wire suspended in 0.01 mol L^{-1} AgNO$_3$ in acetonitrile. The counter electrode was a piece of platinum-coated silicon wafer with a surface area of approx. 25 mm^2.

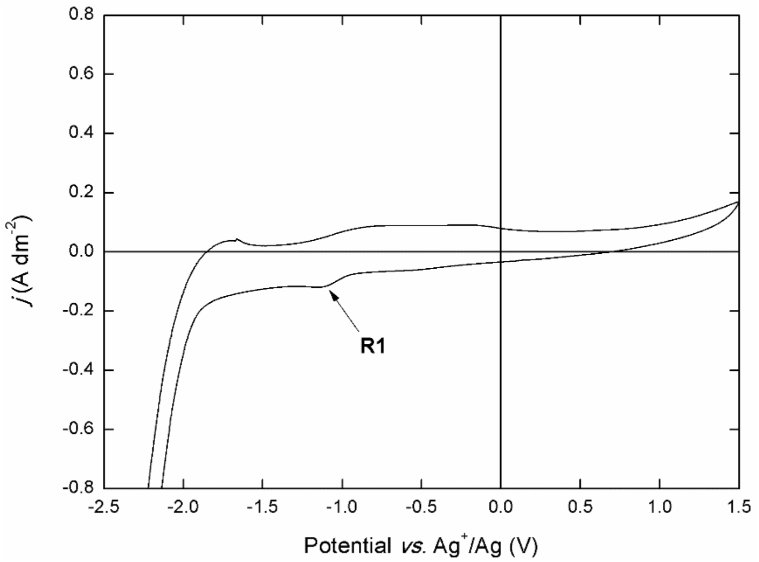

Figure S4. Cyclic voltammogram of 0.1 mol L^{-1} $TEATf_2N$ in acetonitrile, recorded on a platinum disc working electrode (∅ = 0.5 mm) with a scan rate of 50 mV s^{-1}. The reference electrode was a silver wire suspended in 0.01 mol L^{-1} $AgNO_3$ in acetonitrile. The counter electrode was a piece of platinum-coated silicon wafer with a surface area of approx. 25 mm^2.