Electronic Supplementary Information

for

Complementary Interpretation of $E_T(30)$ Polarity Parameters of Ionic Liquids

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Content.

Task A: Effect of the ILs anion on the E_T(30) parameter

1. UV/vis and ^{1}H-NMR spectroscopic investigations of [C_2mim]FAP using TEA

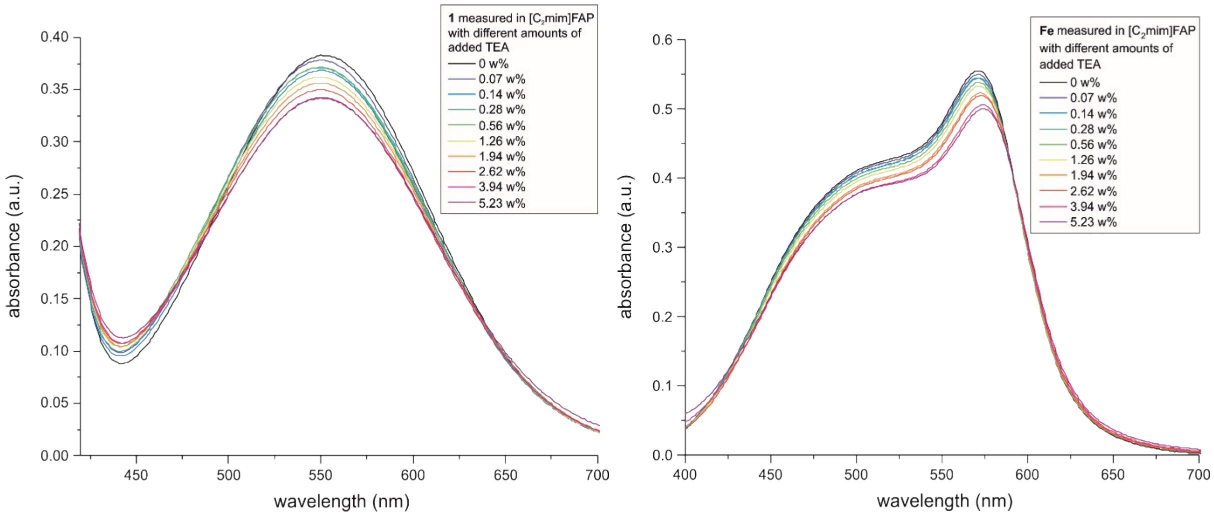


Figure S1. Left: UV/vis spectra of Reichardt's dye **1** in [C_2mim]FAP with different amounts of added TEA, Right: UV/vis spectra of **Fe** in [C_2mim]FAP with different amounts of added TEA.

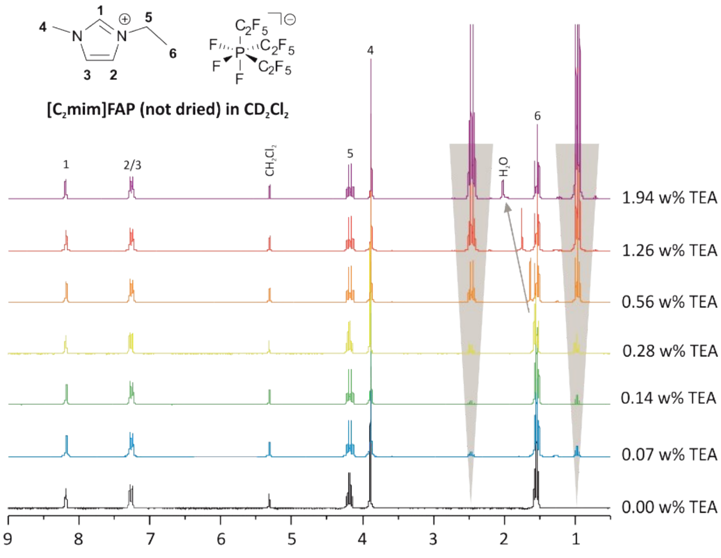


Figure S2. ^{1}H-NMR spectrum of undried [C_2mim]FAP in CD_2Cl_2 with addition of up to 1.94 w% TEA. Signals from TEA are grey shaded, water peaks are marked with a grey arrow.

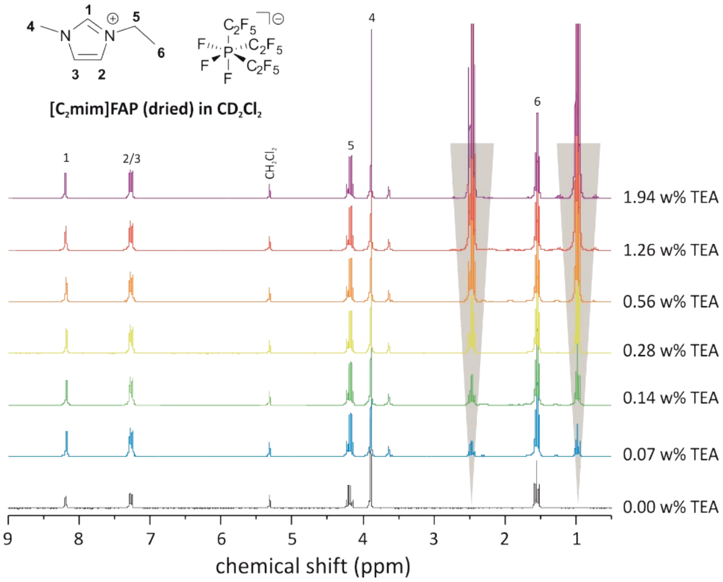


Figure S3. ^{1}H-NMR spectrum of dried [C_2mim]FAP in CD_2Cl_2 with addition of up to 1.94 w% TEA. Signals from TEA are grey shaded.

Task B: Investigation of protic ionic liquids

Table S1. UV/vis absorption maxima of Reichardt's dye **1**, **Fe**, **ABF**, **DMe-ABF**, **Th**, **DENA** and **BMN** in protic ionic liquids.

IL	**1**		**Fe**		**ABF**		**DMe-ABF**		**Th**		**DENA**		**BMN**	
	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})	λ_{max} (nm)	$\tilde{\nu}_{max} \cdot 10^3$ (cm^{-1})
$EtNH_3NO_3$	461	21.7	538	18.6	606	16.5	633	15.8	637	15.7	418	23.9	441	22.7
HO-[C_2mim]NTf_2	471	21.2	545	18.3	577	17.3	645	15.5	628	15.9	416	24.0	436	22.9
HO-[C_2mim]BF_4	459	21.8	544	18.4	592	16.9	635	15.7	633	15.8	417	23.9	438	22.8

1. UV/vis absorption spectra of selected solvatochromic dyes in $EtNH_3NO_3$

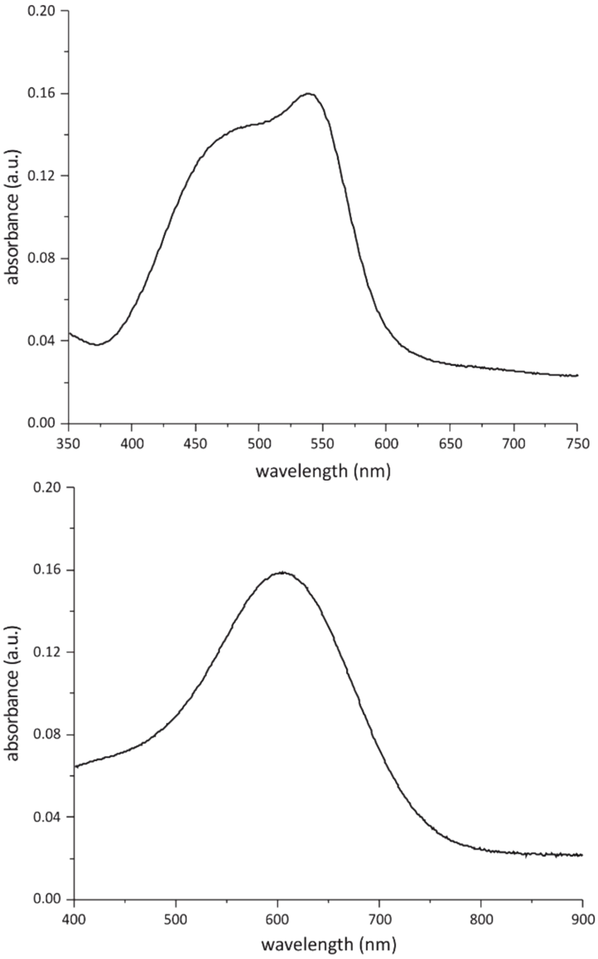


Figure S4. Left: UV/vis absorption spectrum of **Fe** measured in $EtNH_3NO_3$, Right: UV/vis absorption spectrum of **ABF** measured in $EtNH_3NO_3$.

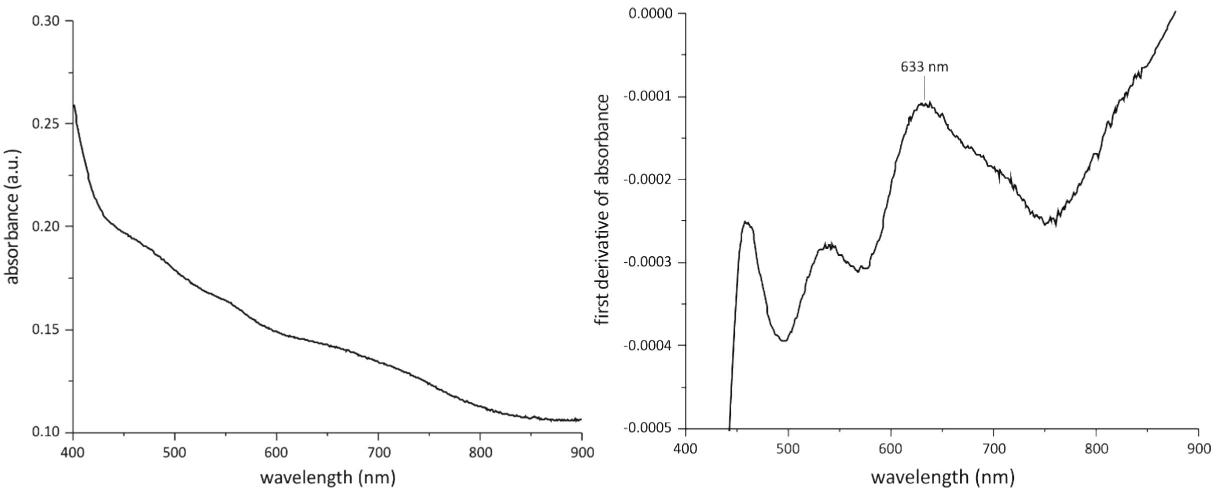


Figure S5. Left: UV/vis absorption spectrum of **DMe-ABF** measured in $EtNH_3NO_3$, Right: first derivation of this UV/vis absorption spectrum.

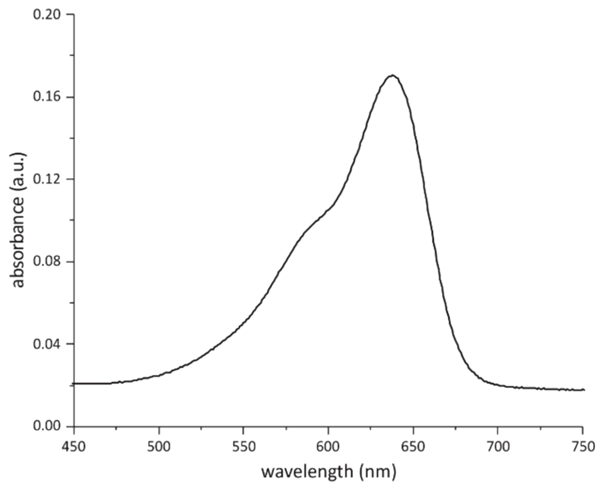
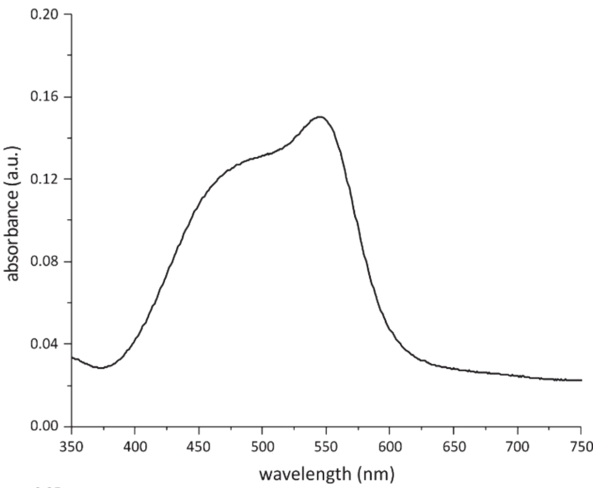


Figure S6. UV/vis absorption spectrum of **Th** measured in $EtNH_3NO_3$.

2. UV/vis absorption spectra of selected solvatochromic dyes in HO-[C_2mim]NTf_2



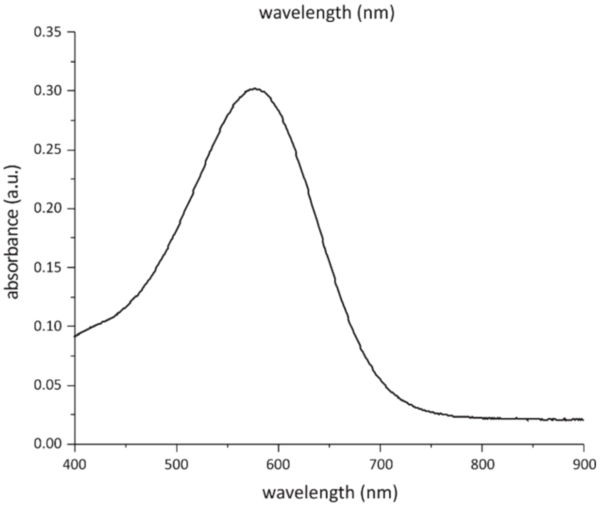


Figure S7. Left: UV/vis absorption spectrum of **Fe** measured in HO-[C_2mim]NTf_2, Right: UV/vis absorption spectrum of **ABF** measured in HO-[C_2mim]NTf_2.

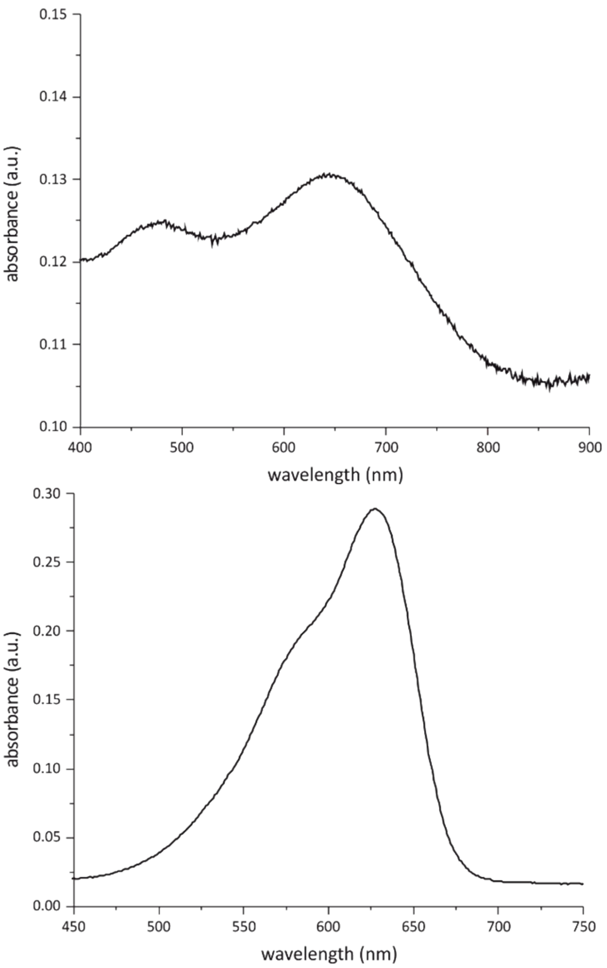


Figure S8. Left: UV/vis absorption spectrum of **DMe-ABF** measured in HO-[C_2mim]NTf_2, Right: UV/vis absorption spectrum of **Th** measured in HO-[C_2mim]NTf_2.

3. UV/vis absorption spectra of selected solvatochromic dyes in HO-[C_2mim]BF_4

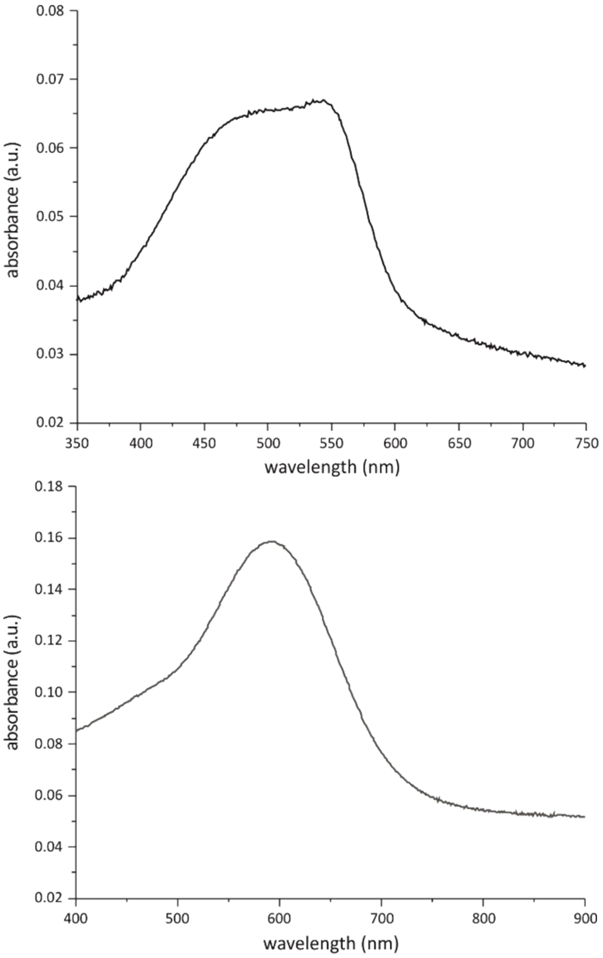


Figure S9. Left: UV/vis absorption spectrum of **Fe** measured in HO-[C_2mim]BF_4, Right: UV/vis absorption spectrum of **ABF** measured in HO-[C_2mim]BF_4.

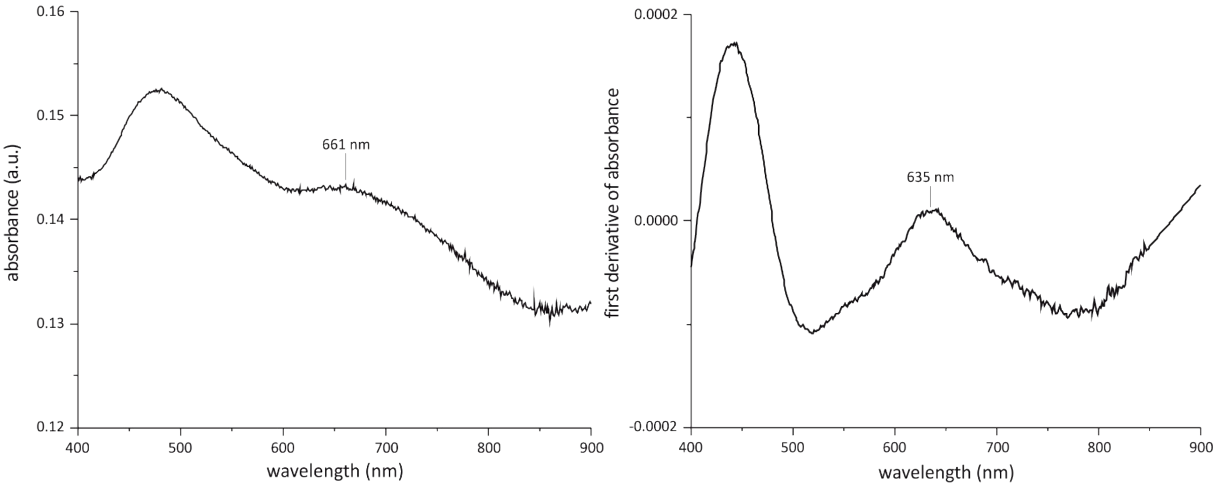


Figure S10. Left: UV/vis absorption spectrum of **DMe-ABF** measured in HO-[C_2mim]BF_4, Right: first derivation of this UV/vis absorption spectrum.

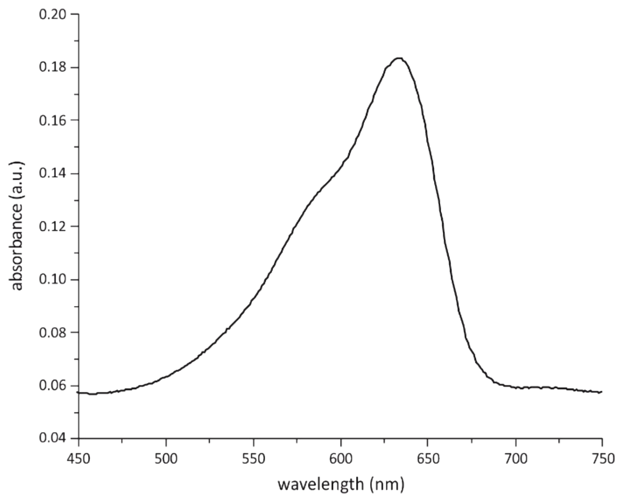


Figure S11. UV/vis absorption spectrum of **Th** measured in HO-[C_2mim]BF_4.

4. UV/vis absorption spectra of Reichardt's dye 1 in various protic ILs with different amounts of added TEA

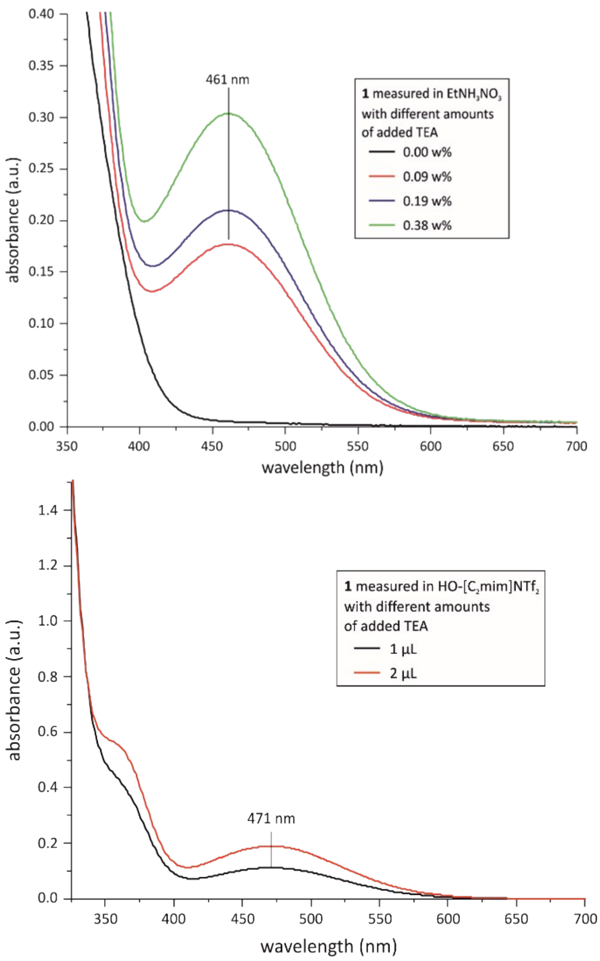


Figure S12. Left: UV/vis spectra of Reichardt's dye (**1**) in $EtNH_3NO_3$ with different amounts of added TEA, Right: UV/vis spectra of Reichardt's dye (**1**) in HO-[C_2mim]NTf_2 with different amounts of added TEA.

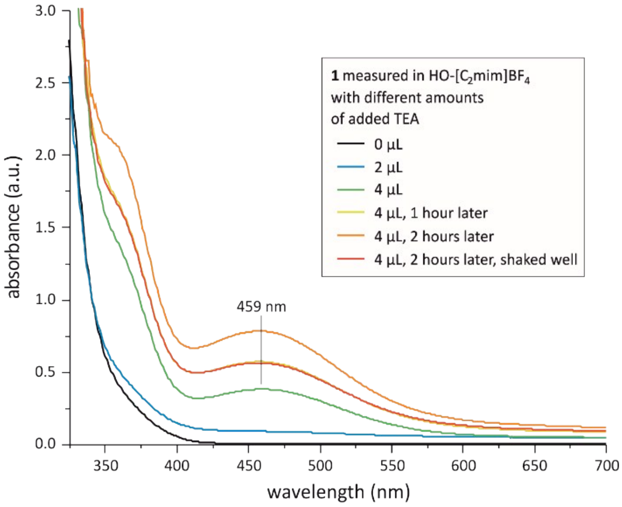


Figure S13. UV/vis spectra of Reichardt's dye (**1**) in HO-[C_2mim]BF_4 with different amounts of added TEA.

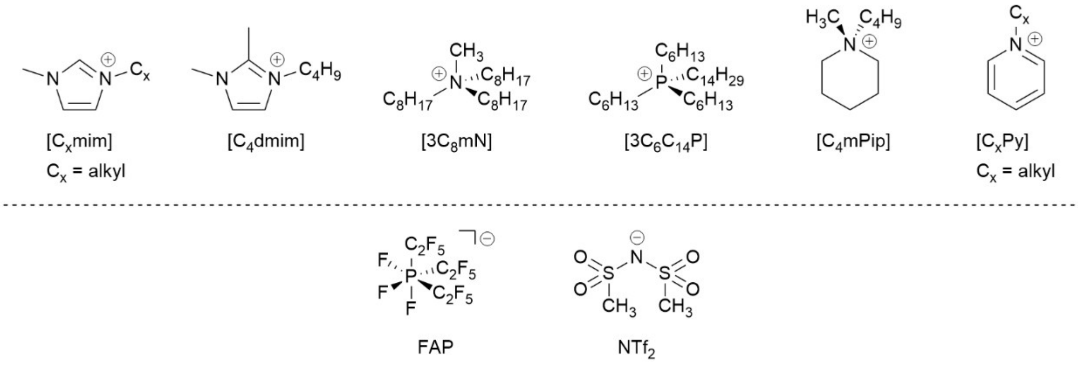
Task C: Correlation of E_T(30) as function of the Kamlet-Taft as well as Catalán solvent parameters of ionic liquids

Table S2. Kamlet-Taft parameters, Catalán parameters and E_T(30) values used for correlation analyses.

IL	α (Fe)[2]	β (ABF)[2]	π^* (Th)[2]	*SA* (Fe)[1]	*SB* (ABF, DMe-ABF)[1]	*SP* (Th, BMN)[1]	*SdP* (Th, BMN)[1]	E_T(30)
[C_1mim]NTf_2	0.60	0.36	0.80	–	–	–	–	52.6[6]
[C_2mim]$N(CN)_2$	0.51	0.61	0.98	–	–	–	–	51.7[10]
[C_2mim]FAP	0.62[a]	0.20	0.71	0.346[a]	0.191	0.755	0.756	51.6[a]
[C_4mim]Cl	0.32	0.95	1.13	0.167	0.869	0.833	1.172	51.0[3]
[C_4mim]Ac	0.36	0.85	1.06	–	–	–	–	48.8[4]
[C_4mim]$MeSO_3$	0.36	0.85	1.04	0.191	0.799	0.837	1.062	49.6[4]
[C_4mim]$OctOSO_3$	0.41	0.77	0.96	0.223	0.691	0.769	1.032	51.9[5]
[C_4mim]$MeOSO_3$	0.39	0.75	1.05	–	–	–	–	51.4[4]
[C_4mim]CF_3CO_2	0.43	0.74	0.90	–	–	–	–	51.1[6]
[C_4mim]NO_3	0.40	0.74	1.04	0.215	0.664	0.868	1.034	51.8[7]
[C_4mim]$N(CN)_2$	0.44	0.64	0.98	–	–	–	–	51.5[4]
[C_4mim]CF_3SO_3	0.50	0.57	0.90	0.271	0.482	0.808	0.934	52.1[4]
[C_4mim]ClO_4	0.50	0.55	0.98	0.271	0.397	0.844	0.994	52.9[8]
[C_4mim]BF_4	0.52	0.55	0.96	0.288	0.466	0.800	1.003	52.4[6]
[C_4mim]PF_6	0.54	0.44	0.90	0.296	0.364	0.808	0.934	52.6[9]
[C_4mim]NTf_2	0.55	0.42	0.83	0.304	0.372	0.793	0867	51.7[6]
[C_4mim]SbF_6	0.58	0.42	0.87	–	–	–	–	52.1[9]
[C_4mim]FAP	0.59	0.25	0.78	0.329	0.233	0.747	0.829	51.5[a]
[C_6mim]Cl	0.31	0.97	1.06	0.159	0.996	0.787	1.139	50.2[5]
[C_6mim]Br	0.36	0.88	1.09	0.191	0.786	0.861	1.101	50.6[5]
[C_6mim]$N(CN)_2$	0.44	0.69	1.00	0.239	0.596	0.866	0.990	51.0[5]
[C_6mim]CF_3SO_3	0.47	0.61	0.92	0.255	0.515	0.798	0.959	52.7[11]
[C_6mim]BF_4	0.44	0.60	0.96	0.239	0.495	0.800	1.003	53.6[9]
[C_6mim]PF_6	0.51	0.50	0.93	0.279	0.463	0.820	0.954	52.3[12]
[C_6mim]NTf_2	0.51	0.44	0.86	–	–	–	–	51.7[6]
[C_8mim]Cl	0.31	0.98	1.03	0.159	1.001	0.784	1.096	48.5[12]
[C_8mim]BF_4	0.45	0.63	0.93	0.247	0.525	0.788	0.983	51.9[5]
[C_8mim]PF_6	0.52	0.53	0.92	0.288	0.392	0.798	0.959	50.1[12]
[C_8mim]NTf_2	0.48	0.47	0.86	0.263	0.373	0.774	0.918	51.4[11]
[C_{10}mim]NTf_2	0.48	0.49	086	0.263	0.396	0.774	0.918	51.0[13]
[$3C_6C_{14}P$]NTf_2	0.36	0.58	087	0.191	0.447	0.827	0.884	46.4[14]
[C_4mPip]NTf_2	0.43	0.42	0.82	–	–	–	–	49.4[15]
[C_4Py]NTf_2	0.51	0.42	0.85	0.279	0.339	0.815	0.863	48.7[17]
[C_6Py]NTf_2	0.50	0.44	0.86	0.271	0.379	0.805	0.888	50.1[16]
[C_4dmim]BF_4	0.41	0.57	1.00	0.215	0.452	0.834	1.019	49.7[9]
[C_4dmim]NTf_2	0.44	0.44	0.86	0.239	0.371	0.774	0.918	50.1[6]

[3C$_8$mN]NTf$_2$	0.39	0.55	0.87	0.207	0.396	0.827	0.884	46.2[14]

[a] Data was determined experimentally.



Scheme S1. Cations used within this study and the corresponding abbreviations. Anions are given as chemical formulas, except for FAP and NTf$_2$.

1. Correlation analyses of E_T(30) with *SA* and *SdP*

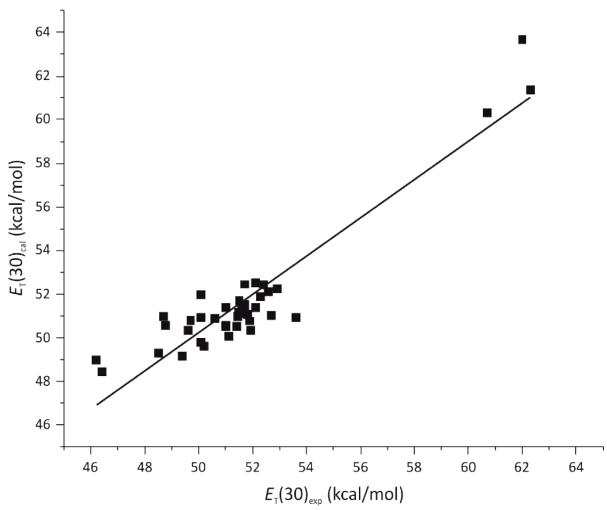


Figure S14. Correlation of the *via* eq. 7 (main text) calculated E_T(30) parameter of ILs *versus* the measured value as function (data for correlation analyses are taken from Table S2).

2. Correlation analyses of E_T(30) with *SA*, *SB* and *SdP*

E_T(30) was correlated with *SA*, *SB* and *SdP*. A smaller significance (F = 96, eq. S1) compared to the correlation with *SA* and *SdP* (F = 125, eq. 9) was obtained.

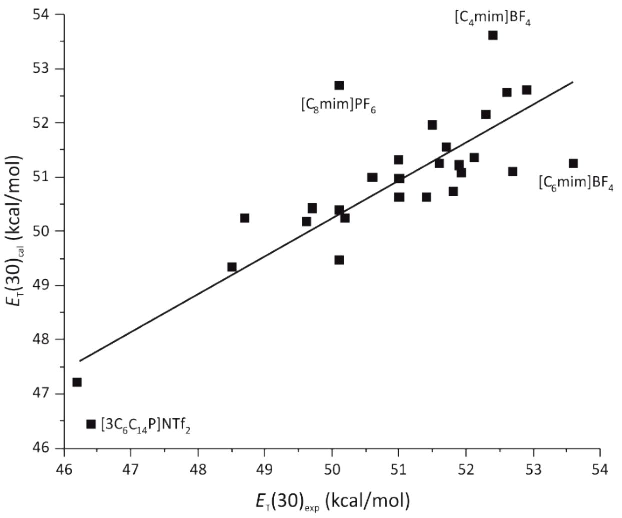


Figure S15. Correlation of the calculated E_T(30) parameter of ILs *via* eq. S1 *versus* the measured value (data for correlation analyses are taken from Table S2).

$$E_T(30) = 48.32\ SA + 0.016\ SB + 20.92\ SdP + 18.71 \qquad \text{(S1)}$$
$$n = 28,\ r = 0.812,\ f = 2.00\cdot10^{-6}$$

3. Evaluation of Catalán solvent parameter *SdP* of ILs regarding their correlation with molar volume properties

Table S3. E_T(30) and *SA* values used for calculating SdP_{cal} *via* eq. 9 (main text) and V_m and *N* of the respective IL.

IL	E_T(30)	*SA*[1]	SdP_{cal}	V_m (cm³/mol)[18,19]	*N* (mol/cm³)
[C_1mim]NTf_2	52.6[6]	0.279[a]	0.889	241.5	0.00414
[C_2mim]$N(CN)_2$	51.7[10]	0.279[a]	0.956	160.9	0.00622
[C_2mim]FAP	51.6[a]	0.346[b]	–	–	–
[C_4mim]Cl	51.0[3]	0.167	1.165	161.7	0.00618
[C_4mim]Ac	48.8[4]	0.191[a]	0.947	185.9	0.00538
[C_4mim]$MeSO_3$	49.6[4]	0.191	1.005	188.4	0.00531
[C_4mim]$OctOSO_3$	51.9[5]	0.223	1.104	326.8	0.00306
[C_4mim]$MeOSO_3$	51.4[4]	0.208[a]	1.099	207.6	0.00482
[C_4mim]CF_3CO_2	51.1[6]	–	–	–	–
[C_4mim]NO_3	51.8[7]	0.215	1.109	174.5	0.00573
[C_4mim]$N(CN)_2$	51.5[4]	0.238[a]	1.036	193.9	0.00516
[C_4mim]CF_3SO_3	52.1[4]	0.271	1.004	211.7	0.00472
[C_4mim]ClO_4	52.9[8]	0.271	1.063	190.5	0.00525
[C_4mim]BF_4	52.4[6]	0.288	0.988	188.1	0.00532
[C_4mim]PF_6	52.6[9]	0.296	0.984	208.3	0.0048
[C_4mim]NTf_2	51.7[6]	0.304	0.899	291.8	0.00343
[C_4mim]SbF_6	52.1[9]	–	–	–	–
[C_4mim]FAP	51.5[a]	0.329	0.827	358.4	0.00279
[C_6mim]Cl	50.2[5]	0.159	1.119	194.9	0.00513
[C_6mim]Br	50.6[5]	0.191	1.078	201.1	0.00497
[C_6mim]$N(CN)_2$	51.0[5]	0.239	1.000	224.3	0.00446
[C_6mim]CF_3SO_3	52.7[11]	0.255	1.086	255.1	0.00392
[C_6mim]BF_4	53.6[9]	0.239	1.190	221.9	0.00451
[C_6mim]PF_6	52.3[12]	0.279	1.000	241.5	0.00414
[C_6mim]NTf_2	51.7[6]	0.279[a]	0.956	326.4	0.00306
[C_8mim]Cl	48.5[12]	0.159	1.001	228.4	0.00438
[C_8mim]BF_4	51.9[5]	0.247	1.039	254.2	0.00393
[C_8mim]PF_6	50.1[12]	0.288	0.900	304.1	0.00329

[C_8mim]NTf_2	51.4[11]	0.263	0.943	360.1	0.00278
[C_{10}mim]NTf_2	51.0[13]	0.263	0.943	395.2	0.00253
[3C_6C_{14}P]NTf_2	46.4[14]	0.191	0.771	716.3	0.0014
[C_4mPip]NTf_2	49.4[15]	–	–	–	–
[C_4Py]NTf_2	48.7[17]	0.279	0.737	287.7	0.00348
[C_6Py]NTf_2	50.1[16]	0.271	0.858	318.8	0.00314
[C_4dmim]BF_4	49.7[9]	0.215	–	–	–
[C_4dmim]NTf_2	50.1[6]	0.239	–	–	–
[3C_8mN]NTf_2	46.2[14]	0.207	0.720	599.5	0.00167

[a] *SA* values were calculated from the $\tilde{\nu}_{max}$ values from ref. 2 using eq. 23 from the main text.
[b] Data was determined experimentally.

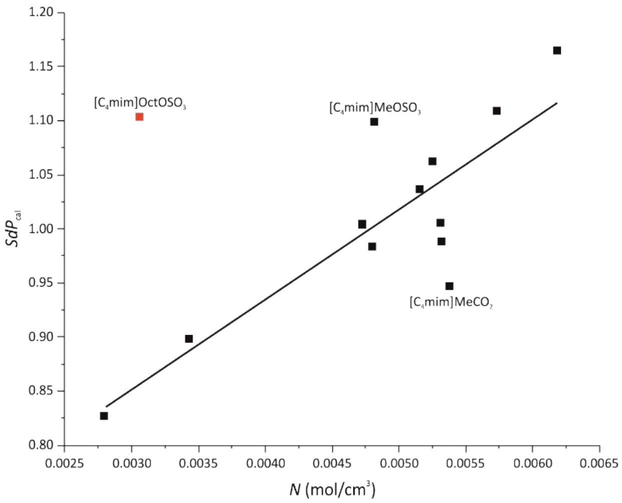


Figure S16. *SdP* calculated *via* eq. 9 of [C_4mim] ILs as function of the molar concentration *N* of the IL (data are taken from Table S3).

$$SdP_{\mathrm{cal}} = 71.465\ N + 0.658 \qquad \text{(S2)}$$

$n = 12$, $r = 0.815$, $f = 7.54 \cdot 10^{-4}$

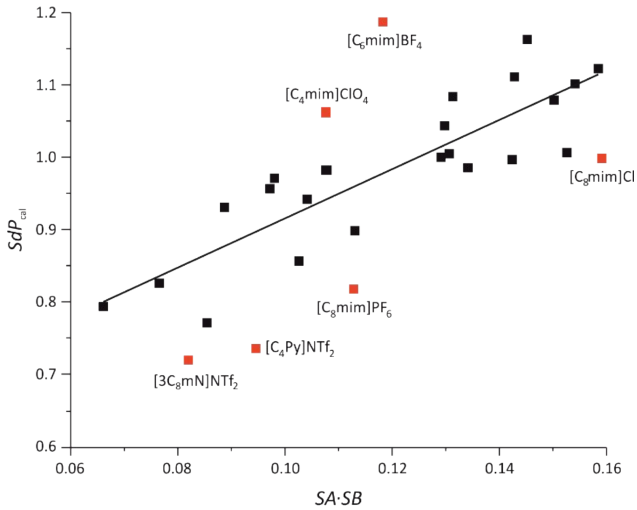


Figure S17. Correlation of *SdP* of ILs as function of the product *SA*·*SB*. Long alkyl chain IL are marked.

4. Correlation of $E_T(30)$ and *SA* with molar concentration of the IL

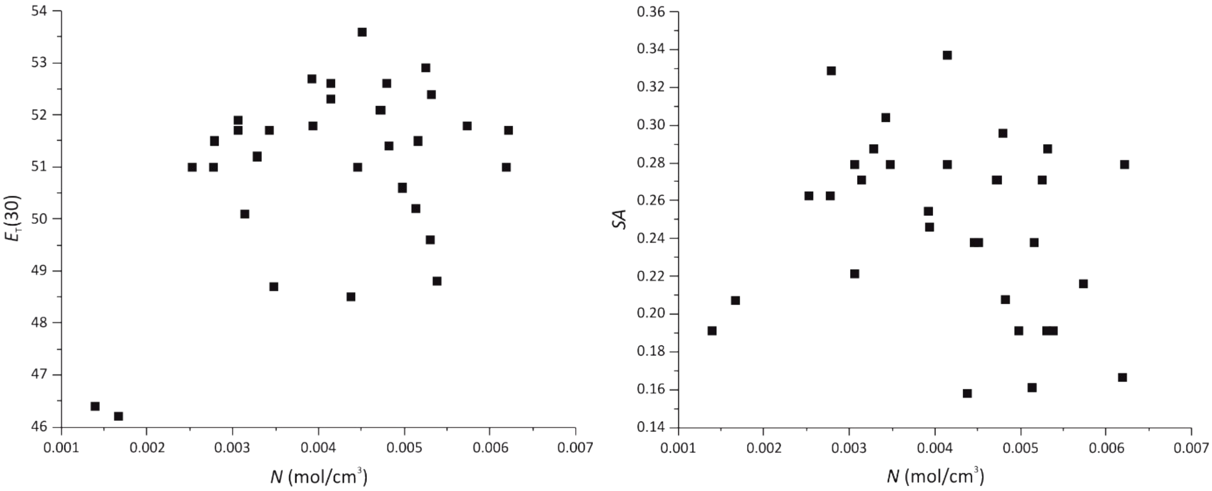


Figure S18. Left: $E_T(30)$ values of all IL from Table S3 as function of *N*, Right: *SA* values of all IL in Table S3 as function of *N*.

References of the SI part

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