Supplementary Material (ESI) for *New Journal of Chemistry*

Supporting information of

New aspects on the hydrogen bond donor (HBD) strength of 1-butyl-3-methylimidazolium room temperature ionic liquids

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Supporting Information

EPR Spectra

Fig. 1: EPR spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in nitromethane.

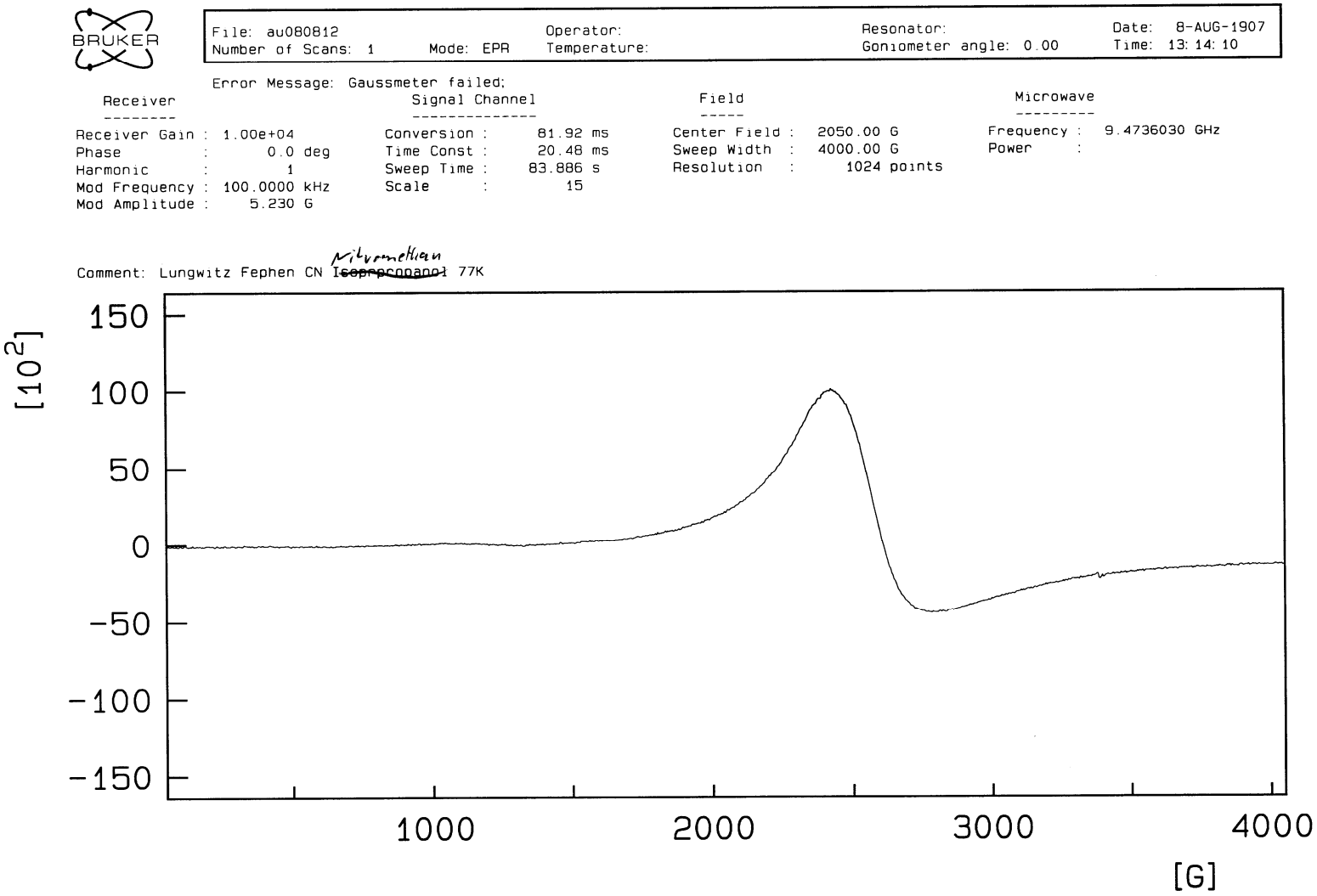


Fig. 2: EPR spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in acetonitrile.

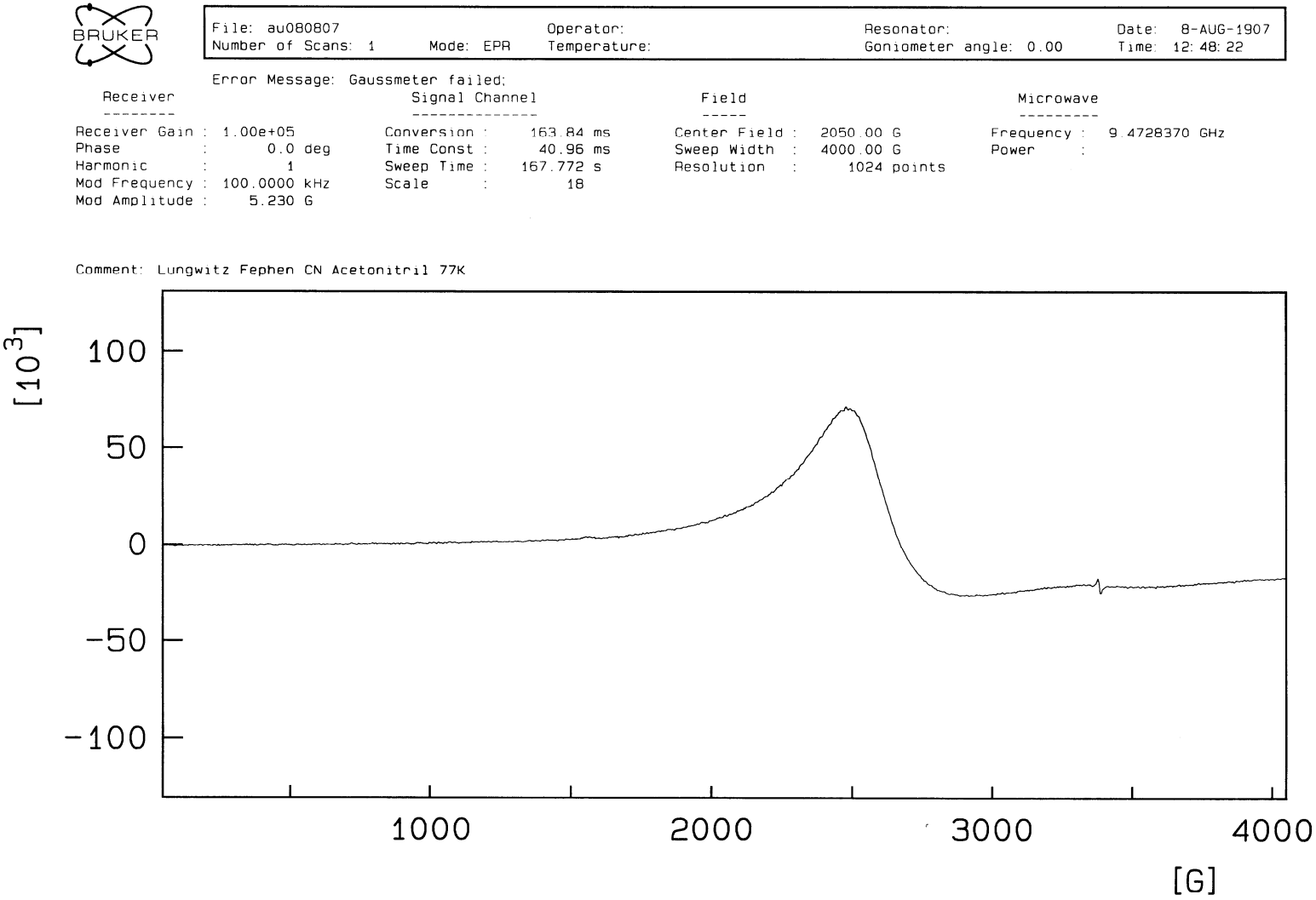


Fig. 3: EPR spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in 2-propanol.

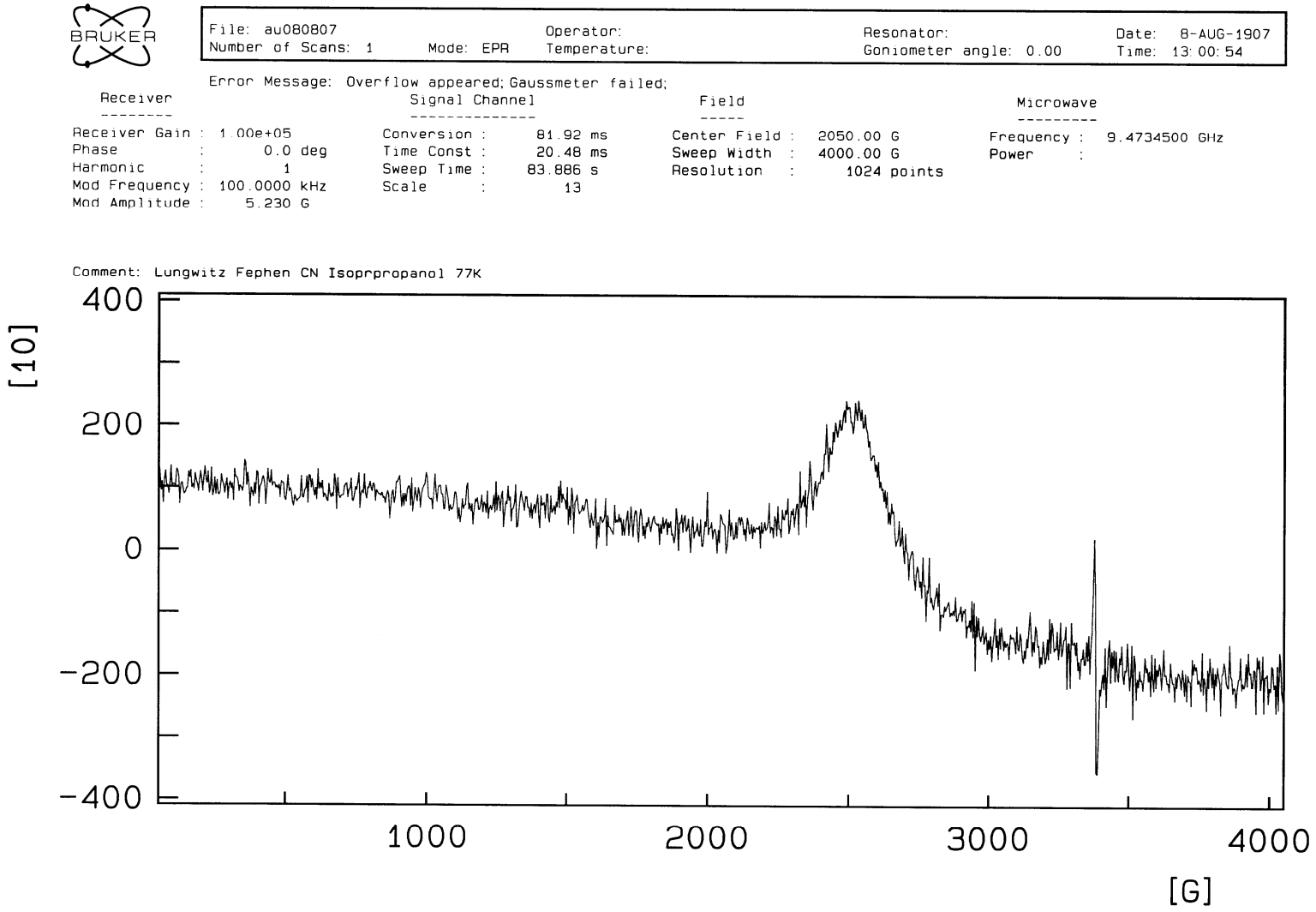
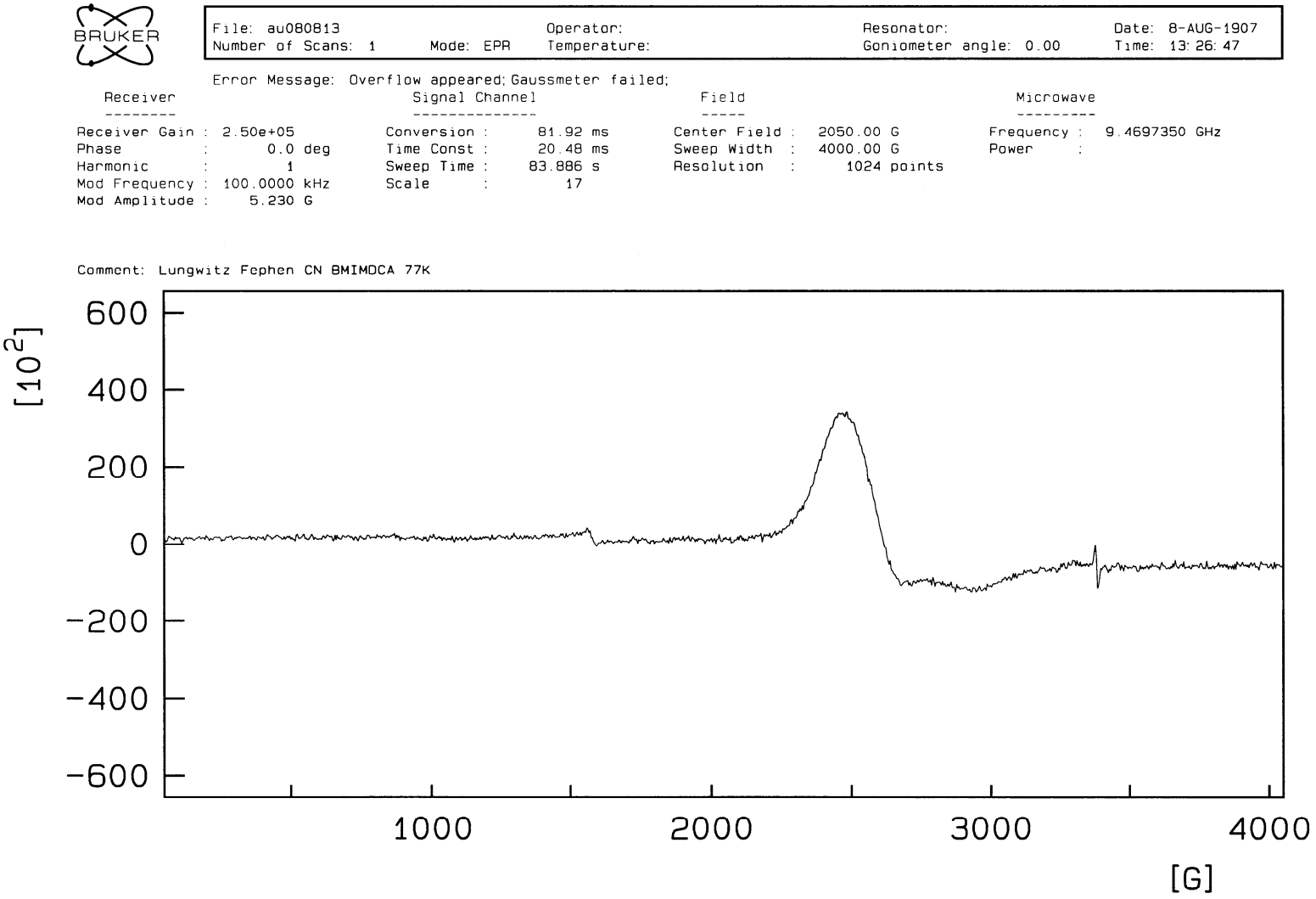


Fig. 4: EPR spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in $[Bmim]N(CN)_2$.



UV/Vis absorption spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in nitromethane and acetonitrile

Fig. 5: UV/Vis absorption spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in nitromethane.

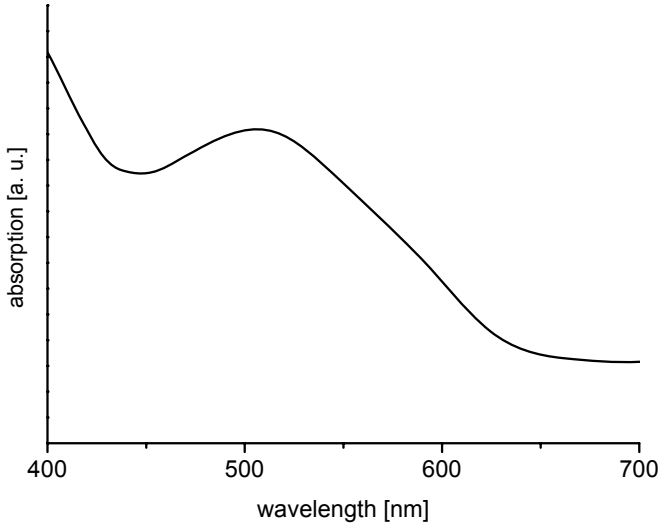


Fig. 6: UV/Vis absorption spectra of $[Fe(phen)_2(CN)_2]ClO_4$ in acetonitrile.

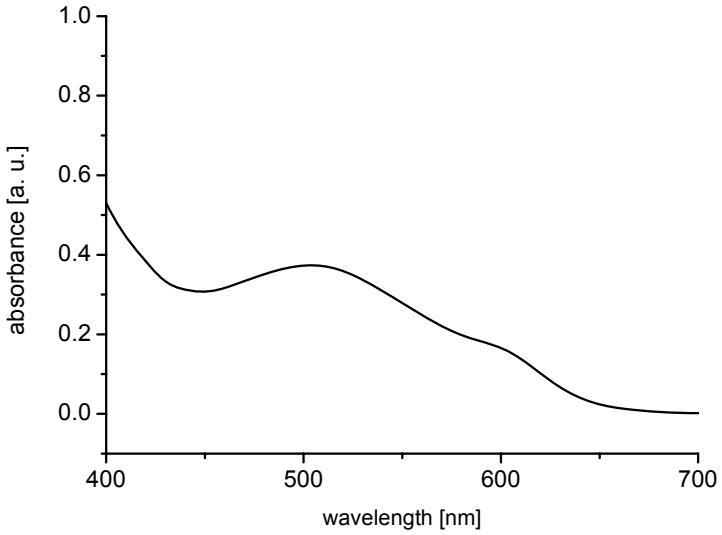


Table 1: UV/Vis absorption maxima of $Fe(phen)_2(CN)_2$ in well behaved solvents.

solvent	λ_{max} (nm)	$\tilde{\upsilon}_{max}$ ($10^{-3}cm^{-1}$)
tetramethylurea	628	15.92
acetone	622	16.08
pyridine	621	16.10
dimethylacetamide	621	16.10
benzonitrile	613	16.31
dimethyl sulfoxide	606	16.50
dichloromethane	602	16.61
chloroform	600	16.67
2-propanol	571	17.51
1-butanol	566	17.67
1-propanol	566	17.67
methylformamide	564	17.73
ethanol	561	17.82
methanol	549	18.21
formamide	547	18.28
ethylene glycol	544	18.38
2,2,2-trifluoroethanol	519	19.27
water	513	19.49
1,1,1,3,3,3-hexafluoropropan-2-ol	502	19.92

Table 2: UV/Vis absorption maxima of $[Fe(phen)_2(CN)_2]ClO_4$ in well behaved solvents.

solvent	λ_{max} (nm)	$\tilde{\upsilon}_{max}$ ($10^{-3}cm^{-1}$)
tetramethylurea	629	15.90
acetone	619	16.16
pyridine	622	16.08
dimethylacetamide	620	16.13
benzonitrile	611	16.37
dimethyl sulfoxide	603	16.58
dichloromethane	598	16.72
chloroform	598	16.72
2-propanol	573	17.45
1-butanol	569	17.57
1-propanol	566	17.67
methylformamide	563	17.76
ethanol	561	17.82
methanol	549	18.21
formamide	546	18.32
ethylene glycol	541	18.48
2,2,2-trifluoroethanol	518	19.30
water	512	19.53
1,1,1,3,3,3-hexafluoropropan-2-ol	505	19.80

Table 3: UV/Vis absorption maxima of $[Fe(phen)_2(CN)_2]ClO_4$ in 1-butyl-3-methylimidazolium ionic liquids.

anion	λ_{max} (nm)	$\tilde{\upsilon}_{max}$ ($10^{-3}cm^{-1}$)
Cl^-	593	16.86 [a]
Br^-	590	16.95 [a]
CH_3COO^-	590	16.95
$CH_3SO_3^-$	590	16.95 [a]
NO_2^-	589	16.98
$CH_3OSO_3^-$	588	17.01
NO_3^-	587	17.04
$OctOSO_3^-$	586	17.06
I^-	586	17.06
CF_3COO^-	585	17.09
SCN^-	585	17.09
$N(CN)_2^-$	584	17.12
$CF_3SO_3^-$	580	17.24
BF_4^-	578	17.30
PF_6^-	577	17.33
$N(SO_2CF_3)_2^-$	576	17.36

[a] measured in the melt

Procedure and results of concentration dependent UV/Vis measurements

Concentration dependent measurements of $[Fe(phen)_2(CN)_2]ClO_4$ in 1-butanol, ethanol, methylformamide, [Bmim]$N(CN)_2$ and [Bmim]Ntf_2

0.10, 0.32 and 0.61 mg of $[Fe(phen)_2(CN)_2]ClO_4$ were dissolved in the respective organic solvent or ionic liquid and stirred for one hour. UV/Vis absorption spectra were recorded using precision quartz cells with a light path of 10 or 2 mm under exclusion of moisture.

Fig. 7: UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$, dissolved in 1-butanol with 3 different concentration.

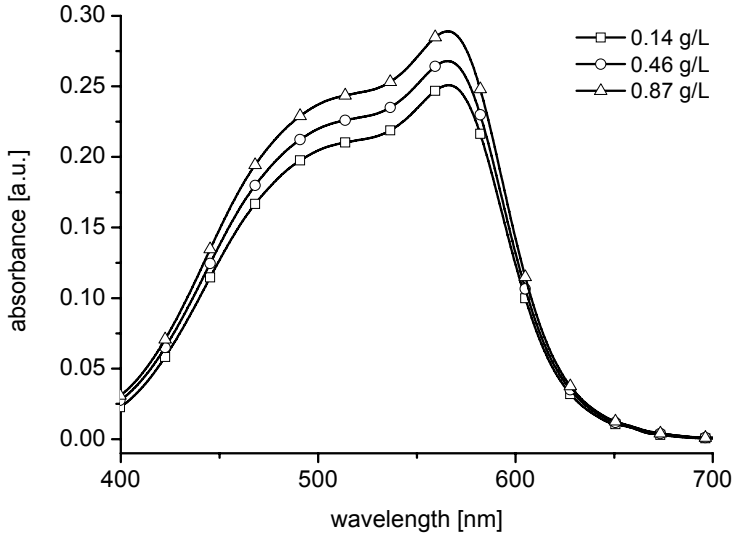


Fig. 8: UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$, dissolved in ethanol with 3 different concentration.

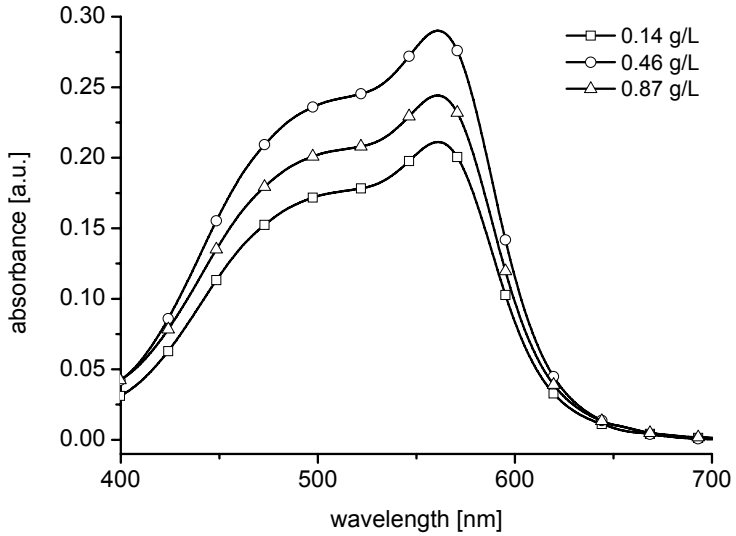


Fig. 9: UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$, dissolved in methylformamide with 3 different concentration.

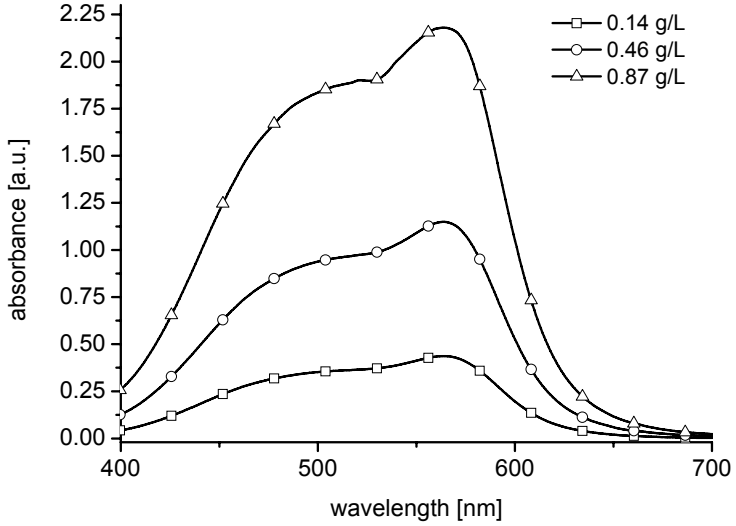


Fig. 10: UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$ dissolved in $[Bmim]N(CN)_2$ with 3 different concentration.

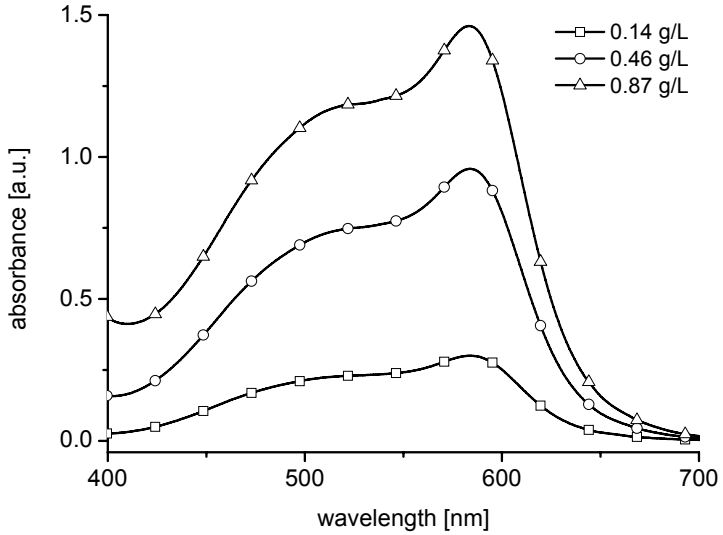
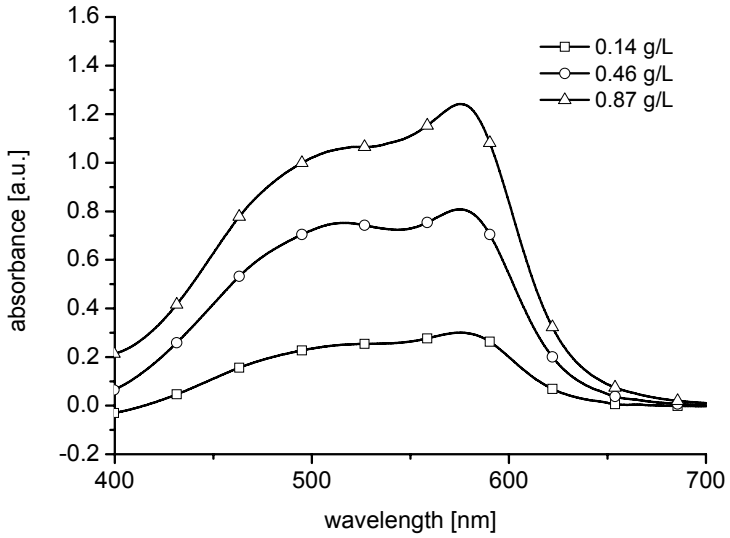


Fig. 11: UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$ dissolved in $[Bmim]Ntf_2$ with 3 different concentration.



Determination of α for [C_6mim]Cl by an UV/Vis titration

A stock solution of 1.00 g 1-hexyl-3-methylimidazolium chloride in 2.00 g dichloro-methane was prepared. 1.3 mL of the solution was added stepwise to 0.20 mL of a saturated $Fe(phen)_2(CN)_2$/dichloromethane solution. The UV/Vis spectra were recorded after each addition step.

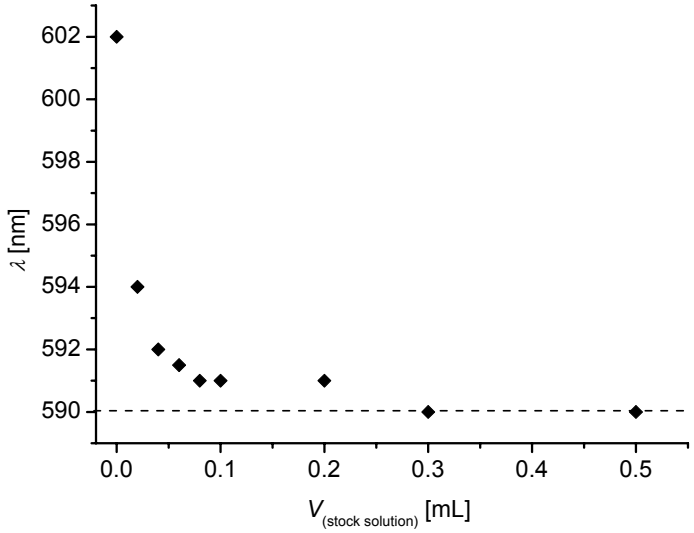


Figure 12: Plot of the measured UV/Vis absorption maxima against the added volume of the stock solution.

A UV/Vis absorption maxima of 590 nm was reached and an α value of 0.31 was calculated according to the following equation (S. Spange, S. Prause, E. Vilsmeier and W. Thiel, *J. Phys. Chem. B*, 2005, **109**, 7280.):

$$\alpha = -7.49 + 0.46\tilde{\upsilon}_{\max} Fe(phen)_2(CN)_2 (10^{-3} cm^{-1})$$

The same α value of 0.31 was determined using $[Fe(phen)_2(CN)_2]ClO_4$ as the solvatochromic probe.