Supporting Information

Optical basicity of ionic liquids

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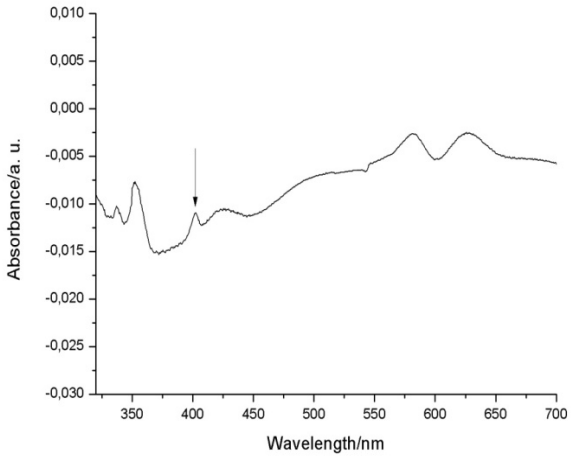
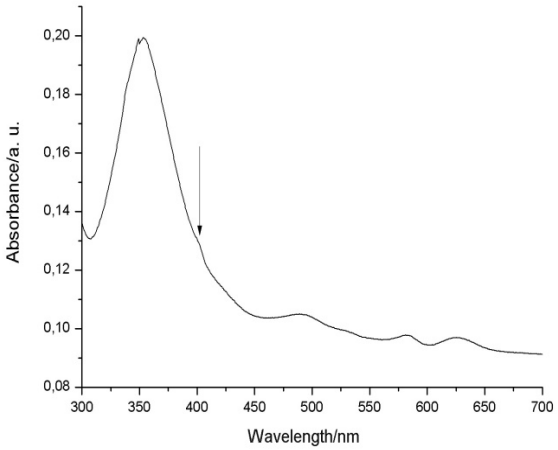
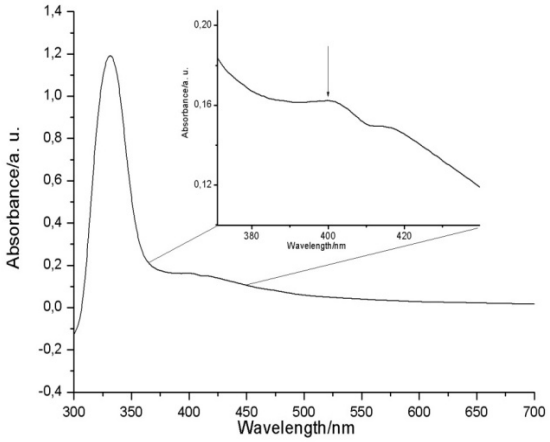
All shown spectra are difference spectra between the neat and $Mn(NTf_2)$ doped ionic liquid.



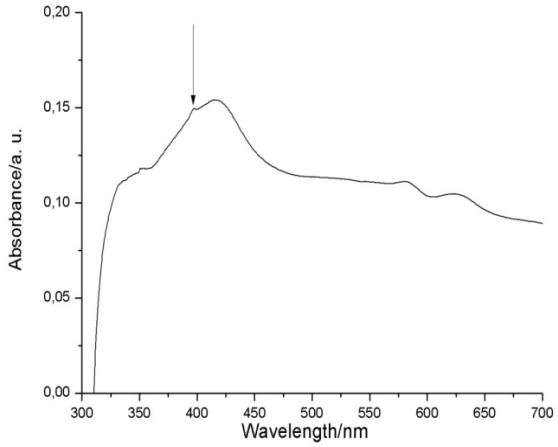
ESI-Fig. 1 UV/Vis spectrum of $C_4C_1mimNTf_2$ doped with $Mn(NTf_2)_2$.



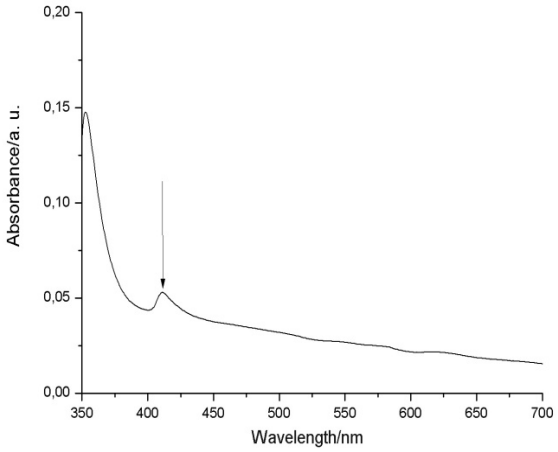
ESI-Fig. 2 UV/Vis spectrum of $C_4mimNTf_2$ doped with $Mn(NTf_2)_2$.



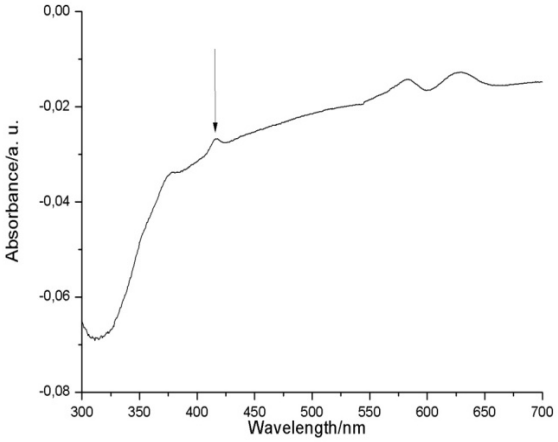
ESI-Fig. 3 UV/Vis spectrum of $C_4mimClO_4$ doped with $Mn(NTf_2)_2$.



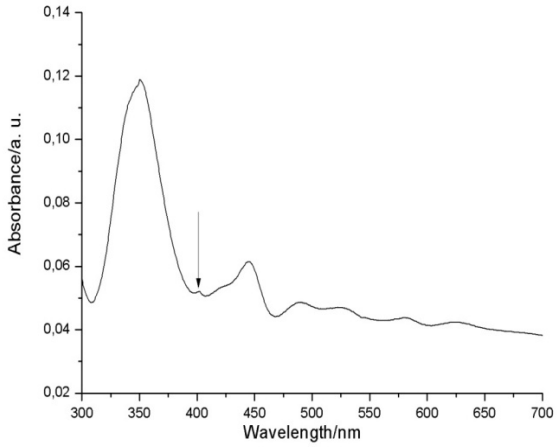
ESI-Fig. 4 UV/Vis spectrum of $C_6mpyridBF_4$ doped with $Mn(NTf_2)_2$.



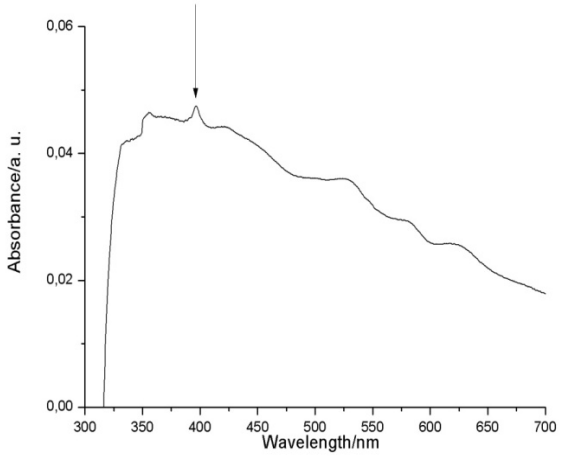
ESI-Fig. 5 UV/Vis spectrum of C_4mimNO_3 doped with $Mn(NTf_2)_2$.



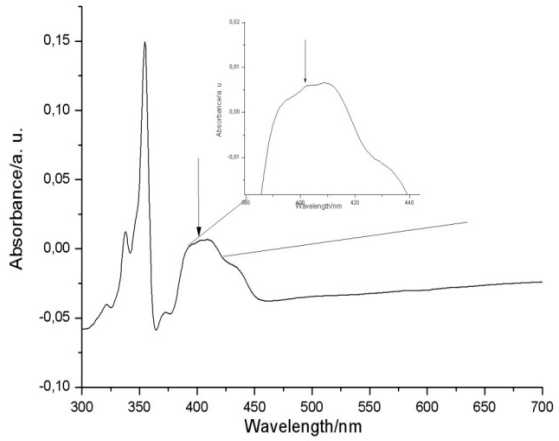
ESI-Fig. 6 UV/Vis spectrum of $C_4mimTFA$ doped with $Mn(NTf_2)_2$.



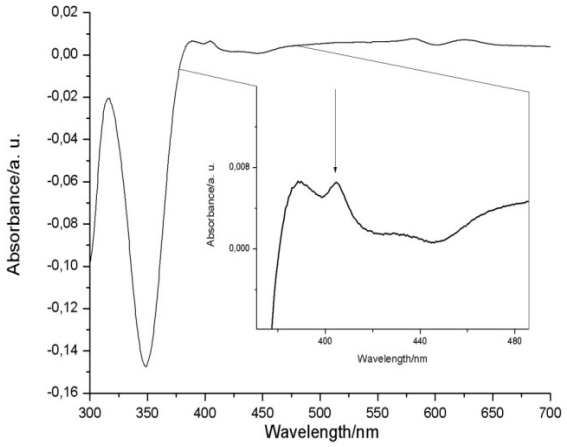
ESI-Fig. 7 UV/Vis spectrum of $C_4mpyrNTf_2$ doped with $Mn(NTf_2)_2$.



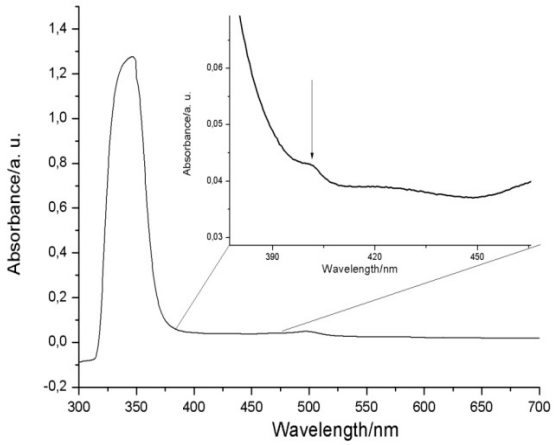
ESI-Fig. 8 UV/Vis spectrum of $C_4pyridBF_4$ doped with $Mn(NTf_2)_2$.



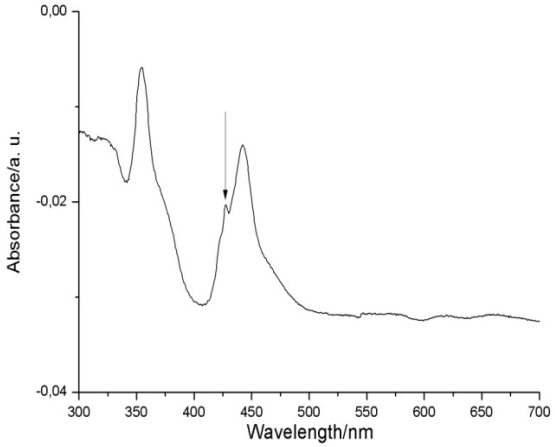
ESI-Fig. 9 UV/Vis spectrum of $C_{10}mimNTf_2$ doped with $Mn(NTf_2)_2$.



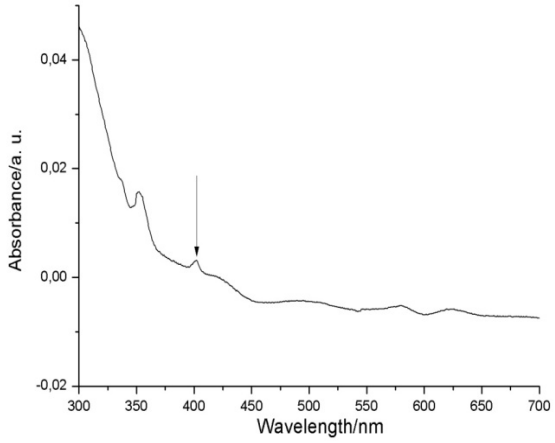
ESI-Fig. 10 UV/Vis spectrum of $CNC_2emimNTf_2$ doped with $Mn(NTf_2)_2$.



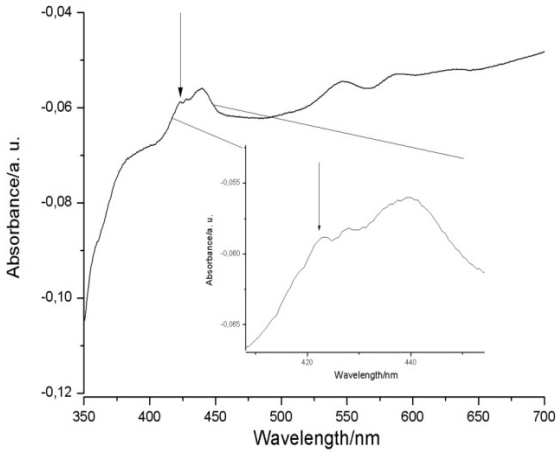
ESI-Fig. 11 UV/Vis spectrum of C_2mimNTf_2 doped with $Mn(NTf_2)_2$.



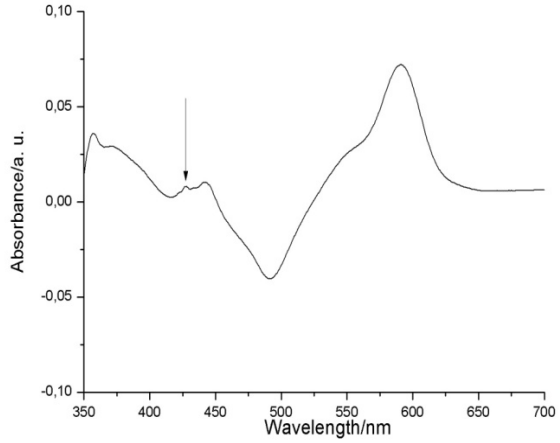
ESI-Fig. 12 UV/Vis spectrum of C_2mim$EtSO_4$ doped with $Mn(NTf_2)_2$.



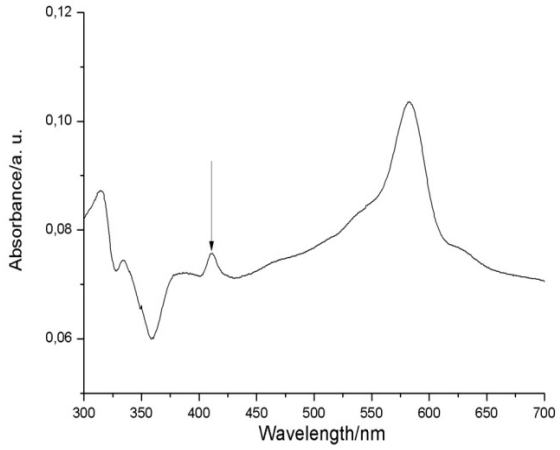
ESI-Fig. 13 UV/Vis spectrum of C_2mim$MeSO_3$ doped with $Mn(NTf_2)_2$.



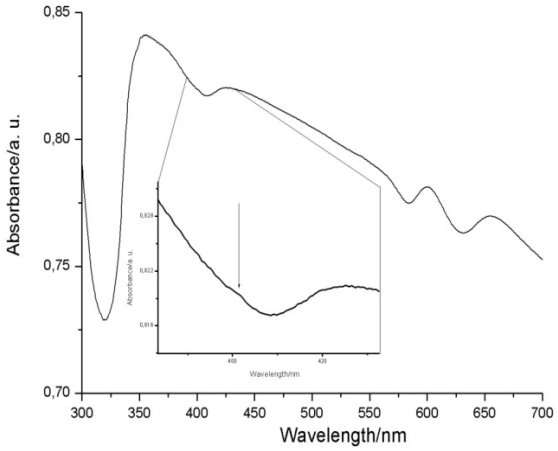
ESI-Fig. 14 UV/Vis spectrum of C_2mimOTos doped with $Mn(NTf_2)_2$.



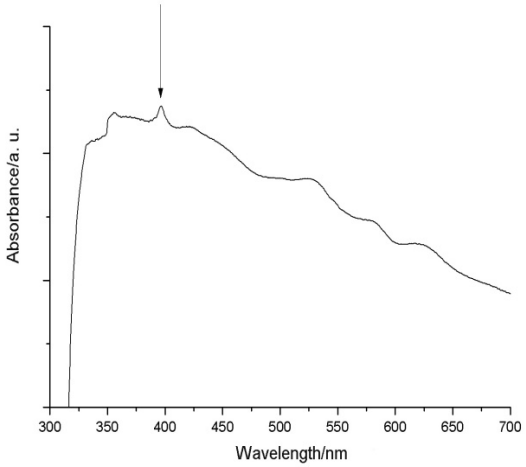
ESI-Fig. 15 UV/Vis spectrum of C_4mpyridEtSO_4 doped with $Mn(NTf_2)_2$.



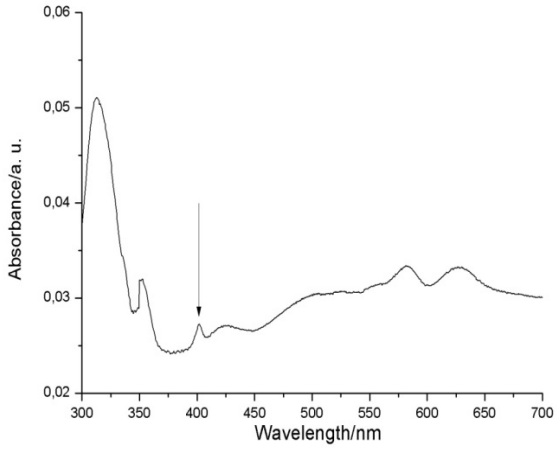
ESI-Fig. 16 UV/Vis spectrum of Et_3NvalCN NTf_2 doped with $Mn(NTf_2)_2$.



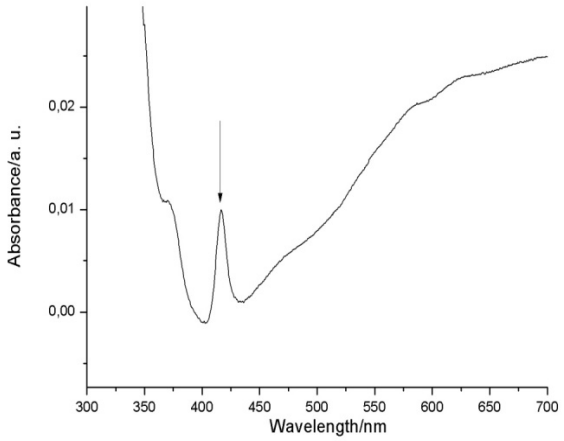
ESI-Fig. 17 UV/Vis spectrum of C_6mimNTf_2 doped with Mn(NTf_2)$_2$.



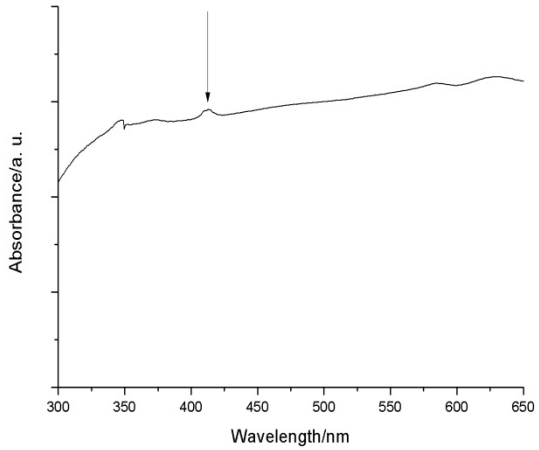
ESI-Fig. 18 UV/Vis spectrum of C_4mpyridBF_4 doped with Mn(NTf_2)$_2$.



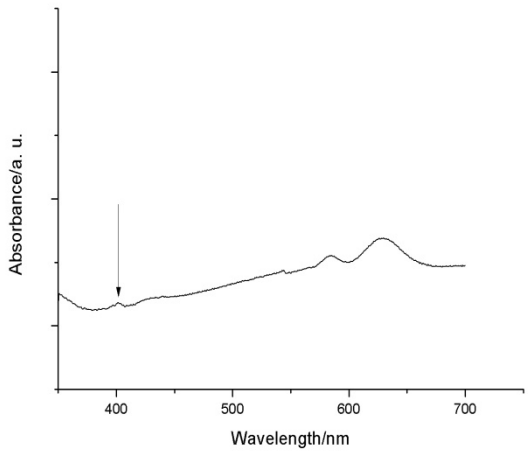
ESI-Fig. 19 UV/Vis spectrum of C_6mpyrNTf_2 doped with Mn(NTf_2)$_2$.



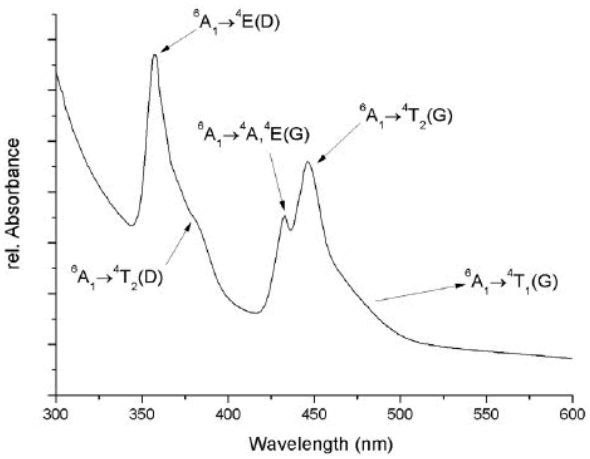
ESI-Fig. 20 UV/Vis spectrum of C_4mimDCA doped with $Mn(NTf_2)_2$.



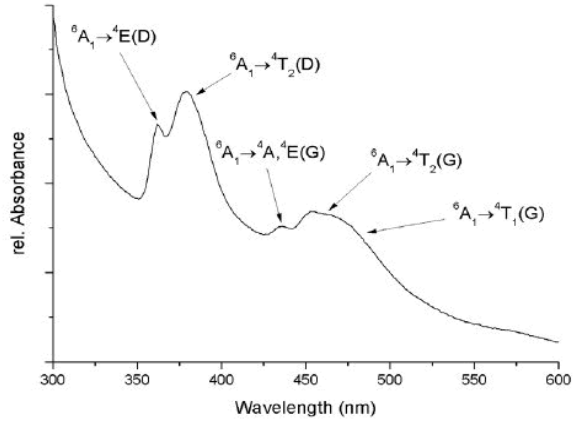
ESI-Fig. 21 UV/Vis spectrum of Acetonitrile doped with $Mn(NTf_2)_2$.



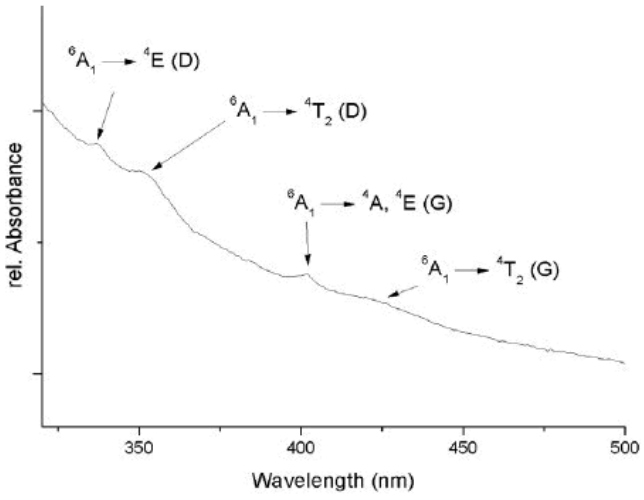
ESI-Fig. 22 UV/Vis spectrum of deionized water doped with $Mn(NTf_2)_2$.



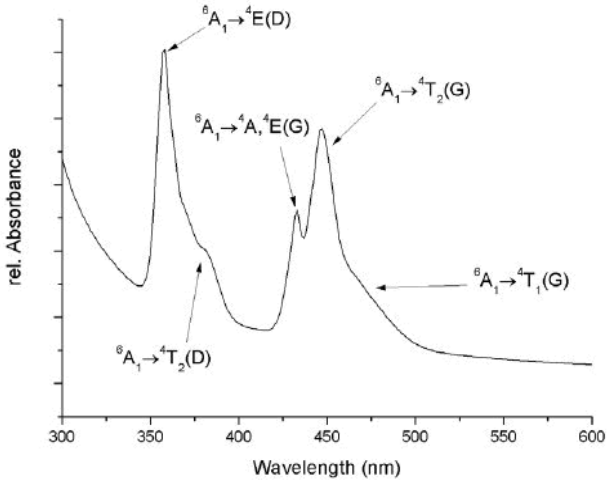
ESI-Fig. 23 UV/Vis spectrum of $[C_2mim]_2[MnCl_4]$.



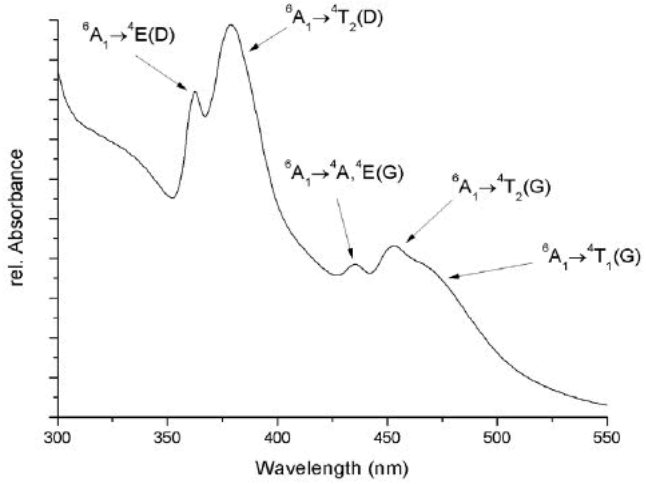
ESI-Fig. 24 UV/Vis spectrum of $[C_2mim]_2[MnBr_4]$.



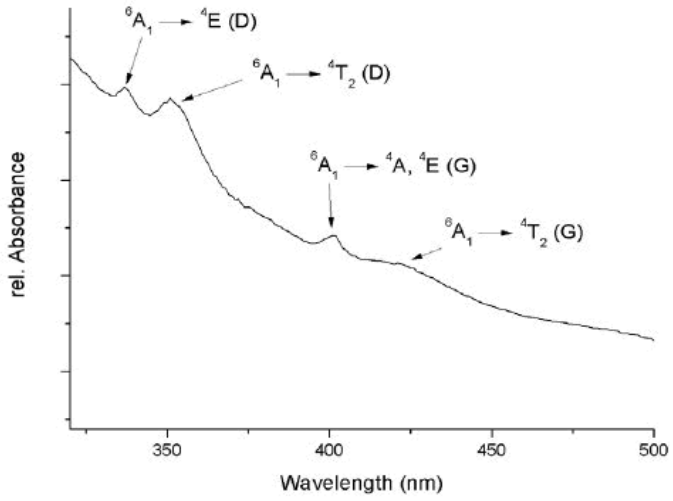
ESI-Fig. 25 UV/Vis spectrum of $[C_2mim][Mn(Tf_2N)_3]$.



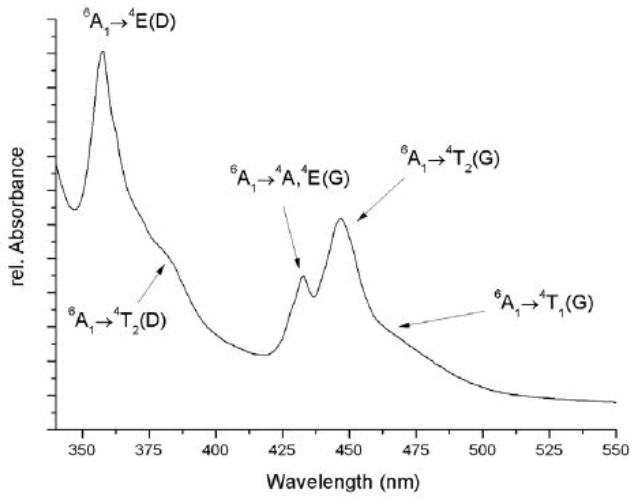
ESI-Fig. 26 UV/Vis spectrum of $[C_3mim]_2[MnCl_4]$.



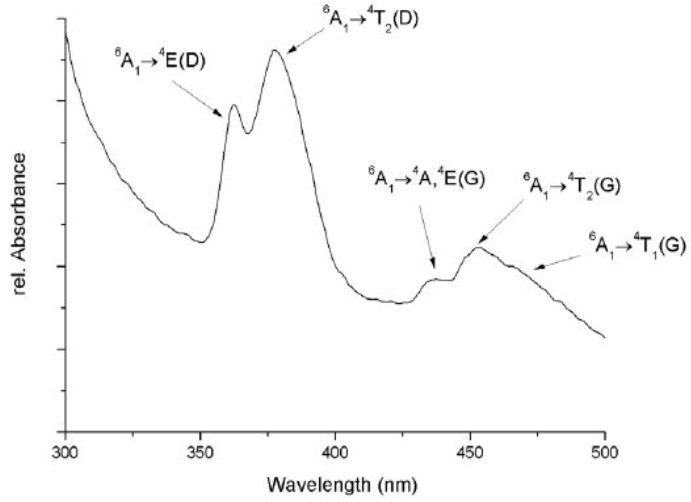
ESI-Fig. 27 UV/Vis spectrum of $[C_3mim]_2[MnBr_4]$.



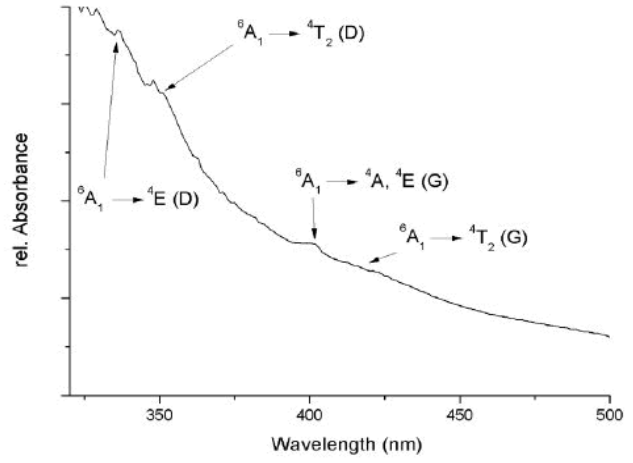
ESI-Fig. 28 UV/Vis spectrum of $[C_3mim][Mn(Tf_2N)_3]$.



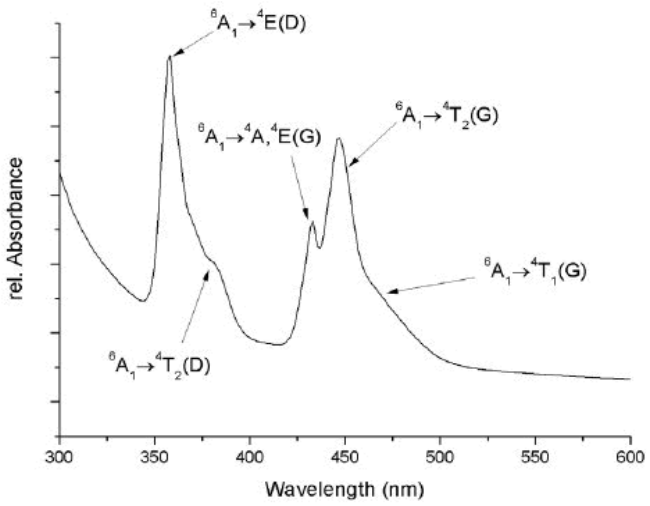
ESI-Fig. 29 UV/Vis spectrum of $[C_4mim]_2[MnCl_4]$.



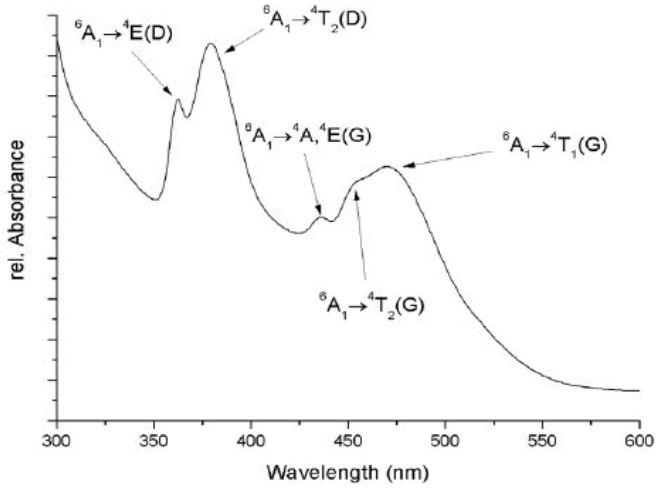
ESI-Fig. 30 UV/Vis spectrum of $[C_4mim]_2[MnBr_4]$.



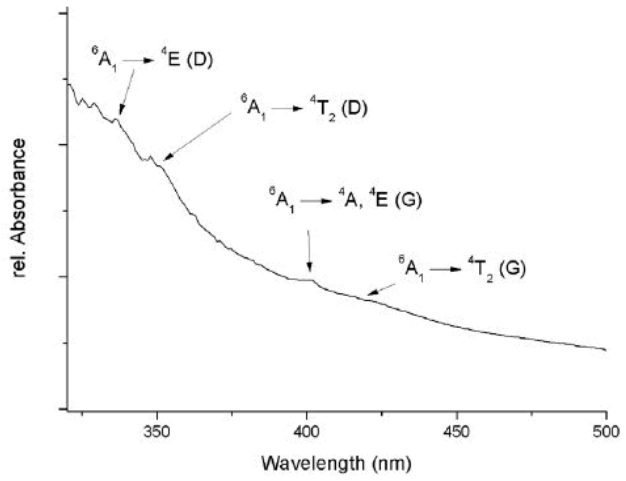
ESI-Fig. 31 UV/Vis spectrum of $[C_4mim][Mn(Tf_2N)_3]$.



ESI-Fig. 32 UV/Vis spectrum of $[C_6mim]_2[MnCl_4]$.



ESI-Fig. 33 UV/Vis spectrum of $[C_6mim]_2[MnBr_4]$.



ESI-Fig. 34 UV/Vis spectrum of $[C_6mim][Mn(Tf_2N)_3]$.

ESI-Table 1. List of the $^6A_1 \rightarrow {}^4A$, $^4E(G)$ transition bands and the nephelauxetic parameters *h* calculated from literature data. The Mn^{2+} site symmetry is assigned to tet (tetrahedral) and oct (octahedral).

compound	$^6A_1 \rightarrow {}^4A$, $^4E(G)$ transition band/cm^{-1}	coordination site	nephelauxetic parameter *h*
MnF_2 [1]	24937	oct	-0.04
MnF_2 @ 4 K [1]	25340	oct	-0.27
$MnCl_2$ [2]	23590	oct	0.74
$MnBr_2$ [2]	23084	oct	1.03
$MnBr_2$ in propanediol-1,2-carbonate [3]	23041	tet	1.05
$MnBr_2$ in acetonitrile [3]	23095	tet	1.02
$MnBr_2$ in Bu_4NBr [4]	22992	tet	1.08
$[Bu_4N]_2[MnBr_4]$ in hexachlorobutadiene [5]	23810	tet	0.61
$[Bu_4N]_2[MnCl_4]$ in Nujol [5]	23310	tet	0.90
$[Et_4N]_2[MnCl_4]$ @ 77 K [6]	23400	tet	0.85
$[Et_4N]_2[MnBr_4]$ @ 77 K [6]	23050	tet	1.05
$[Me_4N]_2[MnCl_4]$ @ 77 K [6]	23290	tet	0.91
$[Me_4N]_2[MnBr_4]$ @ 77 K [6]	23000	tet	1.08
$[Bu_4N]_2[MnCl_4]$ @ 77 K [6]	23470	tet	0.81
$[Bu_4N]_2[MnBr_4]$ @ 77 K [6]	23080	tet	1.03
5% $MnCl_2$ in KCl [7]	23880	oct	0.57
$Mn(H_2O)_6^{2+}$ [8]	25150	oct	-0.16
$Mn(CH_3CN)_6^{2+}$ [8]	24450	oct	0.24

[1] Gmelin *Handbook*, *Mn*, Vol. C 10, 6, **1982**
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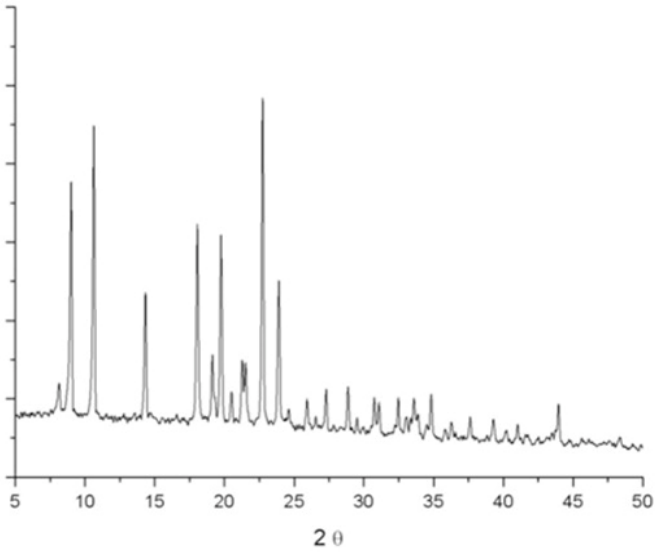

ESI-Fig. 33 PXRD of as-synthesized $Mn(NTf_2)_2$.