Abstract

Synthetic, structural and luminescence studies of (i) crown ether compounds of Mn^{2+} in well defined coordination environments other than T_d or O_h and (ii) Ln^{3+} - MX_4^{2-} anions (M = divalent d-block element; X = halogen; Ln = lanthanide element) crown ether supramolecular complexes, were undertaken in an effort to understand the origin of emitting crystal defects found in cubic *F23* $[(M18C6)_4MnBr_4][TlBr_4]_2$ (M= Rb, K) crystals and Mn^{2+} doped phosphors.

Emission from Mn^{2+} in an eight-coordination environment in stoichiometric complexes is seen, for the first time, from $[Mn(12C4)_2]^{2+}$ cation of the novel compound $[Mn(12C4)_2][(CH_3)_4N]_2[MnBr_4]_2$ **(4)**. Intense emission from Mn^{2+} in a seven coordination environment, also seen for the first time, is observed in $[Mn(15C5)(H_2O)_2]^{2+}$ and $[Mn(15C5)(D_2O)_2]^{2+}$ cations of the novel complexes $[Mn(15C5)(H_2O)_2][TlBr_5]$ **(8)**, $[Mn(15C5)(H_2O)_2][MnBr_4].H_2O$**(10)**, $[Mn(15C5)(H_2O)_2][Br]_2$ **(9)** and $[Mn(15C5)(D_2O)_2][Br]_2$ **(11)**. For **(4)** long lived emission (77 K decay rate 3 × 10 s^{-1}) from $[Mn(12C4)]^{2+}$ is observed ($\lambda_{max} \approx 546$ nm) along with emission of the sensitising T_d $MnBr_4^{2-}$ anion ($\lambda_{max} \approx 513$ nm), which is partially quenched. Intense quenched emission from the seven-coordinate $[Mn(15C5)(H_2O)_2]^{2+}$ species ($\lambda_{max} \approx 592$ nm) in **(10)** which is also sensitised by the $MnBr_4^{2-}$ anion, is also observed. Moderately long-lived

emission (77 K decay rate ≈ 8.0 × 10 s^{-1}) is observed from the deuterate $[Mn(15C5)(D_2O)_2]^{2+}$ in **(11)**, peaking intensity is also at ≈ 592 nm.

The potential of Mn^{2+} emission as a luminescent probe for supramolecular dynamics is demonstrated (for the first time) by the temperature dependent decay rates from $[Mn(15C5)(H_2O)_2]^{2+}$ ions. The $[Mn(15C5)(H_2O)_2]^{2+}$ cations, which are anchored by a net-work of O-H$\cdots$(Br^-)$\cdots$H-O bonds ions in two and one dimensional arrays of $\{[Mn(15C5)(H_2O)_2][TlBr_5]\}_n$ **(8)** and $\{[Mn(15C5)(H_2O)_2][Br]_2\}_n$ **(9)** respectively, probe thermal tuning of the luminescence quenching activity of coordinated H_2O.

Emission from Mn(II) in solution, also reported for the first time, is observed from 3:1 CH_3CN:CH_3OH solutions of **(4)** (with four- and eight-fold Mn^{2+} coordination environments), $[Mg(12C4)_2]_{1-x}[Mn(12C4)_2]_x[(CH_3)_4N]_2[MnBr_4]_2$ **(5)** (with four-fold Mn^{2+} coordination environment); and $[Mn(12C4)_2][(CH_3)_4N]_2[MnBr_4]_x[ZnBr_4]_{2-x}$ **(6)** (with eight-fold Mn^{2+} coordination environment). This expands the potential Mn(II) as a luminescent probe to solution coordination chemistry, biology and materials.

Efforts to probe Mn^{2+} defects associated with the $MnBr_4^{2-}$ anion led to the synthesis and first structural characterisation of lanthanide-crown ether

sandwich complexes $[Pr(15C5)_2][(CH_3)_4N][ZnBr_4]_2$ **(17)** and $[Er(12C4)_2][(CH_3)_4N][ZnBr_4]_2$ **(35)**. Novel complexes of the general stoichiometry $[Ln(H_2O)_8][15C5][Br]_3$(Ln = Er, Dy, Yb), $[Ln(H_2O)_4(15C5)][Br]_3$ (Ln = Eu, Gd, Tb, Er, Dy, Yb), $[(15C5)Ln(H_2O)_4][15C5][ZnBr_4][Br]$ (Ln = Eu - Tb), $LnBr_3(15C5)$ (Ln = Tb, Eu), $[Eu(H_2O)_8][(12C4)][Br]_3.CH_3OH$, $[(12C4)Ln(solvent)_5][solvent]_3[Br]_3$ (Ln = Eu, Gd, Tb, Dy, solvent = H_2O or CH_3OH) and $[(12C4)(H_2O)_2Ln(\mu_2\text{-}OH)Ln(12C4)][ZnBr_4][Br_2]$ (Ln = Er); intermediates to the formation of lanthanide-crown ether sandwich complexes were also isolated and structurally characterised and mechanisms for the formation of both 12C4 and 15C5 lanthanide(III) sandwich complexes are proposed. Successful crystallisation of $[Ln(crown)_2]^{3+}$ sandwiches (crown = 15C5 and 12C4) is attributed to the presence of large poorly binding doubly charged anions {i.e. MBr_4^{2-} (M = 3d metal ion)} and the protection of the resulting complexes from hydrolytic assault. Revealing that through space coulombic interactions between poorly co-ordinating $[Ln(Crown)_2]^{3+}$, $[MBr_4]^{2-}$ and $[(CH_3)_4N]^+$ ions do produce the right supramolecular stabilisation package for $[Ln(Crown)_2][(CH_3)_4N][MBr_4]_2$ lattices. The sandwich and their intermediates show interesting luminescence behaviour including the defect luminescence behaviour associated with Zn^{2+} complexes which was previously attributed to “special ligand-to-metal charge transfer transitions”. Absorption and luminescence studies of the red-orange complex $[Eu(15C5)(Br)_3]$ **(30)** an intermediate to the formation

of $[Eu(15C5)_2][(CH_3)_4N][ZnBr_4]_2$ **(21)**, also clarified the origin of the unusual intense temperature dependent dark brown to red colour seen in anhydrous $EuBr_3$ compounds in contrast to colourless hydrated europium(III) bromides. This behaviour, previously assigned to bromide-to-europium(III) (Br^--Eu^{3+}) charge transfer transitions, has been attributed to inter-configurational electronic transitions ($4f^7 5d^0 \leftrightarrow 4f^6 5d^1$) of Eu^{2+}-Br^- defect sites in the crystal lattice of **(30)** centred at 21, 322 cm^{-1}.