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)$_{4}$MnBr$_{4}$][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$_{3}$)$_{4}$N]$_{2}$[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$_{2}$O)$_{2}$]$^{2+}$ and [Mn(15C5)(D$_{2}$O)$_{2}$]$^{2+}$ cations of the novel complexes [Mn(15C5)(H$_{2}$O)$_{2}$][TlBr$_{5}$] (8), [Mn(15C5)(H$_{2}$O)$_{2}$][MnBr$_{4}$].H$_{2}$O(10), [Mn(15C5)(H$_{2}$O)$_{2}$][Br]$_{2}$ (9) and [Mn(15C5)(D$_{2}$O)$_{2}$][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$_{2}$O)$_{2}$]$^{2+}$ 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 \((77 \, \text{K decay rate} \approx 8.0 \times 10^{-4} \, \text{s}^{-1})\) is observed from the deuterate \(\text{[Mn}(15\text{C}5)(\text{D}_2\text{O})_2]^{2+}\) in (11), peaking intensity is also at \(\approx 592 \, \text{nm}\).

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 \(\text{[Mn}(15\text{C}5)(\text{H}_2\text{O})_2]^{2+}\) ions. The \(\text{[Mn}(15\text{C}5)(\text{H}_2\text{O})_2]^{2+}\) cations, which are anchored by a net-work of O-H***(Br')***H-O bonds ions in two and one dimensional arrays of \{\text{[Mn}(15\text{C}5)(\text{H}_2\text{O})_2][\text{TlBr}_3]\}_n \text{ (8) and } \{\text{[Mn}(15\text{C}5)(\text{H}_2\text{O})_2][\text{Br}]_2\}_n \text{ (9) respectively, probe thermal tuning of the luminescence quenching activity of coordinated } \text{H}_2\text{O}.

Emission from Mn(II) in solution, also reported for the first time, is observed from 3:1 \text{CH}_3\text{CN:CH}_3\text{OH} solutions of (4) (with four- and eight-fold Mn\(^{2+}\) coordination environments), \(\text{[Mg}(12\text{C}4)_2]_{1-x}[\text{Mn}(12\text{C}4)_2][\text{(CH}_3)_4\text{N}]_2[\text{MnBr}_4]_2 \text{ (5) with four-fold Mn}\(^{2+}\) coordination environment); and \(\text{[Mn}(12\text{C}4)_2][\text{(CH}_3)_4\text{N}]_2[\text{MnBr}_4]_x[\text{ZnBr}_4]_{2-x} \text{ (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 \([\text{Pr}(15C5)_2][(\text{CH}_3)_4\text{N}][\text{ZnBr}_4]_2\) (17) and
\([\text{Er}(12C4)_2][(\text{CH}_3)_4\text{N}][\text{ZnBr}_4]_2\) (35). Novel complexes of the general
stoichiometry \([\text{Ln}((\text{H}_2\text{O})_8][15C5][\text{Br}]_3(\text{Ln} = \text{Er}, \text{Dy}, \text{Yb}),
[\text{Ln}((\text{H}_2\text{O})_4][15C5][\text{Br}]_3(\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{Dy}, \text{Yb}),
[(15C5)\text{Ln}((\text{H}_2\text{O})_4][15C5][\text{ZnBr}_4][\text{Br}] (\text{Ln} = \text{Eu} - \text{Tb}), \text{LnBr}_3(15C5) (\text{Ln} = \text{Tb},
\text{Eu}), \text{[Eu(}\text{H}_2\text{O})_8][12C4])][\text{Br}]_3.\text{CH}_3\text{OH}, [(12C4)\text{Ln(solvant)}_8][\text{solvant}]_3[\text{Br}]_3
(\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{solvent} = \text{H}_2\text{O} \text{or} \text{CH}_3\text{OH}) \text{ and } [(12C4)(\text{H}_2\text{O})_2\text{Ln(}\mu_2-
\text{OH})\text{Ln}(12C4)][\text{ZnBr}_4][\text{Br}_2] (\text{Ln} = \text{Er})\); 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 \([\text{Ln}(\text{crown})_2]^3+ \) sandwiches (crown = 15C5 and 12C4) is
attributed to the presence of large poorly binding doubly charged anions
(i.e. \(\text{MBr}_4^{2-} (\text{M} = \text{3d metal ion})\)) and the protection of the resulting
complexes from hydrolytic assault. Revealing that through space
coulombic interactions between poorly co-ordinating \([\text{Ln(Crown)}_2]^3+, \text{[MBr}_4^{2-} \text{ and } [\text{(CH}_3)_4\text{N}]^+ \) ions do produce the right supramolecular
stabilisation package for \([\text{Ln}(\text{Crown})_2][(\text{CH}_3)_4\text{N}][\text{MBr}_4]_2\) lattices. The
sandwich and their intermediates show interesting luminescence
behaviour including the defect luminescence behaviour associated with
\(\text{Zn}^{2+}\) complexes which was previously attributed to “special ligand-to-metal
charge transfer transitions”. Absorption and luminescence studies of the
red-orange complex \([\text{Eu}(15C5)(\text{Br})_3] (30) \) an intermediate to the formation
of [Eu(15C5)2][(CH₃)₄N][ZnBr₄]₂ (21), also clarified the origin of the unusual intense temperature dependent dark brown to red colour seen in anhydrous EuBr₃ compounds in contrast to colourless hydrated europium(III) bromides. This behaviour, previously assigned to bromide-to-europium(III) (Br⁻-Eu³⁺) charge transfer transitions, has been attributed to inter-configurational electronic transitions (4f⁷5d⁰ ↔ 4f⁶5d¹) of Eu²⁺-Br⁻ defect sites in the crystal lattice of (30) centred at 21, 322 cm⁻¹.