Summary of Thesis Findings

Metal Organic Framework Materials: Synthesis, Characterization and Their Luminescent Properties

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This thesis is organized into six chapters. A brief overview of each chapter is presented below.

Chapter 1. Introduction: Metal-organic frameworks (MOFs) are crystalline solids built from metal nodes connected by organic linkers through coordination bonds; the related but broader term coordination polymer (CP) covers any such extended structure, with "MOF" generally reserved for the three-dimensional, porous structures. Their structural diversity, permanent porosity, and chemical tunability have made them significant for gas storage, catalysis, sensing, and energy-related applications. A specific and comparatively hot area related to this chemistry are luminescent MOFs, where emission can originate from the organic linker itself, from the metal centre, or from charge transfer between the two, and where the modular construction is used to incorporate such optically active centres rather than, or alongside, adsorptive or catalytic function. The thesis work presents using bidentate and multidentate organic linker platform combined with different metal (transition and lanthanide metal) centres independently to establish how framework architecture controls the properties of the product materials.

Chapter 2: Objectives and approach. In this thesis work two linked design variables: linker denticity and metal identity. A rigid, tetratopic carboxylate ligand (H_4TCPB) and a simple bidentate ligand (4,4′-bipyridyl) were each combined with Ag(I) to isolate the effect of linker geometry on framework dimensionality, while the same tetratopic ligand was separately combined with two different lanthanide ions (Eu(III) and Tb(III)) to isolate the effect of metal identity on emission colour. All four coordination polymers - CP-1 to CP-4 were grown as single crystals under solvothermal or slow-diffusion conditions chosen to favour ordered nucleation, since single-crystal structure determination, rather than bulk powder data alone, was essential to establishing connectivity and topology in such systems. A thorough characterization techniques were then applied across all synthesized compounds: single-crystal and powder X-ray diffraction for structure and phase purity, infrared spectroscopy to confirm linker coordination, thermogravimetric analysis for thermal stability, and UV-Vis/photoluminescence spectroscopy for optical band gap and emission behaviour, providing a detailed information about the synthesized materials.

Chapter 3: CP-1: a three-dimensional silver-carboxylate framework. Reaction of silver trifluoroacetate with H_4TCPB gave $[Ag_4(TCPB)]_n \cdot 3CH_3OH$ (CP-1), a three-dimensional, highly porous framework with a rare 14-connected bcu-x topology , well above the four- to eight-connected range typical of carboxylate-based frameworks. The high connectivity is reinforced by argentophilic Ag···Ag interactions, Ag-π interactions, and π-π stacking between linker rings, in addition to conventional Ag-O coordination, and it is this dense interaction network that keeps the framework rigid despite relying partly on comparatively soft secondary contacts. CP-1 shows an optical band gap of 3.34 eV, making its wide-band-gap regime consistent with absorption dominated by the conjugated linker rather than by the Ag(I) centres

themselves, and an intense royal-blue emission at 392 nm under 365 nm excitation, attributed to ligand-to-ligand and metal-to-ligand charge-transfer (LLCT/MLCT) pathways enabled by the same metal-metal and metal-π interactions. The synthesized material framework was obtained in pure-phase, thermally stable, and photostable under prolonged UV exposure.

Chapter 4: CP-2: a one-dimensional contrast structure. Replacing the tetratopic linker with the bidentate 4,4′-bipyridyl (bpy), while keeping the metal centre as Ag(I), yields $[Ag(bpy)]_n(NO_3)_n$ (CP-2), which crystallizes in the orthorhombic *Pnna* space group as a one-dimensional Ag-bpy chain linked into a *pseudo-two-dimensional* arrangement only through weak Ag···O contacts with the nitrate ion as counter-ion. The results show that Ag(I)'s d^{10} configuration, which favours low, often two-coordinate linear geometries in the absence of additional bridging ligands, reinforced here by bpy units two donor N-atoms at opposite ends of a rigid linear backbone. Unlike CP-1, CP-2 shows no detectable luminescence and only limited stability under ambient conditions; the coordinatively saturated, two-coordinate Ag centres provide no equivalent metal-metal or metal-π contact network, and the smaller, less conjugated bpy linker appears to be a weaker emitter than TCPB. As the metal centre is same in both CP-1 and CP-2, this contrast in properties depicts linker denticity, rather than metal ion centre is responsible for controlling both dimensionality of the framework structures and their optical properties.

Chapter 5: CP-3 and CP-4: lanthanide-carboxylate frameworks. The reaction of H_4TCPB with Eu(III) and Tb(III) independently gives two three-dimensional frameworks, $[Eu(TCPB)(H_2O)_2]\cdot 3CH_3CN$ (CP-3) and $[Tb(TCPB)(H_2O)_2]\cdot 3CH_3CN$ (CP-4). These frameworks are highly luminescent emits red and green emission. This ligand acts as an antenna for efficient emission properties because lanthanide *4f-4f* transitions are formally forbidden by the parity selection rule and only weakly allowed by symmetry, the TCPB linker instead absorbs the exciting light and transfers the energy non-radiatively to the metal ion of Eu and Tb, which then emits with much higher apparent efficiency than direct excitation would produce in both cases, to overcome the non-radiative quenching normally due to O-H bonds from the coordinated water molecules in each structure. CP-3 shows strong red emission dominated by the Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition at 611 nm, a transition whose hypersensitivity to local symmetry indicates a Eu(III) site lacking inversion symmetry, while CP-4 shows bright green emission dominated by the Tb(III) $^5D_4 \rightarrow {}^7F_5$ transition at 544 nm. Both frameworks retain their three-dimensional connectivity and porosity, demonstrating that a single ligand platform can deliver markedly different emission colours simply by changing the lanthanide ion.

Chapter 6: Summary and Significance. Taken together, the four compounds establish a strong structure-property correlation for this ligand system: linker denticity determines whether the resulting framework is one- or three-dimensional, and that dimensionality, together with the specific secondary interactions available to a given metal centre, determines whether efficient luminescence occurs at all and through which mechanism. CP-1 and the CP-3, CP-4 pair, in particular, combine structural robustness with strong, distinct, and mechanistically well-understood emission, making them good candidates for further development in optoelectronic, chemical-sensing, and solid-state lighting applications. While linker in CP-2 shows no emission properties and stability was relatively low, indicates that linker effect play an important role for the efficient properties of the synthesized systems. To sum up, the multidentate H_4TCPB linker plays a significant role in enhancing the properties of Ag(I) (blue emission), Eu(III) (red emission), and Tb(III) (green emission) systems, making them promising candidates for optoelectronic devices.