IMPACT OF COORDINATION GEOMETRY ON PHOTOLUMINESCENCE WAVEGUIDING IN SINGLE-CRYSTALS

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The design of coordination frameworks requires an in-depth understanding of how metal ionic radii and ligand steric effects govern the resulting architectures. Herein, we report a comparative study of Cd^{II} and Zn^{II} assemblies obtained from novel bis(pyridin-3-ylethynyl) *N*-methylcarbazole, *N*-ethylcarbazole, and 9-fluorenone ligands, combined with coordinatively unsaturated bis-*O*-alkyldithiophosphonato (DTP) complexes[1]. We investigated how metal connectivity and ligand structure influence light transport properties. Substitution of Cd^{II} with Zn^{II} induces a significant change in structural dimensionality: the larger Cd^{II} ion forms one-dimensional sinusoidal coordination polymers (CPs), whereas the smaller Zn^{II} ion preferentially yields discrete complexes. *N*-alkylcarbazole ligands were introduced to modulate steric hindrance and tune photoluminescence emission in comparison with fluorenone-based analogues. All systems display intense ligand-centered photoluminescence. However, their waveguiding efficiency depends on the interplay between structural dimensionality and electronic overlap. Optical loss measurements reveal that extended one-dimensional Cd-based polymeric frameworks significantly outperform discrete Zn-complexes, demonstrating that the transition from discrete to polymeric coordination architectures can be strategically employed to tailor the physical properties of hybrid materials.

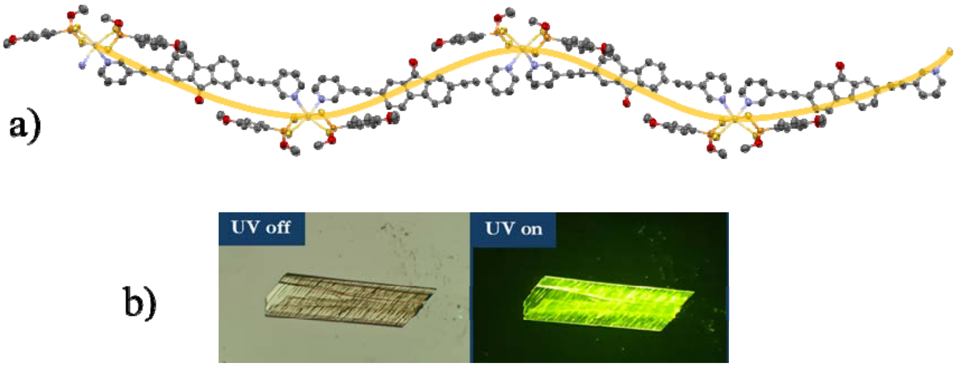

Figure 1 – a) The sinusoidal motif in the SC-XRD structure of the CP obtained from the 9-fluorenone ligand and the Cd^{II} methyl-DTP. Hydrogen atoms are omitted for clarity. b) Single crystals of the same CP under polarized light (left) and UV (365 nm; right) irradiation.

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[1] E. Podda, M. Arca, A. Pintus, V. Lippolis, S. J. Coles, J. B. Orton, S. Porcu, P. C. Ricci, M. C. Aragoni, *JACS Au* **2025**, *5*, 727–739.