This talk strives to highlight the conceptual and practical implications of an interdisciplinary study across molecular syntheses and crystalline networks. Our synthetic endeavor is illustrated by a class of unconventional, backfolded dendrimers (e.g., \( L \)), which, as building blocks, lead to some of the most complex crystalline networks to date. Solid state network structures based on \( L \) and other tailor-made molecules will be presented, with emphasis on the correlation with the associated optical properties, including: white light emission, second harmonic generation, and luminescent sensing of heavy metals and small molecules (e.g., \( \text{NH}_3 \), \( \text{H}_2\text{S} \)).

The second part marries the two distinct fields of metal chalcogenides and coordination polymers, in order to achieve advanced composite electronic materials. Here we use a bifunctional molecule that binds its hard carboxylate groups to Eu(III) and form a robust, porous network, while enclosing AgCl via its soft sulfur side arms. The AgCl is then treated with \( \text{H}_2\text{S} \) to form the dark-colored AgS species, while leaving the enclosing host net intact and upstanding. The resultant composite combines the rich electronic property of metal chalcogenides and the functional diversity of coordination solids, and provides a well-defined medium for exploring novel catalytic and electronic processes in the solid state.