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Editorial

Self–Assembled Complexes: "Love at First Sight"

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Self-assembly is a key process to obtain auto-organized species from disordered components [1–3]. The autonomous process occurs spontaneously, and it allows obtaining diverse substances, from simple molecules to macromolecules, as well as 1D, 2D, and 3D materials of different natures. Thus, self-assembly is responsible for the formation of a huge variety of substances, such as oligomeric metal complexes [4–9], coordination polymers [10–14], varied (metallo)supramolecular materials [15–22], metal–organic frameworks [23,24], complex materials [25–28], biomaterials [29–31], and nanomaterials [32–36]. Furthermore, they can present amazing properties [37–42], so they are useful in diverse fields [43–50].

This Special Issue is centered on coordination, one of the most studied fields of self-assembly. It collects different aspects of several coordination complexes, where self-assembly plays a key role, especially for those with high nuclearity, as coordination polymers. Different techniques were used for their characterization, including powder and single-crystal X–ray diffraction. The compounds collected here exhibit different properties, related to aspects such as magnetism or luminescence.

The article published by Housecroft et al. deals with heteroleptic copper(I) complexes of ligands of 1,1′–biisoquinoline, along with bis(2–(diphenylphosphanyl)phenyl)ether or 9,9–dimethyl–9H–xanthene–4,5–diyl)bis(diphenylphosphane) [51]. In solution and at ambient temperatures, the cationic complexes undergo several concurrent dynamic processes, evidenced in their multinuclear NMR spectra. The photophysical and electrochemical behaviors of these copper (I) complexes were investigated, and the effects of changing from biquinoline to 1,1′–biisoquinoline are described.

Complexes containing purine nucleobases are a subject of interest for the comprehension of mutations and biochemical structures in life sciences. Lillo and coworkers present a new dinuclear ruthenium(III) complex based on guanine (gua), and simultaneously bridged by the two guanines and two chloride anions, with the formula $[\{Ru(\mu\text{–}Cl)(\mu\text{–}gua)\}_2Cl_4]\cdot 2H_2O$ [52]. Its well-resolved voltammetric response could provide a step towards developing new ruthenium-based platforms, devices, and modified electrodes, adequate for studying this purine nucleobase.

Increasing the nuclearity, a dianionic cubane-like complex $[Tb_4(OH)_4(tfa)_6(hfac)_4]^{2-}$ is presented by Hishida [53], in the presence of two counter cations of $[Ni(hfac)(2pyIN)_2]^+$, where Htfa, Hhfac, and 2pyIN are the abbreviations of trifluoroacetic acid, 1,1,1,5,5,5–hexafluoropentane–2,4–dione, and 4,4,5,5–tetramethyl–2–pyridylimidazolin–1–oxyl, respectively. In the crystal structure of the complex, the cuboid is formed by alternate Tb^{III} cations and hydroxy groups. Each terbium center is coordinated to one hfac ligand, while each Tb···Tb diagonal is bridged with a trifluoroacetate anion. The magnetic studies revealed that the complexes are magnetically isolated from each other, and the Tb–O–Tb

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superexchange coupling is negligible. Practically no 4*f*–4*f* superexchange interaction was detected, while there was some ferromagnetic coupling.

The review by Rigamonti and coworkers [54] is focused on the template methods for obtaining oligomeric Schiff base complexes of transition metals, with special attention on the activity of copper(II). They review the reaction of carbonyl compounds (mainly salicylaldehyde) and primary diamines, as well as how the less-common simple condensation, or the typical double condensation occurs. Furthermore, N_2O adducts holding a free amino group can further react to yield classic tetradentate salen-type ligands. Several different aspects are studied: the influence of the amine; of the metal cation; of the concentration of reactants; and the possibility of demetalation or transmetalation.

Coordination polymers are one of the key results of self-assembly. Here, the novel coordination polymer $\{[Ho_2(DHTA)_3(H_2O)_5]\cdot H_2O\}_n$ (DHTA = 2,5–dihydroxy–1,4–terephthalate) was obtained by Su et al. [55], from a hydrothermal synthesis. The crystallographic data show that the polymer contains two eight-coordinate Ho^{III} centers in different coordination environments. This material presents high thermal stability and green luminescence.

Finally, Nieckarz presents a lattice Monte Carlo (MC) simulation technique to extract some chemical information for the supramolecular construction of surface-supported metal–organic networks (SMONs), which are composed of low-coordinated metal atoms and π–aromatic bridging linkers [56]. In this particular case, the studies are centered on a family of ten Y-shaped positional isomers, which are co-adsorbed with trivalent metal cations on a flat metallic surface with (111) geometry. The distribution of active centers within the simulated molecular bricks conditions the two-dimensional (2D) openwork pattern obtained the following: aperiodic mosaics and metal–organic ladders. The theoretical findings could be especially useful for the comprehension of surface-assisted construction of complex nanomaterials stabilized by directional coordination bonds, using scanning tunneling microscopy (STM).

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