English abstract of the doctoral thesis entitled “Application of policyanidometalate complexes of d block metals in construction of new multifunctional molecular materials” by M.Sc. Tomasz Charytanowicz

One of the most important trends in current development of technology is global miniaturization of electronics and sensor devices. The answer to this rising need may be the molecular materials, especially compounds that exhibit spin transitions, slow relaxations of magnetization, and photoluminescent compounds. Such materials can be widely applied in sensors, molecular switches, magnetic memory, and light-processing devices. The molecular building block approach is one of the most efficient synthetic methods for molecular materials. Among many available types of molecular building blocks, polycyanidometallates appear to be one of the most effective, offering the possibility to obtain multicentered structures thorough bridging cyanido ligands.

This doctoral thesis presents the results of research aimed at obtaining new, functional molecular materials utilizing polycyanidometallate ions. **Publications P1-P4** contain the results concerning the usage of octacyanidorhenate(V) ion in the construction of Fe(II)-based spin crossover (SCO) materials. **Publication P5** describes the application of octacyanidotungstate(IV/V) ions in construction of materials, revealing slow relaxations of magnetization. The magnetic properties of Ln(III)-based, cyanido-bridged compounds were further studied in **Publication P6**, but the main emphasis was put on the unique photoluminescent properties, observed in the obtained systems.

The conducted studies resulted in the obtaining of many new molecular materials, characterized by various properties. In the case of **Publication P1**, coordination layers of $\{[\mathrm{Fe^{II}}(4\text{-Brphpy})_4]_3[\mathrm{Re^{V}}(\mathrm{CN})_8]_2\}\cdot n\mathrm{solv}$ were obtained, exhibiting magnetic behavior that strongly depends on the presence of guest molecules in the crystal structure. When there are methanol molecules in the structure, no spin transition is observed; however, the presence of the water molecules induces a two-step, gradual SCO effect, which is well correlated with the optical properties of the system. In addition, the structure crystallizes in a chiral space group. In the context of the recent studies, underlining the influence of sterically bulky organic ligands on spontaneous resolution of chiral systems, further investigations were conducted using sterically large pyridine derivatives. Those resulted with two new compounds, described in **Publication P2**, coordination layers $\{[\mathrm{Fe^{II}}(3\text{-benzpy})_4]_3[\mathrm{Re^{V}}(\mathrm{CN})_8]_2\}\cdot 2\mathrm{H_2O}$ and 3-D network $\{[\mathrm{Fe^{II}}(4\text{-benzpy})_4]_5[\mathrm{Re^{V}}(\mathrm{CN})_8]_3\}(\mathrm{ClO_4})\cdot 2(4\text{-benzpy})\cdot 6\mathrm{H_2O}\cdot\mathrm{MeOH}$. Both compounds exhibit a thermally-induced SCO effect, but only the 3-D network crystalizes in chiral space group. Moreover, in the case of the 3-D network, the spin transition is notably more complex, prompting comprehensive SC-XRD structural studies alongside Mössbauer spectroscopy experiments. The obtained pair of compounds is an excellent illustration of the profound impact of ligand isomerism on both structural and magnetic properties. The further studies in this field resulted in **Publication P3**, which describe new, non-centrosymmetric coordination chains of $(\mathrm{TBA})\{[\mathrm{Fe^{II}}(\mathrm{phIN})_4][\mathrm{Re^{V}}(\mathrm{CN})_8]\}(\mathrm{phIN})$. This material exhibits a sharp, hysteretic spin transition. The detailed structural studies allowed the magneto-structural correlation, even in the range of the hysteresis loop. Moreover, the experiments enabled the correlation the observed magnetic transitions with optical (light absorption and second harmonic generation) and dielectric (dielectric permittivity and conductivity) properties. The resulting compound is a unique example of multilevel bistability observed in molecular materials. In **Publication P4**, the main focus was on the switchability of magnetic properties, utilizing guest molecules (observed previously for $\{[\mathrm{Fe^{II}}(4\text{-}\mathrm{Brphpy})_4]_3[\mathrm{Re^{V}}(\mathrm{CN})_8]_2\}\cdot n\mathrm{solv}$ (**P1**)) . A new two-dimensional coordination polymer compound was synthesized, $\{[\mathrm{Fe^{II}}(4\text{-}\mathrm{phpy})_4]_3[\mathrm{Re^{V}}(\mathrm{CN})_8]_2\}\cdot n\mathrm{solv}$, revealing two stable phases: one stable in the air and the other stable in the mother solution. Both phases displayed the thermally induced SCO effect, but with dramatically different characteristics. To thoroughly study the observed effects, thermal-dependent SC-XRD and Mössbauer studies were conducted for both phases. Additionally, magnetic experiments were performed on both phases, incorporating pressure and light irradiation to assess their impact on the spin transition. These observations allow us to conclude that the obtained material serves as an exemplary molecular sensor responsive to both physical and chemical stimuli.

While **Publications P1-P4** focus on the use of the diamagnetic $[\mathrm{Re^{V}}(\mathrm{CN})_8]^{3-}$ ion, subsequent studies employed its paramagnetic analogue - $[\mathrm{W^{V}}(\mathrm{CN})_8]^{3-}$ ion. By combining two paramagnetic building blocks - the octacyanidotungstate(V) ion and Co(II) complexes - it become possible to obtain a new family of the coordination polymers, as described in **Publication P5**. The new polymers $\{[\mathrm{Co^{II}}(\mathrm{bpp})\mathrm{X}_{0.5}(\mathrm{H_2O})_{0.5}]_2[\mathrm{W^{V}}(\mathrm{CN})_8]\}\cdot 2\mathrm{H_2O}$ (X = Cl, Br) exhibited metamagnetic behavior. In the low-temperature, antiferromagnetic phases were observed with slow magnetic relaxations originating from SCM behavior. Moreover, it was possible to synthesize an isotopological system $\{[\mathrm{Co^{II}}(\mathrm{bpp})(\mathrm{H_2O})]_2[\mathrm{W^{IV}}(\mathrm{CN})_8]\}\cdot 6\mathrm{H_2O}$, based on diamagnetic octacyanidotungstate(IV). This unique situation enabled a comparative analysis of both types of systems and facilitated a series of theoretical studies, providing insights into the mechanisms of the observed magnetic properties.

In further exploring the magnetic properties of polycyanidometallates-based coordination polymers, , the hexacyanidoruthenate(II) ions were used together with lanthanide(III) complexes, which are known for their high magnetic anisotropy. The obtained systems did not show strong magnetic relaxations, while due to the presence of Ln(III) complexes, unique emission properties were observed, leading to the observation of white and/or switchable luminescence. The conducted experiments led to the findings presented in **Publication P6**. In the first step, four homo-lanthanide compounds $\mathrm{KLn^{III}}[\mathrm{Ru^{II}}(\mathrm{CN})_6]\cdot n\mathrm{H_2O}$ (Ln = La, Ce, Sm, Tb) were obtained, each exhibiting bright-blue, blue, red and green emission colors, respectively. In the next step, two families of compounds were prepared, featuring a mixed composition of lanthanide ions: a mixture of Sm(III) and Ce(III) and a mixture and Tb(III) and Ce(III). The different ratios between lanthanide ions were explored to determine the optimal composition. The strong, blue luminescence of the Ce(III) dominated the collected emission spectra, leading to the determination of the optimal Ce(III) content at approximately 1‰. In the final step, the optimal ratio of Sm(III), Tb(III) and Ce(III) was defined, resulting in the final hetero-lanthanide compound $\mathrm{KSm_{0.4}Tb_{0.599}Ce_{0.001}}[\mathrm{Ru}(\mathrm{CN})_6]\cdot 4{,}5\mathrm{H_2O}$, which exhibited multi-colored emission, including different hues of white light that depended on the excitation wavelength.

In conclusion, the research presented in this thesis highlights the key role of polycyanidometallate ions in developing new functional molecular materials, paving the way for new synthetic approaches toward multifunctional materials. The thesis underlines the structural properties of synthesized compounds and their correlation with the observed physical properties. Moreover, various physical measurements were conducted to characterize the obtained compounds thoroughly. This approach integrates multiple branches of chemistry – such as physical chemistry, inorganic chemistry, organic chemistry, and crystallography – emphasizing the multidisciplinarity of this thesis.