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Abstract in English

Doctoral dissertation entitled "Investigations of nonlinear optical properties of coordination polymers" was carried out in the Advanced Materials Engineering and Modelling Group at the Faculty of Chemistry, Wrocław University of Science and Technology, under the supervision of dr hab. Marcin Nyk, Assoc. Prof. of WUST. The dissertation has been prepared in English.

The main purpose of the work was to characterize in broad spectral range nonlinear optical properties of selected coordination polymers. The investigated nonlinear optical properties included both parametric optical processes such as second- and third harmonic generation (SHG and THG, respectivelty), and nonparametric ones, such as two- and three-photon absorption (2PA and 3PA, respectively).

The dissertation can be divided into two main distinct parts: theoretical, including literature review, and experimental one. The theoretical part starts with an introduction to the subject of coordination polymers (CPs) and of their subclass, metal-organic frameworks (MOFs), their recommended nomenclature, specific structural features, and a brief historical outline of the development of this field. Next, an introduction to the fundamental phenomena of nonlinear optics is presented. Structural factors that contribute to the nonlinear optical properties of CPs are overviewed, with particular emphasis being put on the ligands’ structure as well as on the so-called aggregation effects. Recent literature describing the harmonic generation of radiation, 2PA and multiphoton absorption for these materials and their state-of-the-art applications are presented.

The research part can be divided into two core areas. The first area is dedicated to spectrally-resolved characterization of SHG and THG phenomena in CPs. These measurements have been conducted on CPs constructed from cobalt (II) ions and a tetraphenylmethane-based tetraphosphonate diester. It was demonstrated that in both cases, the excitation spectra of SHG and THG response are dominated by the effects of self-absorption of pumping radiation and the self-absorption corresponding harmonic frequencies. These observations were based on the comparative

analysis of the second and third harmonic excitation spectra with the absorption spectra of investigated solids.

The second, much wider, research area explored was the spectrally-resolved characterization of 2PA and multiphoton absorption in CPs. This part of doctoral dissertation involved the characterization of CPs in the form of nanoparticle dispersions in solvents with the use of Z-scan technique. Prussian Blue nanoparticles, dispersed in D_2O, featured a strong 3PA in the infrared range, with a maximum at approx. 1375 nm (σ_3 value of $0.41 \cdot 10^{-80}$ $cm^6s^2g^{-1}mol$); noteworthy, Prussian Blue nonlinear response is of comparable intensity to that of e.g. organometallic dendrimers. The mechanism of 3PA was attributed to the absorption of a third photon from the two-photon excited state, which was inferred from time-resolved measurements. ZIF-8 and Co/ZIF-8 nanoparticles constituted another class of CPs, whose nonlinear optical were investigated using the Z-scan technique. Z-scan measurements of dispersions of ZIF-8 nanoparticles in dimethyl sulfoxide at 600 nm and of 50Co/ZIF-8 nanoparticles at 950 nm revealed that the 2PA cross sections of these materials are very small (σ_2 values of 8 and 18 GM, respectively).

Next subsections within the research part were devoted to measurements of nonlinear absorption of CPs in the form of microcrystalline materials. A series of isomorphous MOFs based on aluminum, gallium, indium, and 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid have been characterized using the ISTPEF method (Internal Standard Two-photon Excited Fluorescence). Strong two-photon absorption was identified, reaching a maximum at about 690 nm (σ_2 value of 325 GM for a gallium-based analogue). For the first time, the fluorescence quenching phenomenon by nitrocompounds has been investigated under both, one-photon (377 nm) and two-photon (820 nm) excitation. The kinetic parameters of MOF fluorescence quenching were found to be strongly dependent on the excitation mode. It is proposed that the observed differences are related to the different attenuation and scattering of the latter (long-wavelength) excitation, but also stems from low penetration depth of nitrocompound molecules into the studied MOFs.

New CPs constructed from lanthanide ions (Gd^{3+}, Eu^{3+}, Tb^{3+}), 1,10-phenanthroline, and 1,3,5-trimesic acid as ligands are presented. A set of spectroscopic measurements showed that lanthanide CPs, which are usually excited using ultraviolet, can be excited as well using femtosecond pulsed laser radiation in the near-infrared range (800 nm). This approach allows the use of these and similar CPs in so called near-infrared-to-visible noncontact temperature measurement. Systematic differences were observed in the values of thermometric parameters obtained under one- and three-photon excitation, which necessitates the independent determination of calibration curves.

With the use of SSTPEF (Solid State Two-Photon Excited Fluorescence) technique, measurements of nonlinear absorption of two MOFs based on zinc ions, 4,4'-bipyridine and tetracarboxylic acid based on tetrabiphenylethane skeleton were carried out. These measurements were also made for the ligands themselves in the solid state form. It was observed that the MOFs show reduced 2PA cross sections, compared to ligands. This was explained on the basis of a comparison of the ligand conformations in the crystal structures of the above materials. In particular, the dynamics of phenylene rotors in MOFs was ascribed as the origin of their specific spectroscopic properties.

In summary, this dissertation contains research results of fundamental and methodological significance, as well as those that may form the basis for future applications. The research presented in this dissertation was carried out as part of the Maestro research project of the Polish National Science Center "New directions in the study of nonlinear optical phenomena and their physicochemical consequences", led by prof. Marek Samoć. Most of the research presented in this dissertation has been published in international journals covering the fields of chemistry and materials engineering.