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Report on Mr Zaręba's manuscript for the degree of Doctor of Philosophy

The PhD manuscript of 190 pages, entitled: "Investigation of nonlinear optical properties of coordination polymers", is organized into ten sections. It starts with a general introduction, followed by a section listing the main objectives of this work. The third section, dealing specifically with the experimental results gathered during this PhD is itself composed of two sub-sections dealing specifically with spectrally resolved harmonic generation and multi-photon absorption in coordination polymers (CP). It is followed by a general conclusion and outlook (fourth section). The fifth, sixth and seventh sections contain, respectively, the bibliography (334 references), the experimental part and the appendixes of this PhD (listing the main experimental setups and methods used throughout this work). These are followed by three additional sections containing (i) the listing of the publications to which the author of the PhD has contributed and (ii-iii) the abstracts of this PhD Thesis in Polish and English.

The general introduction defines the notion of a CP and gives some general background about nonlinear optics (NLO) and the ways these properties can be measured for CPs, before specifically addressing the NLO properties presented by several classes of coordination polymers through an exhaustive literature review of the field. After pointing out the scarcity of the available data on these materials in the literature, this section is concluded on some emerging applications of multiphotonic absorption for CPs.

The next section briefly outlines some of the challenges to overcome in order to exploit CPs as new NLO-active materials for various applications. These are (i) obtaining better understanding of the spectral dependence of the various harmonic generation phenomena, (ii) developing better experimental ways to measure the multiphotonic absorption cross-sections in practice, (iii) comparing multiphotonic excitation *vs.* one-photon excitation for temperature or molecular sensing purposes and (iv) exploring the use of ligands subject to aggregation induced emission (AIE) for molecular engineering of CPs. All these points are then specifically addressed in the following section.

The third section, which is the largest of all, contains all the new experimental data acquired during this PhD work on several families of CPs.

It starts with an investigation focused at the spectral resolution of second- (SHG) and third harmonic generation (THG) of CPs obtained from Co(II) ions and tetraphenylmethane-based tetraphosphonate diester ligands. It is convincingly shown that the spectral response of these materials is largely shaped by their self-absorption of the generated harmonic.

Next, the accurate measurement of multiphoton absorption by Z-scan for definite CPs in the visible-near IR range is addressed. In this part, a strong three-photon absorption is evidenced for Prussian Blue at *ca.* 1375 nm, making such CPs potentially interesting for various applications in the telecommunication field. The latter phenomenon results from a net two-photon absorption followed by an excited state absorption (ESA) involving an additional photon. In contrast, two CPs featuring various Co(II) contents, proved nearly inactive when studied by the same technique. These results outline the interest of using Z-scan for studying the nonlinear absorption of colloidal suspensions of CPs.

When luminescent and microcrystalline CPs have to be studied for which no suspension of nanoparticules can be obtained, other techniques are advisable such as "SSTPEF" or "ISTPEF". This is subsequently illustrated through the characterization of multiphoton absorption cross-sections of three families of CPs; (i) fluorescent Eu(II) and Tb(III) centers co-doped CPs obtained from trimesic acid and *o*-phenanthroline; (ii) highly porous metal organic frameworks (MOFs) based on 1,3,6,8-tetrakis(*p*-benzoate)pyrene ligands with In(III), Ga(III) or Al(III) centers and (iii) a related MOF family featuring an extended 1,3,6,8-tetrafunctional pyrene ligand with Zn(II) complexes and 4,4'-bipyridine.

The first family shows temperature-dependent luminescence. It is thus shown that rare-earth co-doped CPs can be conveniently used as thermal probes for remote temperature measurements following either one- or many-photon excitation. For the first time, differences between both modes of excitation were evidenced before being rationalized.

The second family exhibits a remarkably large porosity. It can therefore be conveniently used for molecular luminescence-based sensing purposes. Its two-photon absorption properties were first determined by ISTPEF. Differences in the sensing ability of different functional nitroaromatics were again evidenced depending on whether one- or two-photon excitation was used and these differences were rationalized later on.

The last family of CPs incorporates a tetrafunctional pyrene ligand which undergoes AIE in its free state. It was therefore of fundamental interest to examine if this ligand, once constrained in the MOF, would show an enhanced luminescent quantum yield or not, and this after excitation via either one- or two-photon processes. The two-photon absorption properties were accurately determined by SSTPEF and the luminescence properties were also characterized, revealing that both the two-photon absorption cross-section and the luminescence quantum yield of the ligand in the MOF were consistently lower than these recorded for the free ligand in the aggregated state. This behavior was traced back to an enhanced mobility of the ligand in the MOF compared to its motional freedom in the aggregated state.

As a result, the manuscript of Mr Zaręba is extremely well written with results consistently presented. The discussion is conducted in a very pedagogical way, especially the introduction about the CPs that makes a good parallel with organic polymers. Then, the presentation of nonlinear optical properties and the description of the various NLO phenomena is very well balanced between general notions and specific point of interest pertaining to CPs, such as the role of aggregation on the NLO properties of the constitutive units, keeping the readers interests high. Also, a good understanding of the underlying photophysical problems associated with the determination of the nonlinear optical properties of the CPs is apparent throughout the manuscript. Finally, I also appreciated the very complete bibliographic coverage of the topic, with a unique reference section at the end of the manuscript, rather than many "chapter-by-chapter" bibliographic sections, as often encountered in PhD manuscripts. The Figures and Schemes are clear and well dimensioned for the reader (especially these reporting the various spectra).

Then the most impressive aspect of the interdisciplinary work is its novelty, since, as mentioned in several places in this manuscript, basically not much had been undertaken so far to determine the NLO properties of CPs. As such, Mr Zaręba had to identify the various problems associated with the experimental determination of the NLO parameters of interest, a task often complicated by the poor solubility of the CPs, and to find out ways to express them in such a way that they might be compared to those of related CPs. All these challenges were overcome by Mr Zaręba who used a set of distinct CPs presenting different solubilities and crystallinities. Based on his data, he was able to discuss the advantages of using multiphotonic excitations rather than one-photon excitation for various promising applications involving CPs, such as thermal sensing or molecular sensing. Finally, during the last part of his work, Mr Zaręba could even point out the deleterious effects of the MOF structure on the fluorescence quantum yield and multiphoton absorption cross-section of the tetracarboxylate ligand used as linker. He could even come up with a convincing explanation for the negative effect stated.

Finally, I would like to recall here that Mr Zaręba was in a completely "uncharted territory" while conducting his PhD work. In this respect, this PhD thesis which successfully sums up all the key data of this emerging field and paves the way for addressing these issues in the future is even more valuable. Without surprise, this work has already given rise to six publications in high standard international journals in which Mr Zaręba is first author (and three of which he is also the corresponding author) and some more are apparently to come on the last part of the work (3.2.2.3. and 3.2.2.4.).

Although most of the experimental material presented and discussed in this PhD is largely concerned with physico-chemical or optical measurements, Mr Zaręba has himself prepared most of the CPs that were required for his studies, except for the CPs described in parts 3.2.2.3. and 3.2.2.4. Furthermore, Mr Zaręba has also had a very intense activity in chemistry on topics not related to this work, since he contributed to fifteen other publications since 2013, five of which he was the corresponding author (two as first author). Obviously Mr Zaręba is a hard working student who had lots of experimental results. Remarkably, he was smart enough to select the most telling parts of his work to put this PhD manuscript together.

In conclusion, owing to the novelty of the studies done and their importance for the field of molecular photonics and coordination polymers, I really think that Mr Jan K. Zaręba largely deserves the degree of Doctor of Philosophy in Chemical Sciences and I conclude that he should be admitted to the public defense. Additionally I would like to propose his doctoral thesis for an additional award given its outstanding quality.

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