

UNIVERSITY OF PÉCS

Physics Doctoral School

Nonlinear Optics and Spectroscopy Programme

**Application of fluorescence methods in the
investigation of nanostructures**

PhD thesis

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1. Introduction

The aim of my study was to apply fluorescence spectroscopy on various type of cavitands and SiC nanocrystals (SiC NCs) to accomplish the following tasks:

- Quantitative and qualitative description of the fluorescence quenching in tetrakis(ketocarboxamide)cavitand and anthracene system and the comparison of the applicable models.
- Detailed investigations of UV-light induced fluorescence enhancement of tetra-triazole-pyridazine cavitand and the explanation of this effect.
- Decompose the luminescence spectra of SiC NCs to distinct spectral- and lifetime- components and identify the origin of these components.

As a result of their conformationally rigid cavity, the cavitands have been used as hosts in host-guest complexes, as it makes possible the reversible transport of guest molecules from the solution into the particle cavity and back again. The selective and highly variable functionalization of the basic

deepened cavitand skeleton is a prerequisite for any further applications including molecular recognition and selective transport processes. I intended to elaborate methods for investigation of wide range of cavitand's fluorescence properties. Based on the achieved analysis my aims were the explanation of the revealed behaviour and explore the connection between the function and the structure of the molecules.

SiC NCs are proven to be favorable biological labels due to their good biocompatibility, hemocompatibility and excellent solubility in polar solvents. Moreover, they contain many surface groups that are suitable for further chemical modifications for targeted biomolecules. The aim of my study was to investigate methods which help us to understand the connection between the structure and the luminescence properties of SiC NCs.

2. Summary

The fluorescence lifetime and intensity of anthracene were investigated in the presence of various concentration of newly derived tetrakis(ketocarboxamide)cavitand (cavitand (**1**)). The cavitand (**1**) possess some absorption at the applied excitation wavelength, so the measured values were corrected for this artifact. Both the fluorescence lifetime and intensity decreased as a result of increased concentration of cavitand (**1**). It has been shown, that the cavitand (**1**) causes simultaneous dynamic and prompt quenching of anthracene fluorescence. The dynamic quenching was explained by the collision mechanism, while the Smoluchowski-model of “sphere of action” quenching was applied to describe the contribution of the prompt effect. The derived constants are in good agreement with the corresponding parameters calculated from the size of molecules, and they correlate well to the values previously reported in the literature for other quenchers. The measured quenching indicates weak molecular level interaction between the anthracene and the cavitand (**1**),

however, it does not prove unambiguously the complex formation.

UV-light induced changes in the fluorescence properties of cavitand series were also investigated. As members of this series, the synthetic intermediates leading to a tetra-triazole-pyridazine cavitand were chosen for the investigation. Namely, the parent ('naked') cavitand with methyl substituents at the upper rim only, and multi-level cavitand(s) with additional moieties such as benzene, triazole and substituted pyridazine levels were involved in our experiments. Significant difference in terms of their spectroscopic behaviour was revealed between cavitands (**2**), (**3**), (**4**) and (**5**), (**6a**), (**6b**). Appearing of photoreacting group was characterized by the elevated absorbance of cavitand (**5**) and this effect is more pronounced at (**6a**), (**6b**). The observed changes in the emission spectrum and the increased value of quantum yield as a result of 282 nm light irradiation prove, that cavitand (**6a**) (tetra-triazole-pyridazine cavitand) produces elevated fluorescence emission around the wavelength of 465 nm. The measured quantum yield values of cavitand (**6a**) are in good accordance with the

values available for similar cavitands. In order to quantify the kinetics of cavitand (**6a**)'s fluorescence emission on a long timescale, a proper model was applied (Eq. **Hiba! A könyvjelző nem létezik..**). The model describes the observed behaviour as a sum of an initial intensity and two asymptotically growing term. It seems an established model, that the observed light-induced enhance of the tetra-triazole-pyridazine cavitand's fluorescence intensity is caused by light-triggered transition between its rotational conformational isomers. The presence of two individual emitting species, corresponding to the "Dark" and "Light" state of molecule was confirmed by the analysis of time-resolved fluorescence decay curves. The increase of the fluorescence intensity and the elongation of the average fluorescence lifetime are explained by the efficiency changes of the intramolecular quenching caused by conformational alteration. This hypothesis was evidenced by fluorescence anisotropy decay measurements. Significant increase of rotational correlation time after UV-light irradiation is the hard evidence for UV-light induced conformational change. Computational studies of Tímea Kégl revealed the existence of

two conformational state. Before irradiation, the generality of molecules has tubular structure, while the UV-light irradiation alters this to a merry-go-round geometry. The transition between these conformational states increases both fluorescence lifetime and quantum yield by decreasing the chance of non-radiative relaxation processes, while the absorption spectrum remains basically unaltered.

Time resolved optical properties of various type of SiC nanocrystals (SiC NCs) were investigated in order to identify their luminescent centres. The as-prepared sample served as a reference for the series of measurements. Both SiC NC solved in methanol and SiC NC doped with aluminium were involved in the investigation, moreover a series of SiC NCs treated with different surface reduction methods were investigated in the experiments. TCSPC measurements were successfully achieved to obtain the TRES surfaces of the SiC NCs. The analysis of the constructed TRANES curves revealed the presence of well separated emission centres in all of the samples. With the application of DAS method we went further and we were able

to reconstruct the emission spectra of these centres by using appropriate temporal model. The propriety of DAS method was confirmed by the excellent match between the calculated and the steady-state measured spectra. We demonstrated successful identification of surface- and doping-dependent luminescence centres of SiC NCs. Our method is useful for explanation of the luminescence mechanism in other complex quantum dot and related systems.

3. New scientific results

T1 I measured the fluorescence lifetime of anthracene in the presence of various concentrations of tetrakis(ketocarboxamide)cavitand (cavitand (**1**)). I recorded the fluorescence emission spectra of anthracene in the presence of cavitand (**1**) and I corrected them in order to eliminate the effect of apparent quenching, which is the decline of excitation intensity due the absorption of cavitand (**1**) at the excitation wavelength. Based on the results I proved that the cavitand (**1**) is an efficient quencher of the anthracene's fluorescence. I revealed that both dynamic and prompt

quenching processes are simultaneously involved in the anthracene's fluorescence quenching in the presence of cavitand (**1**). I explained the dynamic quenching by collision and I successfully applied the Smoluchowski's "sphere of action" model to describe the prompt quenching. The parameters provided by the models are in good agreement with the corresponding values calculated from the size of molecules, and they correlate well to the values previously reported in the literature. [S3]

T2 I achieved absorption and fluorescence measurements on the series of cavitands. Based on the results of these measurements I revealed, that in cavitand (**2**), (**3**) and (**4**) both the absorption and the emission is done by the 3-di-alkoxy benzene moieties in the cavitand ring while in cavitand (**6a**) and (**6b**) it is done by the triazole-pyrazine moieties on the rim. [S2]

T3 I demonstrated unexpected fluorescence behaviour of cavitand (**6a**). Its fluorescence emission around 465 nm is significantly enhanced as a result of 282 nm light irradiation

while its absorption remains unaltered. I constructed an empirical model to describe the fluorescence intensity of cavitand (**6a**) during the irradiation. This model correlate well to the observed values on the investigated 0.1-60 min time interval. [S2]

T4 I performed fluorescence lifetime measurements on cavitand (**6a**). These measurements revealed the presence of two individual emitting species with different lifetimes. I proved the light induced conformational changes of cavitand (**6a**) by the analysis of the results delivered by the achieved fluorescence anisotropy decay measurements. I explained the observed UV-light induced fluorescence intensity increase with conformational changes in cavitand (**6a**). Due to light irradiation the arms of cavitand (**6a**) twist out resulting some increase in the volume of the molecule. The increased distance between the arms decrease the probability of intramolecular quenching, it is the reason of the UV-light irradiation induced elevation of fluorescence intensity. [S2]

T5 I recorded Time-Emission Matrices with increment of 10 nm on series of silicon carbide nanocrystals (SiC NCs). Beside the as-prepared, SiC NCs solved in methanol and doped with aluminium and a series of SiC NCs treated with different surface reduction methods were involved in the measurements. I constructed series of Time Resolved Area Normalized Emission Spectra (TRANES) curves, which revealed the presence of well separated emitting centres in all of the samples. [S1]

T6 I applied the Decay Associated Spectra (DAS) method in order to clarify the contribution of separated spectral components to the total fluorescence intensity. I demonstrated, that the spectra from DAS provide essential basic information about the origin of luminescence and with them it is possible to find connection between the emitting centres and the separated spectra. [S1]

4. Publications related to the topics of this thesis

S1:

D. Beke, **T. Z. Jánosi**, B. Somogyi, D. Á. Major, Zs. Szekrényes, J. Erostyák, K. Kamarás, A. Gali

"Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals"

J. Phys. Chem., vol. 120, pp. 685–691, 2016.

<http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.5b09503>

S2:

T. Z. Janosi, G. Makkai, T. Kegl, P. Matyus, L. Kollar, and J. Erostyak

"Light-Enhanced Fluorescence of Multi-Level Cavitands Possessing Pyridazine Upper rim"

J. Fluoresc., vol. 26, no. 2, pp. 679–688, 2016

<http://link.springer.com/article/10.1007/s10895-015-1754-3>

S3:

T. Z. Janosi, J. Korppi-Tommola, Z. Csok, L. Kollar, P. Myllyperkio, and J. Erostyak

"Anthracene Fluorescence Quenching by a Tetrakis (Ketokarboxamid) Cavitand"

J. Spectrosc., vol. 2014, pp. 1–8, 2014.

<http://www.hindawi.com/journals/jspec/2014/708739/>