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Photophysical properties and intracomplex energy transfer of complexes of quantum dots and chlorin e6 in organic solution

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Photodynamic therapy (PDT) is an effective and delicate method of treating cancer. PDT is based on the ability of special molecules of organic photosensitizers to selectively accumulate in tumor tissues and being excited to destroy tumor cells because of singlet oxygen (SO) generation. The major advantages of PDT are: it is inexpensive and noninvasive therapy approach, and it can be applied locally without cumulative toxicity effect [1, 2]. Tetrapyrrole molecules, for example chlorin e6, that is a typical PDT drug, are bright representatives of photosensitizer molecules. Although tetrapyrroles are now widely used in biomedical applications, they have several disadvantages. Careful selection of excitation source is needed due to narrow absorption bands of tetrapyrroles. They have also a limited capacity for accumulation in cancer cells, slow elimination from the body and poor solubility in water [3]. Therefore, the development of new drugs for PDT that would have improved properties is extremely important [4].. Combining a tetrapyrrole molecules with semiconductor quantum dots (QDs) in one moiety can help to overcome the limitations and restrictions of traditional photosensitizers and will result in more efficient and safer PDT drugs.

QDs have been extensively used now for biomedical applications as biomarkers for molecular diagnostics, tumor imaging and ultrasensitive in vitro assays. QDs have unique optical properties among nanosized materials, such as high quantum yield of photoluminescence (PL), broad absorption spectrum, narrow and sharp PL spectrum and long PL lifetime. The high brightness of PL QDs is a result of high molar adsorption coefficients (several times higher than those of fluorescent dyes and proteins). The surface of an inorganic nanocrystal plays an important role in the determining of its structural, optical, thermodynamic, and transport properties, high photo- and chemical stability, along with the ease of surface modification, it allows the formation of hybrid nanostructures with molecules of photosensitizes on their basis [5]. It is proposed to use QDs as effective energy donors, providing “indirect excitation” of tetrapyrrole molecules through Förster resonance energy transfer (FRET), increasing the generation of singlet oxygen by tetrapyrrole molecules in complexes with QDs [6].

We present the results of the study of complexes of CdSe/ZnS QDs with photosensitizer Ce6 (QD/Ce6). QD/Ce6 complexes have been formed and characterized by stationary absorbance and PL spectroscopy combined with single photon correlation microscopy in tetrachloromethane. We demonstrate the falling dependence of FRET efficiency on chlorin e6 concentration due to Ce6 aggregation on the QD surface, while an optimization of QD/Ce6 complexes, i.e. for QD/Ce6 complexes with three Ce6 monomer molecules per QD, allows doubling SO concentration generated by the complexes in comparison of free Ce6 molecules that is demonstrated in Figure.

The Figure demonstrates SO luminescence spectra registered from the solutions of free Ce6 molecules and QD/Ce6 complexes with the same Ce6 concentration. The PL was excited at 405 nm, PL signals from QDs and Ce6 were cut off using filters.

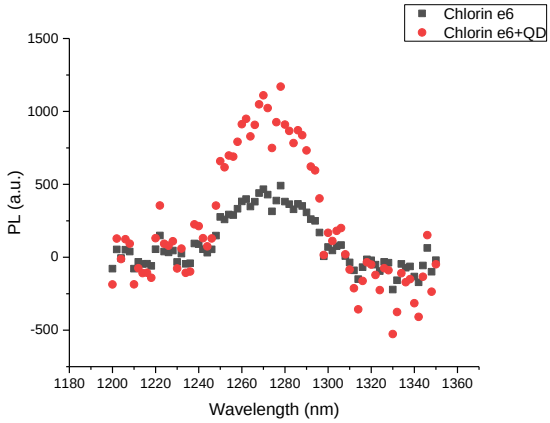

Figure. Luminescence spectra of singlet oxygen generated by samples of Ce6 (black squares) and QD/Ce6 complex (red circles) solutions; the excitation wavelength was 405 nm

In the course of developing new efficient PDT drug based on QDs, we are going to make fully biocompatible QD/Ce6 complexes using chitozan molecules as stabilizing agent and test their impact in living cancer cells.

References:

1. Charron, G., et al., *Insights into the mechanism of quantum dot-sensitized singlet oxygen production for photodynamic therapy*. The Journal of Physical Chemistry C, 2012. **116**(16): p. 9334-9342.
2. Zenkevich, E.I., et al., *Quantitative analysis of singlet oxygen (1O2) generation via energy transfer in nanocomposites based on semiconductor quantum dots and porphyrin ligands.* The Journal of Physical Chemistry C, 2011. **115**(44): p. 21535-21545.
3. Allison, R.R., et al., *Photosensitizers in clinical PDT*. Photodiagnosis and photodynamic therapy, 2004. **1**(1): p. 27-42.
4. Visheratina, A., et al., *Water-Soluble Conjugates of ZnS: Mn Quantum Dots with Chlorin e6 for Photodynamic Therapy*. Optics and Spectroscopy, 2018. **125**(1): p. 94-98.
5. Martynenko, I.V., et al., *Energy transfer in complexes of water-soluble quantum dots and chlorin e6 molecules in different environments.* Beilstein journal of nanotechnology, 2013. **4**: p. 895.
6. Douda, J., et al., *Synthesis and characterization of II–VI (CdSe) quantum dot encapsulated liposomes.* Journal of Materials Science: Materials in Electronics, 2018: p. 1-9.