

Influence of gold nanostructures on excited state intramolecular proton transfer in multidomain HTTH dye

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Abstract. Organic multidomain dyes exhibiting excited state intramolecular proton transfer (ESIPT) are known due to large Stokes shifts and dependence of their luminescence spectral characteristics on the properties of the environment. In this work, influence of gold nanostructures on the spectral characteristics of a “polycarbonate matrix – gold nanostructures – HTTH” system was studied using thiazole dye HTTH as an example. A hypothesis about the possibility of plasmon resonance energy transfer (PRET) between the HTTH molecules in different states, namely the ground state (enol form) and the state after proton transfer (keto form), mediated by gold nanostructures was experimentally tested. Presence of gold nanostructures in the vicinity of HTTH molecules was found to lead to the changes in the ratio of the luminescence peak intensities for the enol and keto form of these molecules. This phenomenon opens up the possibility of additional regulation of the spectral characteristics and may evidence the PRET effect in the systems containing ESIPT-exhibiting dyes and plasmonic nanostructures. The obtained results improve our understanding of the physical processes in the systems similar to the studied one and imply new practical applications of them such as fabrication of organic light-emitting diodes, sensors, super-resolution microscopy tools and ultraviolet-to-visible radiation convertors.

Keywords: excited state intramolecular proton transfer, gold nanostructures, luminescence, plasmon resonance energy transfer.

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1. Introduction

Excited state intramolecular proton transfer (ESIPT) is a four-level photo-chemical process discovered by Weller [1]. For dyes exhibiting ESIPT phenomena, two forms of radiation are possible: photoluminescence without proton transfer (enol form) and with proton transfer (keto form), which correspond to two different molecular structures. The characteristic feature of the keto-form luminescence is the large Stokes shift of more than 200 nm (Fig. 1).

As a molecule is photoexcited, a proton can very quickly (within less than 10^{-12} s) move from an oxygen atom to a nitrogen one. After that, the molecule changes to the ground state by emitting light and returns to the initial state after reverse proton transfer [2–4]. This phenomenon can be influenced by the environment such as by external electromagnetic field [5].

Localized surface plasmon resonance (LSPR) is known to induce a near-field enhancement in the vicinity of a metallic nanostructure [7]. Therefore, possible influence of plasmonic nanostructures on ESIPT has to be studied. It should be also remembered that the LSPR phenomenon may lead to both enhancement and quenching of photoluminescence [7] as well as provide conditions for plasmon resonance energy transfer (PRET) [8].

Recently, a possibility of applying multidomain dyes for monitoring stability of nanoparticle coatings was investigated [9]. It was demonstrated that damage of the polymer coating on gold nanoparticles containing ESIPT-exhibiting dye can be detected with high sensitivity. Moreover, this result was confirmed for the systems with donor and acceptor dyes interacting *via* the Forster resonance energy transfer (FRET) mechanism. Such dyes were used to combine ESIPT, FRET and aggregation-

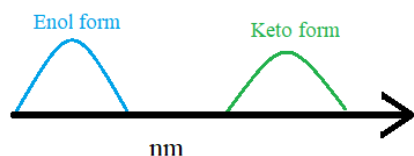


Fig. 1. Difference between the enol-form and keto-form luminescence spectra.

induced emission effects in order to create systems for artificial light harvesting [10]. Recently, a combination of the ESIPT and FRET phenomena as well as nanostructures in combination with ESIPT dyes and polymer films were used. It was shown in [11] that imaging with the resolution near 70 nm, which exceeds the light diffraction limit, is possible using ESIPT dyes in poly(methyl methacrylate) films with polycaprolactone nanostructures. Hence, it would be reasonable to study the systems with ESIPT dyes and nanostructures to extend our understanding of the physical processes in such systems, which may contribute to the respective research field and have practical implications.

Usually, the ESIPT phenomenon is considered as a separate case of resonance transfer, because, unlike PRET or FRET, the transferred object is a proton, not energy. This is true, but in a real system ESIPT dye molecules can exist in two different states and energy transfer between them (from enol form to keto form) may be possible *via* the FRET or PRET mechanism, leading to the increase of the contribution of keto-form photoluminescence.

From this point of view, one would see combination of the ESIPT and FRET mechanisms, where enol-form dye is a donor and keto-form dye is an acceptor [12–19]. If two such dye molecules are located near the gold nanostructure (Fig. 2), the PRET mechanism may also become possible [20–25]. At this, the interaction will be mediated by a localized surface plasmon of the nanostructure. As a result, resonance energy transfer between two dye molecules in different forms may occur *via* the nanostructure, leading to a competition between the ESIPT and PRET mechanisms and a rise in the peak intensity of keto-form photoluminescence.

2. Materials and methods

In order to test this hypothesis, a system consisting of an array of gold nanostructures on a glass substrate (nanochip) covered with a layer of polycarbonate matrix containing the saturation concentration of HTTH dye as well as a control sample containing no gold nanostructures have been fabricated.

By thermal heating and cooling of the system, dye molecules have been brought closer to the gold nanostructures. Diffusion in polycarbonate matrix is enhanced due to the increase of the system temperature. This leads to both faster diffusion of the dye molecules to the gold nanostructures and transfer of the latter from the nanochip into the polycarbonate matrix. An advantage of the diffusion mechanism is that the morphology of the

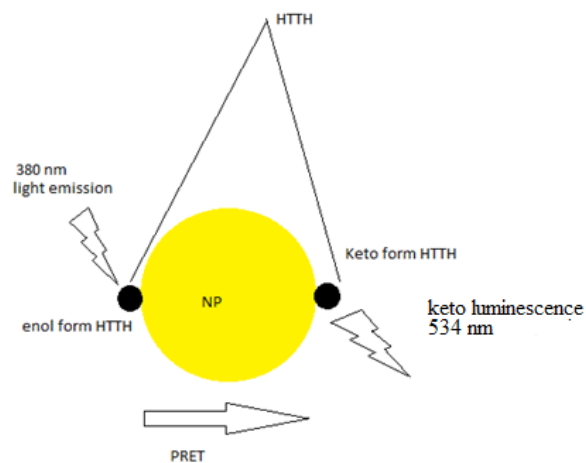


Fig. 2. Schematic representation of the HTTH dye molecule excited in the enol form and energy transfer to the HTTH dye molecule in the keto form *via* the PRET mechanism.

gold nanostructures remains almost unchanged, while the transfer takes place from one environment to another [26]. Since the diffusion mechanism is sensitive to the temperature, concentration gradients, and shape and size of both nanostructures and dye, a saturated diffusion level exists that limits the concentration of dye molecules near the gold nanostructures [26]. At the same time, this mechanism enables the release of the gold nanostructures from the surface of the glass substrate practically unchanged [26, 27].

Generally, nanostructures can absorb hydrogen [28] when they approach dye molecules. This process, however, is very slow and not important in our case, when the measurement time is less than 10 min.

3. Experimental

Nanochips were fabricated by thermal annealing of gold island films. This technique allows producing random arrays of gold nanostructures with the sizes and LSPR spectral positions in a wide range [29]. In this work, the nanochip obtained from a gold island film with the thickness 12 nm, which provides the LSPR wavelength position after annealing at about 550 nm [30] was used.

In the present research, we used the ESIPT-exhibiting dye 2,2'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(4-tert-butylphenol) (HTTH) synthesized by our colleagues from Taiwan [4]. The structure of this dye molecule is shown in Fig. 3.

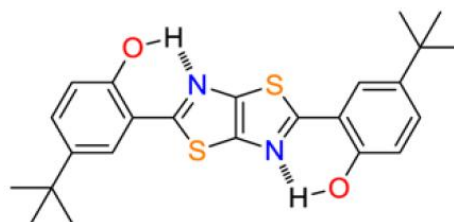


Fig. 3. Structure of HTTH molecule.

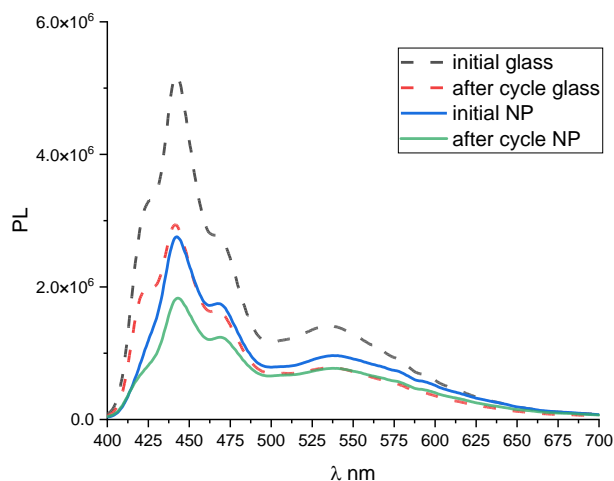


Fig. 4. Photoluminescence spectra of the “polycarbonate matrix – gold nanostructures – HTTH” system on the nanochip (solid lines) and the control sample on glass (dashed lines) in the initial state and after the thermal treatment cycle. (Color online)

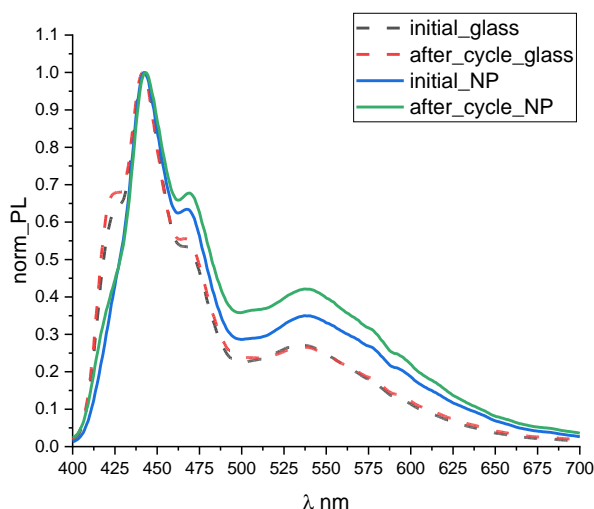


Fig. 5. Photoluminescence spectra of the “polycarbonate matrix – gold nanostructures – HTTH” system on the nanochip (solid lines) and the control sample on glass (dashed lines) in the initial state and after the thermal treatment cycle, normalized by the intensity of the central peak at 442 nm. (Color online)

To study the influence of gold nanostructures on the ESIPT phenomenon, a sample of the nanocomposite material “polycarbonate matrix – gold nanostructures – HTTH” was fabricated as follows. A solution of polycarbonate (class “crystal clear”) and HTTH dye (at the saturation concentration) in toluene (purity $\geq 99.7\%$) was applied onto the nanochip with the gold nanostructures using a pipette. A 100 μl solution was used to cover the nanochip surface of 1×2 cm, followed by drying at the room temperature for 90 min. The same method was applied to produce the control sample.

Photoluminescence excitation and emission spectra (the excitation wavelength is 380 nm) of the prepared samples were measured using the Shimadzu RF-6000 spectrofluorophotometer. Long exposures may lead to

degradation of the polycarbonate surface layer [31]. However, such degradation may be neglected for the short measurement time of 2 min used by us.

During the next step, the samples were heated on a heating plate at the temperature of 100 $^{\circ}\text{C}$ for 3 min and then cooled in a refrigerator at the temperature of 5 $^{\circ}\text{C}$ for 2 min in order to stabilize the sample parameters. After that, photoluminescence excitation and emission spectra were measured again for both samples.

4. Results and discussion

As a result of the experiment, a set of photoluminescence spectra of the “polycarbonate matrix – gold nanostructures – HTTH” system on the nanochip and the control sample on glass were obtained (Fig. 4). Different intensities of the spectra complicate the analysis of the spectral components and their comparison for different samples. Therefore, the peaks were additionally normalized.

After normalizing by the intensity of the central peak at 442 nm (Fig. 5), it is evident that the intensity of the keto-form peak grows after thermal treatment in the presence of gold nanostructures. At the same time, the photoluminescence spectra of the control sample are almost the same before and after the thermal treatment. One can also see that the keto-form peak for the system on the nanochip has a higher intensity in both cases. It is worth noting that the highest energy peak for the sample on the nanochip is completely quenched.

Additional characterization of the samples was performed by measuring photoluminescence excitation spectra with subsequent normalization by the intensity of the central peak at 386 nm. The intensity of this peak correlates with the one of the peak at 442 nm according to the Levshin rule (Fig. 6).

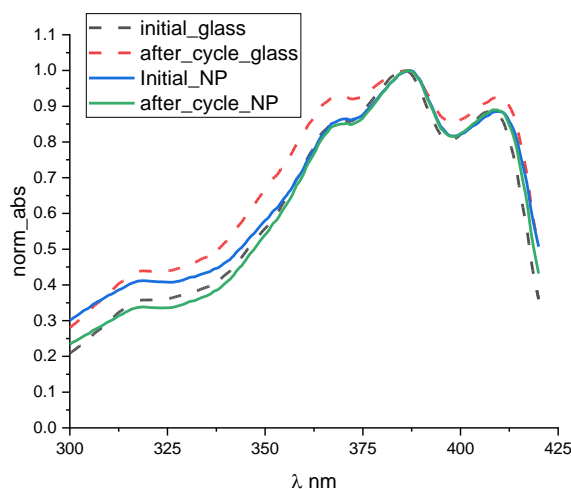


Fig. 6. Photoluminescence excitation spectra of the “polycarbonate matrix – gold nanostructures – HTTH” system on the nanochip (solid lines) and the control sample on glass (dashed lines) in the initial state and after the thermal treatment cycle, normalized by the intensity of the central peak at 386 nm. (Color online)

It can be seen that the photoluminescence excitation spectrum of the control sample changed after the thermal treatment cycle (Fig. 6, dashed lines), which was manifested by the increase of the peak intensities in a way that brought the other peaks closer to the central one. However, this had no significant influence on the photoluminescence emission spectra according to the Kasha rule. Moreover, all the measured photoluminescence excitation spectra exhibit the peak near 320 nm correlated with the keto-form emission peak at 538 nm. At this, the intensity of this peak after the thermal treatment cycle decreased only for the sample with gold nanostructures. This implies that the PRET phenomenon has a significant influence on the “polycarbonate matrix – gold nanostructures – HTTH” system, which is manifested by the enhancement of the photoluminescence of HTTH molecules in the keto part of its spectrum.

5. Conclusions

Influence of gold nanostructures on the spectral characteristics of photoluminescence of the nanocomposite material “polycarbonate matrix – gold nanostructures – HTTH” was experimentally determined. Presence of gold nanostructures was found to lead to the increase of the low-energy photoluminescence peak intensity, which is related to the keto form of the HTTH molecule. After bringing the HTTH molecules closer to the gold nanostructures by diffusion, this influence further increased. This finding confirms that resonance energy transfer between an HTTH molecule in the normal (enol) form and an HTTH molecule in the keto form mediated by a plasmonic nanostructure, essentially PRET, is possible. Hence, a dye molecule stays longer in the keto form, which is supported by the energy donated by a dye molecule in the enol form.

A decrease in the intensity of the photoluminescence excitation peak, which is related to the keto form of the HTTH molecule, was registered after the thermal treatment cycle. Accompanied by the increase in the intensity of the keto-form photoluminescence mentioned above, this phenomenon is explained by the growing influence of PRET. In general, the presented experimental results confirm the hypothesis that the HTTH molecule can be a donor or acceptor in different forms, which agrees with the results published in [10]. The experiments have shown that the ESIPT phenomenon can be involved in more than just the transfer of a proton in an excited molecule, and ESIPT-exhibiting molecules in different forms can be organized into new systems with complex interaction mechanisms.

This peculiarity paves the way toward manipulation of the spectral characteristics *via* the PRET effect in the systems containing ESIPT-exhibiting dyes and plasmonic nanostructures. The presented results improve our understanding of the physical processes in such systems and may be useful for practical applications such as fabrication of organic light-emitting diodes, sensors, super-resolution microscopy tools and ultraviolet-to-visible radiation convertors.

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Вплив наноструктур золота на внутрішньомолекулярний перенос протона у збудженому стані у багатодоменному барвнику НТТН

I.I. Гудзенко, А.М. Лопатинський, В.І. Чегель

Анотація. Органічні багатодоменні барвники, для яких характерний внутрішньомолекулярний перенос протона у збудженому стані (ВППЗС), відомі великими стоксовими зсувами та залежністю спектральних характеристик люмінесценції від властивостей навколишнього середовища. У цій роботі на прикладі тiazольного барвника НТТН проведено дослідження впливу наноструктур золота на спектральні характеристики в системі: «полікарбонатна матриця – наноструктури золота – НТТН». Експериментально перевірено гіпотезу про те, що між різними формами барвника – в основному стані (енол-форма) і після переносу протона (кетон-форма) – можливий ефект плазмон-резонансної передачі енергії (ПРПЕ) за участю наноструктур золота. Встановлено, що наявність наноструктур золота в околі молекул НТТН приводить до зміни співвідношення інтенсивностей піків люмінесценції, характерних для кетон- та енол-форм молекули барвника. Ця особливість відкриває можливості додаткового регулювання спектральних властивостей, а також може свідчити про можливий ефект ПРПЕ у системах, у яких відбувається явище ВППЗС та які містять плазмонні наноструктури. Отримані результати сприяють кращому розумінню фізичних процесів у таких системах та можуть покращити ряд практичних застосувань у виготовленні органічних світлодіодів, сенсорів, мікроскопії з надвисоким розширенням та для переведення випромінювання з ультрафіолетового спектра до видимого.

Ключові слова: внутрішньомолекулярний перенос протона у збудженому стані, наноструктури золота, люмінесценція, плазмон-резонансна передача енергії.