

Concentration-dependent spectral rearrangement of photoluminescence in the nanocomposite material “polycarbonate matrix – gold nanostructures – multidomain HTTH dye”

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Abstract. In this work, the thiazole organic multidomain dye HTTH, which exhibits excited state intramolecular proton transfer (ESIPT) phenomenon, is used as a sample to investigate the influence of the component concentration of the “polycarbonate matrix – gold nanostructures – HTTH dye” system on its photoluminescence spectral characteristics. A hypothesis that different forms of the dye, such as enol form (in the ground state) and keto form (after proton transfer), may be involved in Förster resonance energy transfer (FRET) and plasmon resonance energy transfer (PRET) mediated by gold nanostructures was experimentally verified. The concentration dependence and spectral rearrangement in the photoluminescence of the developed thin-film nanocomposite based on gold nanostructures and HTTH with a transverse concentration gradient were demonstrated and explained by the efficiency of FRET and PRET phenomena depending on the system parameters. The ascertained features open up the possibility of additional manipulation of the spectral properties of the system based on ESIPT-exhibiting molecules by optimization of their parameters, particularly the concentration of components.

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

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1. Introduction

The excited state intramolecular proton transfer (ESIPT) phenomenon was discovered by Weller in molecules of salicylic acid and its derivatives [1, 2]. It is a four-level photochemical process that occurs in compounds with a special structure (for example, in organic dyes), in which the hydrogen atom is valence bonded to nitrogen or oxygen and through a hydrogen bond to nitrogen or oxygen (Fig. 1). Accordingly, four possible variants of the proton transfer in the excited state of the molecule are possible: from nitrogen to nitrogen, from nitrogen to oxygen, from oxygen to oxygen or from oxygen to nitrogen. During the process, an excited hydrogen atom transforms its valence bond in the ground state into a hydrogen bond, and a hydrogen bond is transformed into a valence bond, after which the luminescence in the excited state and reverse proton transfer occur [3, 4]. The ground state of the molecule is called the enol form

and the excited state is called the keto form, therefore, luminescence without proton transfer in such molecules is called enol luminescence, and in the case of proton transfer of the molecule it is called the keto luminescence. A significant Stokes shift distinguishes the keto luminescence because the energy is used to transform the chemical bonds [5]. It is known that the ESIPT phenomenon can be affected by the external electromagnetic field, chemical environment, *etc.* [6]. In particular, metal ions usually block the ESIPT phenomenon completely [7].

Since the external electromagnetic field influences this phenomenon, it would be especially interesting to consider the effect of gold nanostructures in the localized surface plasmon resonance (LSPR) excitation mode, because an enhanced near field is induced around such nanostructures [8]. For this, the organic dye 2,2'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(4-tert-butylphenol) (HTTH) [9] (Fig. 2), which exhibits ESIPT properties and emits light within the spectral range corresponding to

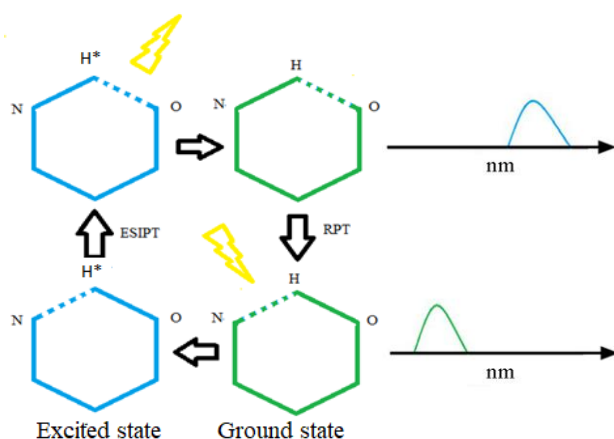


Fig. 1. Illustration of the ESIPT phenomenon: molecular structure transformation (left) and corresponding luminescence spectra (right).

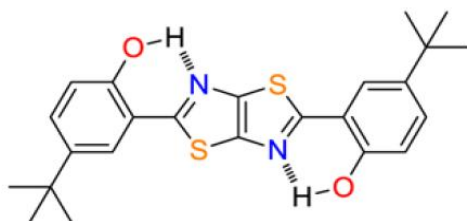


Fig. 2. Molecular structure of the HTTH dye.

the LSPR spectrum of the gold nanostructures, can be used [10]. In addition, it is worth noting that the LSPR phenomenon can cause the enhancement as well as quenching of the luminescence of molecules near metal nanostructures [11].

As shown in [12], ESIPT-exhibiting dyes can be used to detect the damage in the shell around nanostructures. An interesting finding in this work is that the donor-acceptor systems, between which Förster resonance energy transfer (FRET) is possible, were used as a control sample that showed similar results to those of ESIPT-exhibiting dyes, but with a slightly slower reaction time. The FRET is a resonant mechanism of the nonradiative energy transfer due to a dipole-dipole interaction between a donor and an acceptor at nanometer distances [13, 14]. Therefore, it will be appropriate to investigate whether similar processes occur between ESIPT-exhibiting dyes, where the donor is a dye molecule in the enol form and the acceptor is a dye molecule in the keto form. In this case, for high concentrations of dye molecules, the FRET phenomenon will be possible, which will enhance the keto luminescence and weaken the enol luminescence (Fig. 3).

It is known that if light-absorbing molecules are located near the noble metal nanostructures and irradiated with the LSPR wavelength, the plasmon resonance energy transfer (PRET) phenomenon is possible [15–18]. This mechanism is a case of FRET, which extends the range of interaction between donor and acceptor *via* the plasmonic nanostructure [19]. Therefore, this mechanism of resonance energy transfer is also called plasmon-coupled resonance energy transfer (PC-RET) [20].

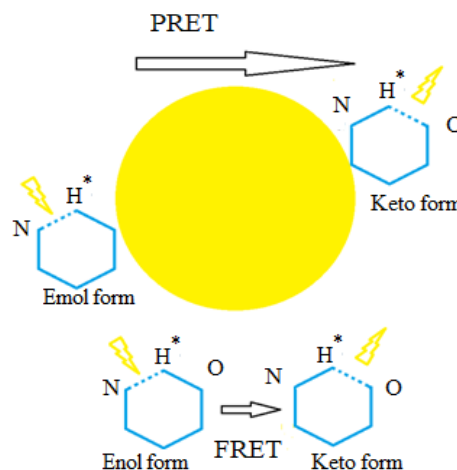


Fig. 3. Proposed illustration of the keto luminescence enhancement phenomenon *via* FRET and PRET mechanisms.

Our previous paper [21] considers the phenomenon of ESIPT in the organic dye HTTH in the context of FRET and PRET resonance energy transfers. If the FRET is possible between donor (in ESIPT “off” state) and acceptor (in ESIPT “on” state) of HTTH molecules, then the plasmonic nanostructures can enhance energy transfer by increasing the radius of possible dipole-dipole interaction between enol and keto forms of HTTH molecules in the role of donor and acceptor. However, the distances between the molecules in enol and keto forms may exceed the distance sufficient for resonance transfer due to FRET and/or PRET, in which case two options should be considered. If the concentration of molecules is insufficient to activate the FRET mechanism but is sufficient to activate the PRET mechanism, then a significant increase in keto luminescence should occur. If the concentration of molecules is low for the effective occurrence of both resonance transfer phenomena, then only the absorption of the luminescent radiation of nanostructures within the LSPR spectral band of plasmonic nanostructures will be manifested. Therefore, in this work, we investigate the dependence of ESIPT spectral features on the concentration of HTTH dye and plasmonic nanostructures.

2. Experimental

To test the hypothesis, two samples containing HTTH dye in a thin-film matrix were created: one on a glass substrate with size 10×20 mm and the other on the same size glass substrate with a random array of gold nanostructures located on the surface (a nanochip), after which the matrices were detached from the substrates. The nanochip (Fig. 4) was manufactured using the method of thermal annealing of gold island films [22], which provided the LSPR position at a wavelength close to 550 nm [23].

The following protocol was used to prepare the HTTH-containing thin film matrix. In 150 ml saturated solution of HTTH in toluene (purity ≥ 99.3%), 4.4 g of polycarbonate (according to ISO 10993-1 standards) was dissolved. After that, 1000 μl of the solution was applied to the surface of each sample with further complete drying. After detaching of the prepared polycarbonate

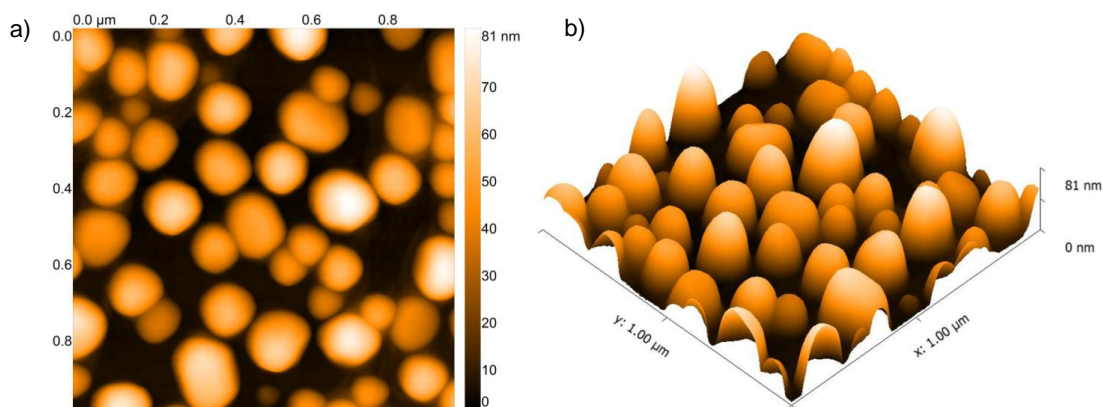


Fig. 4. AFM images of the glass substrate covered with a random array of gold nanostructures (a nanochip) [23]. (Color online)

matrix with HTTH from the substrate, two samples were obtained, the characteristics of which differ by the concentration gradient of both HTTH and gold nanostructures. First, the side of the sample that was adjacent to the substrate had a higher concentration of HTTH dye, while the outer side was formed with a lower concentration of HTTH because the HTTH dye solution in toluene is saturated and it precipitates when the solvent dries. Second, in the case of a nanochip as a substrate, a sample was obtained with a large concentration of plasmonic nanostructures on the inner side and with its small number on the outer surface, due to desorption and subsequent diffusion.

Photoluminescence spectra of the obtained samples were measured (at the excitation wavelength 380 nm) on both sides of the obtained matrices using a Shimadzu RF-6000 spectrofluorophotometer. To compare the results, the spectra were normalized on the intensity of the central peak, since it is the least dependent on the enol or keto form of the luminescent molecule. The samples were measured within a time that does not exceed 20 s for each sample, so the influence of the excitation light on the structure of the matrix can be neglected.

3. Results and discussion

Fig. 5 shows the photoluminescence spectra measured for each side of the polycarbonate plastic matrices with HTTH molecules made using a nanochip with gold nanostructures and an ordinary glass substrate. It is worth noting that the intensity of the peaks in the luminescence spectra is different for each of the cases being considered. So, to reveal how exactly the gold nanostructures affected the photoluminescence, the spectra have been normalized on the intensity of the peak at 442 nm.

The distribution of the intensity of the photoluminescence peaks (Fig. 6) shows that both the matrix created on a nanochip with gold nanostructures and the matrix created on a glass substrate have a common feature that the peak of keto luminescence has a greater intensity in the spectrum of the inner side (adjacent to the substrate).

The mentioned difference in the peak intensity in the spectra of the inner and outer sides of the polycarbonate matrix is the manifestation of the influence of the concentration of the HTTH dye molecules on the ESIPT phenomenon. Namely, the increase in the intensity of the keto-luminescence peak can be explained by the occurrence or the strengthening of effectiveness of the FRET phenomenon between HTTH molecules in the enol form as a donor and HTTH molecules in the keto form as an acceptor at the increasing of their concentration.

In addition, it was found that the intensity of the keto-luminescence peaks is higher in the spectra of polycarbonate matrix with HTTH containing gold nanostructures compared to the same matrix without nanostructures (Fig. 6). This circumstance, as well as the fact that the difference between the intensities of the keto-luminescence peaks for the inner and outer sides of the polycarbonate matrix is larger at the presence of nanostructures, shows that gold nanostructures also affect the ESIPT phenomenon.

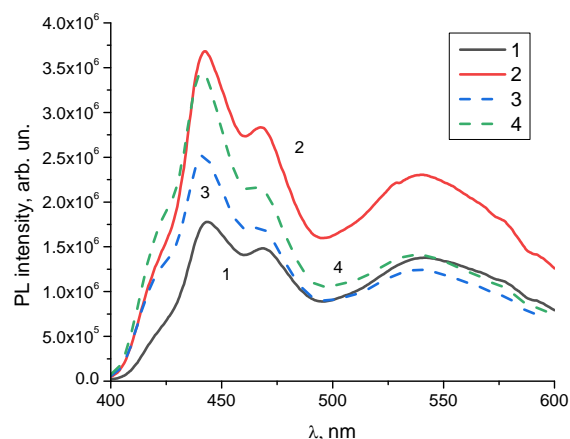


Fig. 5. Room-temperature photoluminescence spectra of polycarbonate matrix with HTTH containing (solid lines 1 and 2) and not containing (dashed lines 3 and 4) gold nanostructures, measured from the side adjacent to the substrate (lines 1 and 3) and outside of the samples (lines 2 and 4). (Color online)

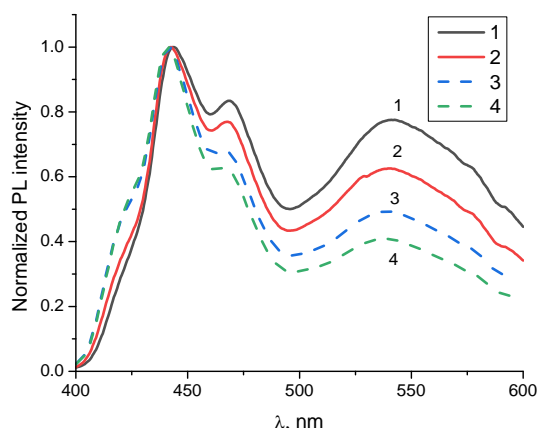


Fig. 6. Normalized photoluminescence spectra of polycarbonate matrix with HTTH containing (solid lines 1 and 2) and not containing (dashed lines 3 and 4) gold nanostructures, measured from the side adjacent to the substrate (lines 1 and 3) and outside of the samples (lines 2 and 4). (Color online)

Thus, we can assume that the additional increase in the intensity of keto-luminescence is caused by the PRET mechanism in the presence of gold nanostructures and depends on their concentration.

4. Conclusions

The influence of gold nanostructures on the photoluminescence spectral characteristics of the nanocomposite material “polycarbonate matrix – gold nanostructures – HTTH dye” was experimentally shown. The nanocomposite thin film with a transverse gradient of the component concentration exhibits the different intensities of the keto-luminescence of HTTH measured in opposite surfaces of the polycarbonate matrix. The redistribution in the photoluminescence bands intensity in the spectra of the polycarbonate matrix with HTTH in the presence of gold nanostructures was observed. The noted redistribution can be explained by the complex of the following factors: the concentration of HTTH molecules and gold nanostructures, and the efficiency of the FRET and PRET resonance energy transfer phenomena. Thus, the optimization of the parameters of the systems based on ESIPT-exhibiting molecules, particularly, the concentration of components, will potentially allow control of the rearrangement of their luminescence spectral properties within wide limits.

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Концентраційно-залежна спектральна перебудова фотолюмінесценції у нанокompозитному матеріалі «полікарбонатна матриця – наноструктури золота – багатодоменний барвник НТТН»

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Анотація. У цій роботі на прикладі тіазольного органічного багатодоменного барвника НТТН, який виявляє властивість внутрішньомолекулярного переносу протона у збудженому стані (ВППЗС), проведено дослідження впливу наноструктур золота на спектральні характеристики фотолюмінесценції системи «полікарбонатна матриця – наноструктури золота – НТТН» в залежності від концентрації її компонентів. Експериментально перевірено гіпотезу про те, що між різними формами барвника – в основному стані (енол-форма) і після переносу протона (кето-форма) – можливі ефекти ферстерівської резонансної передачі енергії (ФРПЕ) та плазмон-резонансної передачі енергії (ПРПЕ) за участю наноструктур золота. З використанням розробленого тонкоплівкового нанокompозиту на основі наноструктур золота та НТТН з поперечним градієнтом концентрації компонентів продемонстровано концентраційну залежність та спектральну перебудову фотолюмінесценції системи, що визначаються ефективністю явищ ФРПЕ та ПРПЕ в залежності від параметрів системи. Ці особливості відкривають можливості додаткового регулювання спектральних властивостей систем на основі молекул, що демонструють ВППЗС, шляхом оптимізації їх параметрів, зокрема, концентрації компонентів.

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