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Perylene derivative dyes luminescence in polysiloxane matrix in presence of gold nanoparticles

Perylene derivatives, including 1,6,7,12-tetrachloroperylene-3,4,9,10-tetradicarboxydianhydride *(dye I) and* 3,4:9,10-bis(1,2-benzimidazole)- 1,6,7,12-tetra(4-tert-octylphenoxy) perylene (syn/ anti-isomers) (dye III), were used for preparation of polysiloxane samples (PSi) containing different concentrations of gold nanoparticles (GN). Dyes I and III demonstrate significant fluorescence enhancement upon addition of GN independent on excitation energy. For Lumogen Red composition in PSi some increase of fluorescence intensity was observed upon addition of small concentrations of GN while further increase of GN concentration quenches fluorescence. The increase of Lumogen Red emission intensity which is depending on energy of excitation is probably due to increase of radiation decay rate since excitation rate decreases. Effect of GN for Lumogen Orange was expressed as quenching of fluorescence even at small concentrations of GN. Calculations at DFT level of approximation for dye III suggest location of GN in plane of perylene core for observed fluorescence enhancement.

Key words: Perylene derivative dyes, gold nanoparticles, surface plasmon resonance, fluorescence enhancement.

1. Introduction

Metallic nanoparticles play important role in many different scientific and technological fields like photography [1], catalysis [2], medicine [3], electronic devices [4], data storage [5] and spectroscopy [6].

Nanoparticles of noble metals demonstrate unique optical properties due to surface plasmon resonance (SPR), which refers to collective coherent oscillation of free electrons in resonance of electromagnetic wave. Plasmon oscillation is considered as photon confined in nanosized space of metallic particle. SPR leads to strong absorption or scattering of light by nanoparticles at resonance frequency. Collective oscillation of free electrons creates local electric field.

In case of presence of luminescent material in local electric field the rates of absorption and excitation may change and that leads to change of radiative and non-radiative decay rates and quantum yield. If the wavelength of SPR overlaps spectrum of absorption of luminescent material then the rates of absorption and excitation increase [7]. These interactions were the subjects of theoretical [8] and experimental [9–12] studies.

This mechanism provides possibility to extend the range of application of luminescent materials, which may be used in luminescent solar concentrators in order to collect long-wavelength light.

We have considered effect of presence of GN on the fluorescent properties of perylene derivative dyes. The reason for using of GN is that there is a great number of published results devoted to application of metal nanoparticles. For instance, in paper [13] the review on spectral properties of nanoparticles of transition metals is presented as well as the potential of their application for luminescent solar concentrators (LSC). In [14] authors have demonstrated enhancement of fluorescence intensity of the dye Lumogen F Red 305 in presence of GN. In papers [15, 2] this effect is considered in detail, particularly effect of distance between GN and a dye on fluorescence intensity enhancement. The results and methods of study represented in these works demonstrate that application of GN allows to achieve significant enhancement of dyes fluorescence thus increasing the efficiency of LSC. Perylene derivative dyes demonstrate relatively high photostability, ability to emit light in long wavelength region therefore this type of dyes could be a good candidates for LSC application.

In this paper for the first time we present data on luminescent properties of some perylene derivative dyes in PSi composition with GN. Such materials may be used in LCS with high efficiency.

2. Material and methods

2.1 Chemicals

Dye 1,6,7,12-tetrachlorperylene-3,4,9,10-tetradicarboxydianhydride, CAS # 156028-26-1 was purchased from Synthon Chemicals GmbH&Co, Mw 530, 1g/mol.

o-Phenylendiamine, Cat. #P23938; Propionic acid, Cat.#P1386; Potassium carbonate, Cat.#P5833; 1-Methyl-2-pyrolidinon, Cat.# 443778; Silica gel, Cat.# 236802; 4-tret-Octylphenol, Cat.# 290823; Chloroauric acid, Cat.# 50790 were purchased from Sigma-Aldrich GmbH.

Components of PSi RTV141A and RTV141B were purchased from Rhodia Silicones.

1.2 Synthesis

1.2.1 Intermediate product 3,4:9,10-bis(1,2-benzimdazole)-1,6,7,12-tetrachlorperylene (Sin and Anti isomers) (II).

1,6,7,12-tetracholperylene-3,4,9,10-tetradicarboxydianhydride (2 g, 3.8 mM) ando-Phenylendiamine (1.85 g, 17.1 mM) were placed in 100 ml round bottom flask, in which 100 ml of propionic acid was added. The mixture was mixed at 140 °C for 6 hours, later it was cooled down to 80–90 °C and filtered out using Shot funnel at this temperature. Intermediate product was washed with 15 ml of warm propionic acid with following rinse of plenty of water. The precipitate was dried out on air at 80 °C for 10 hours.

The yield of final product was 2.4 g (62%).

^{1}HNMR (CDCl$_3$): 8,56–8,42 (m, 4H), 7,83–7,79 (m, 2H), 7,50–7,43 (m, 4H), 7,33–7,20(m, 12 H), 7,01–6,84(m, 6H), 1,85–1,56(m, 16H), 1,33–1,27(m, 20H), 0,91–0,43(m, 36H).

2.2.2 3,4:9,10-bis(1,2-benzimdazole)-1,6,7,12-tetra(4-tret-oktylphenoxy) perylene (Sin and Anti isomers) (III).

Tetrachloroperynone (5g, 7.4 mM) (I), 4-tret-octylphenol(9.08 g, 44 mM) and potassium carbonate (6.07 g, 44 mM) were placed into 150 ml of N-methylpyrrolidone. Reaction mixture was stirred at 140 °C for 24 hours, and then it was cooled down to room temperature. Next reaction mixture was processed with 10 ml of cooled concentrated hydrochloric acid in ice bath till stopping of the emission of gas. The obtained precipitate was filtered out through the Shot funnel, rinsed with water several times and then rinsed with 30 ml of methane 5 times. After that the product was cleaned out by column chromatography using silica gel as stationary phase and 40-70% mixture of dichloroethane-hexane. Final yield is 2.0 g of mixture of sin/anti-isomers [16].

^{1}HNMR (CDCl$_3$): 8,51-8,37 (m, 4H), 7,79–7,78(m, 2H), 7,49–7,45 (m, 3H), 7,33–7,20 (m, 13 H), 7,01–6,84(m, 6H), 1,84–1,76 (m, 8H), 1,65–1,55 (m, 24H), 0,89–0,83 (m, 36H).

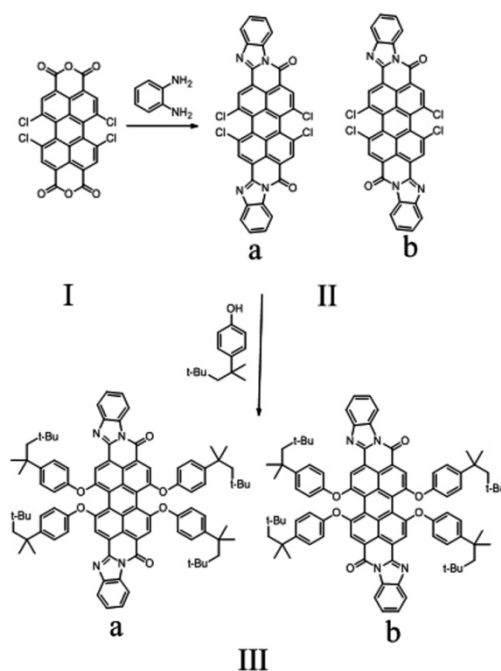Scheme of reaction of obtaining of dye III is shown in Figure 1.

Figure 1. Scheme of reaction of obtaining of dye III

2.3 Obtaining of PSi matrix

Into the oligomer of PSi RTV141A the curing agent RTV141B was added in the weight proportion of RTV141A: RTV141B equaled to 10:1. The obtained mixture was stirred till the uniform white muddy foam appears and then the air was removed from the foam by vacuum pump until uniform clean transparent product forms.

The obtained product is then heated at 60 ^{0}C during 30 minutes and then at 120 ^{0}C during 15 minutes. The obtained sample is totally transparent elastic dense product. If sample is not heated at 120 ^{0}C then it becomes less elastic and easily liable to rupture.

Introduction of dye into polymer matrix by diffusion was performed by following method. Using the method described above 10 samples of PSi were prepared and placed in the methylenechloride solution of the dye of 10 different concentrations. The containers with PSi samples in dye solutions were tightly closed and left for stirring at room temperature for 12 hours. After that the samples were removed from solutions and dried at room temperature until constant weight of samples was obtained. For obtained samples the measurements of UV-vis and fluorescence spectra were conducted.

Introduction of dye into PSi matrix during the curing process was performed by following method. Methylenechloride solution of dye of particular concentration was introduced in the oligomer RTV141A, intensively stirred until uniformly colored foam forms and then evacuated at 60 ^{o}C and pressure of 10 kPa. The obtained colored transparent solution of dye in the oligomer was divided into 10 samples of different amounts and placed into 10 test tubes and then the total weight of each sample was risen to 6 g by adding of clean oligomer RTV141A. The 0.6 g of curing agent RTV141B was added to each sample, and then they were intensively stirred and evacuated several times until uniform mass was obtained. Next these samples were cured according to the following regime: 40 ^{o}C — 15 min.; 50 ^{o}C — 15 min.; 60 ^{o}C — 15 min.; 120 ^{o}C — 15 min. The UV-vis and fluorescence spectra are measured for these samples.

Introduction of GN in PSi matrix was performed according to earlier published method [14]. The mixture of component A, component B and the dye was poured out in amount of 6 g into test tubes then the solution of chloroauric acid of different volumes was added to every test tube which were then evacuated and left for drying.

It should be noticed that color of obtained polymer slowly changes from yellow to gray-crimson due to reduction of gold atoms from 3 to 0 valence.

In works [2, 14, 15, 17] the detailed procedures of obtaining of GN, description of process of formation of GN in various media are presented also the reliable results of obtaining and measuring of GN properties are demonstrated. Since we have thoroughly followed the methods of obtaining of GN described in [14, 17] therefore we do not demonstrate results proving the presence of GN and their properties because there is no doubt that the size and other properties of GN will not be significantly different from previously described works.

As it is described in experimental part the introduction of dye into PSi matrix could be performed by two ways: diffusion or direct introduction of solution into curing mixture with following solvent removing.

The advantage of first method is its ability to introduce into the PSi matrix the dyes which are poorly dissolved in component A. The disadvantage of the first method is a requirement of large time for samples preparation (12 hours for diffusion and 12 hours for solvent removing). Besides in case of fast or non-uniform evaporation of solvent the samples start to break due to heterogeneity between more swollen and less swollen parts of a sample.

The advantage of the second method is its fastness as well as the absence of problem of rupturing of samples since solvent evaporation is not required. Therefore in case of good solubility of the dye in component A the second method is preferable.

For the dyes I and III the few samples of different dyes concentrations in PSi were prepared in order to determine a concentration which provides maximal fluorescence intensity.

It was found that maximal fluorescence intensity corresponds to the concentration of 7.4×10^{-5} M/l for the dye I and 5.01×10^{-5} M/l for the dye III. And these particular concentrations were used then for studying GN effect on fluorescent properties of the dyes.

2.4 Equipment:

For measuring UV-vis spectra a spectrophotometer Specord 250 Plus was used. Fluorescence and excitation spectra were measured using spectrofluorimeter Fluorat-02 Panorama.

3 Results and discussion

3.1 Effect of gold concentration on fluorescent properties of the dyes

Method of gold introduction was described in the experimental part. It should be noted that in case of using diffusion method for introducing dye in PSi the gold was introduced in the polymer in advance and only after that the samples were placed into methylenechloride solution of the dye.

In case of direct introduction of the dye into curing mixture the solution of chloroauric acid in dichloroethane was introduced into the mixture of component A and dye with following removing of dichlorethane by evacuation at 70 °C and 10 kPa.

UV-vis and fluorescence spectra of the obtained samples for the dye III in PSi and different GN concentrations are shown below (see Fig. 2–5).

A

excitation wavelength – 530 nm

B

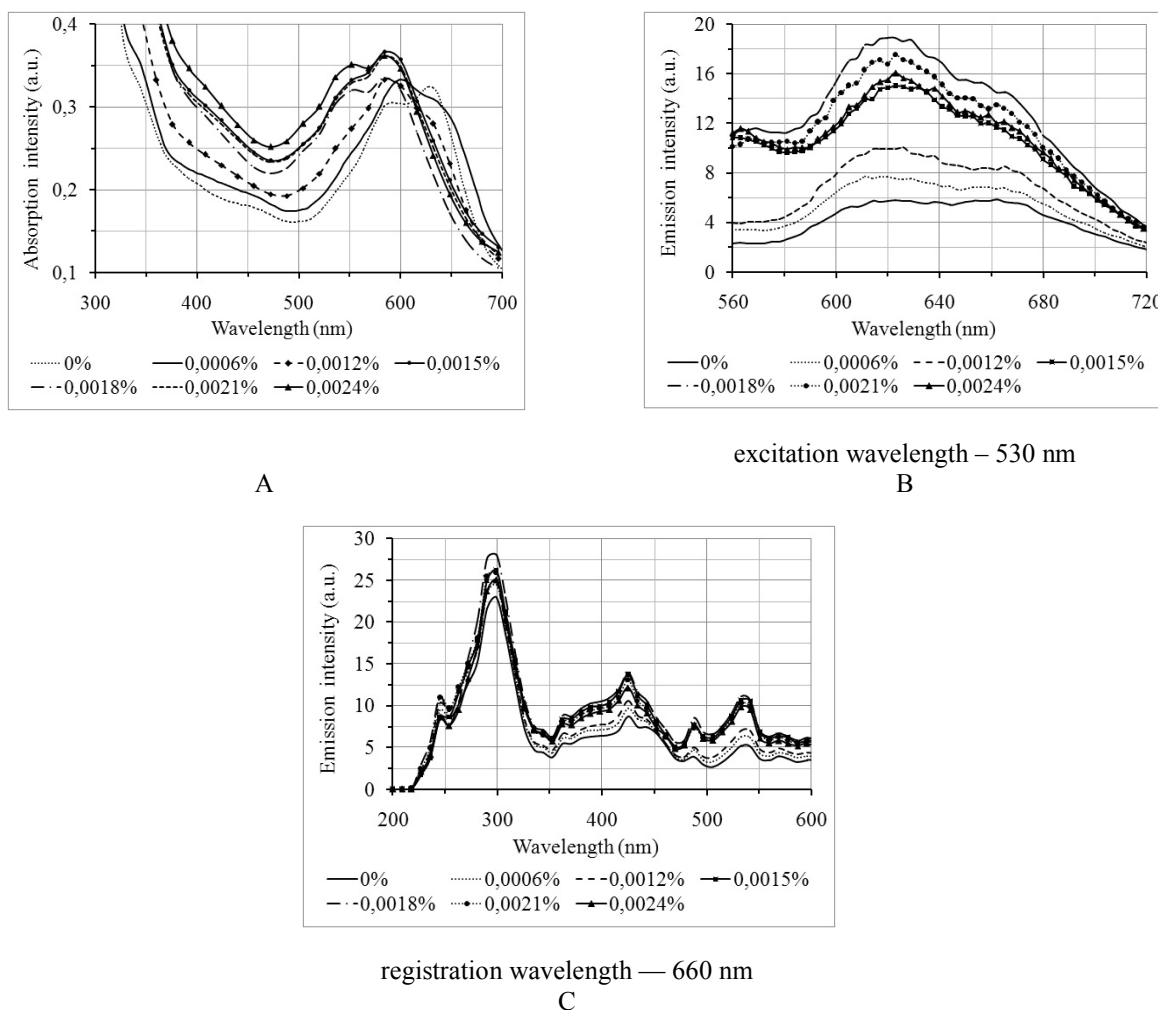registration wavelength — 660 nm

C

Figure 2. UV-vis spectra (A), fluorescence spectra (B) and excitation spectra (C) of the dye III in PSi for different GN concentrations (see inset). Dye concentration 5.01×10^{-5} M/l

Figure 2A shows that gradual increase of GN concentrations shifts main absorption band of PSi composition from 630 nm to 590 nm and increases its intensity. This is due to the fact that GN usually have plasmon band around 520 nm. According to Figure 2B presence of GN in PSi matrix containing dye III molecules provides fluorescence intensity enhancement. In the range of GN concentrations between 0.0006 % and 0.0018 % luminescence intensity increases gradually and reaches its maximum in case of 0.0018 % respectively. For this concentration luminescence increases by factor of 3 comparing to luminescence of pure dye III PSi composition. The subsequent increase of GN concentration leads to decrease of emission intensity but still remains much higher comparing to initial luminescence intensity of dye III without GN in PSi. The shape of emission spectrum does not change in presence of GN indicating the absence of any chemical or physical transformations in the dye III molecules.

It is known that luminescence enhancement of organic dyes in presence of GN may strongly depend on relative positions of excitation wavelength, plasmon band and a dye absorption peak. Therefore we have measured excitation spectra to test effect of excitation energy on luminescence enhancement. Figure 2C shows excitation spectra of dye III PSi composition in presence of different concentrations of GN.

Changing of excitation wavelength does not change the behavior of fluorescence spectra since the intensity increases gradually as concentration of GN rises from 0 to 0.0018% although this increase is less than 3 times. Following rise of GN concentration (0.0021% and 0.0024%) leads to decrease of fluorescence intensity but still it remains higher comparing to the sample without GN.

As one can see from Figure 2B and 2C GN provide enhancement of luminescence of the dye III under excitation of different wavelengths and this allows to use such polymer composition in luminescent solar concentrators (LSC). It is also known that addition of GN may provide enhancement of photostability of organic dyes in polymer matrix [18]. This also favorites to use such dyes in combination with GN in creation of LSC.

Next we have considered effect of GN on dye I fluorescence in PSi. Figure 3A demonstrates UV-vis spectra of PSi samples containing dye I and GN. As one can see from Figure 3A addition of GN provides increase of absorption intensity in short wavelength region 300 – 400 nm and some redistribution of intensity between two peaks located in region 470 – 500 nm. The peak at 500 nm rises in intensity while band at 470 decreases slightly. Increase of band at 500 nm could be explained by fact that plasmon band of GN locates in region 500–520 nm.

excitation wavelength — 485 nm

A   B
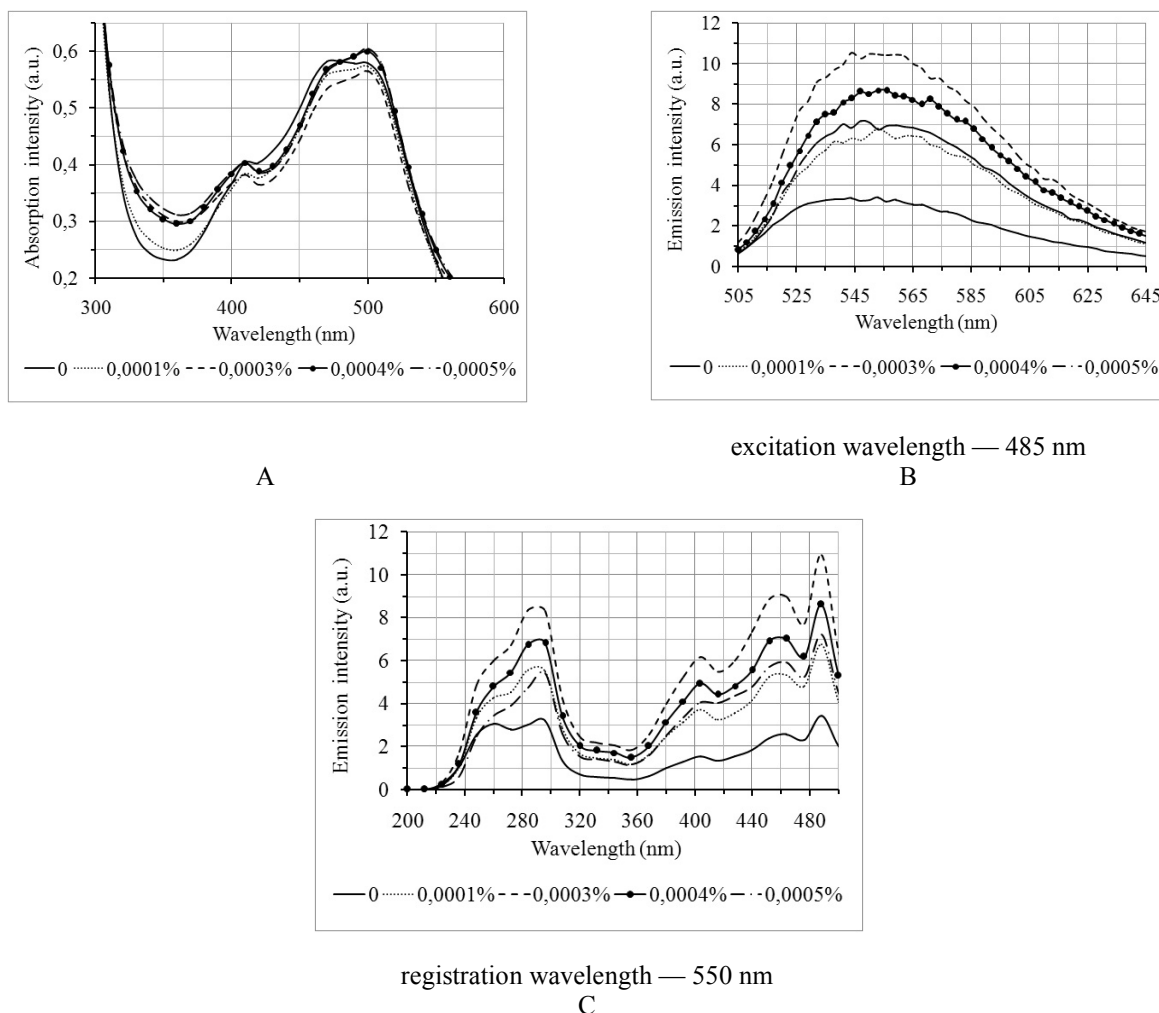

registration wavelength — 550 nm

C

Figure 3. UV-vis spectra (A), fluorescence spectra (B) and excitation spectra (C)
of the dye I in PSi for different GN concentrations (see inset). Dye concentration in PSi was C=7.4×10^{-5}M/l

Since the dye I in PSi demonstrates high absortion intensity in region of 470–500 nm we have used excitation energy of 485 nm for measuring fluorescence spectra corresponding to different GN concentrations (Fig. 3B). Fluorescence intensity reaches the maximum at GN concentration of 0.0003% and the enhancement coefficient is about 3 which is about the same as in case of dye III molecule. Lower or higher concentration gives smaller gain of emission. It should be noted that smaller amount of GN is needed for enchancing of dye I molecule emission than in case of dye III. This may indicate that longer distance between dye I molecule and GN in PSi matrix provides maximal fluorescence enhancing comparing with the one for the dye III and GN composition in PSi.

To test enhancement efficiency for different energies of excitation we have measured excitation spectra of PSi matrices containing dye I and GN (Fig. 3C). The results show that excitation in wide range of wavelength provides fluorescence enhancement of dye I in PSi with GN.

For comparison the UV-vis (Fig. 4A) and fluorescence (Fig. 4B) spectra for samples containing dye Lumogen Red are shown. Samples with Lumogen Red were prepared using the same method as for samples of dye III since it is quite soluble in oligomer of PSi RTV141A. Concentration of Lumogen Redin all samples was 2.6×10^{-5} M/l. Fig. 4A demonstrates that addition of GN leads to the decrease of absorption intensity without changing of spectrum shape. Such behaviour may indicate that presence of GN leads to decrease of excitation rate in Lumogen Red molecule since it directly depends on local electric field. It is known from literature that GN may create the local regions of reduced electric field compared to excitation far-field value [19].

A

excitation wavelength — 530nm
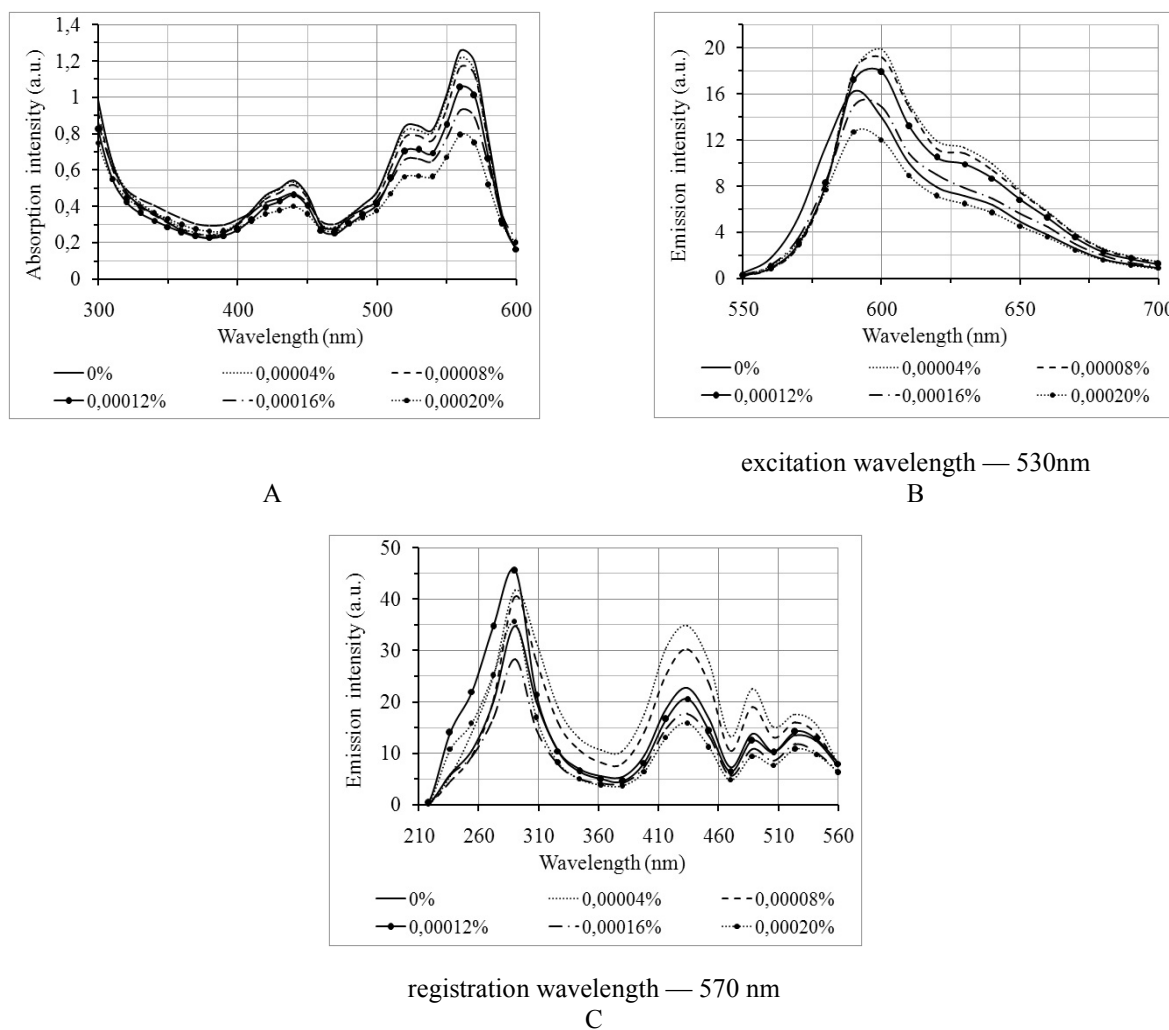
B

registration wavelength — 570 nm

C

Figure 4. UV-vis spectra (A), Fluorescence spectra (B) and Excitation spectra (C)
of Lumogen Red in PSi for different GN concentrations (see inset). Dye concentration in PSi was C=2.6×10^{-5} M/l

Addition of 0.00004% of GN leads to increase of fluorescence intensity by about 30% althougth further addition of GN starts to reduce the intensity. Besides, all considered amounts of GN more than 0.00016% provide quenching of initial emission of Lumogen Red molecule. Thus we may conclude that at longer distances (small concentrations of GN) between the dye molecule and GN fluorescence intensity increases and at shorter distances (high concentrations of GN) the initial dye emission decreases. Our results correlate with data provided by authors [15] for dependance of Lumogen Red emission on distance to GN layer. Next in order to test the effect of excitation energy on fluorescence intensity of the dye we have measured excitation spectra of PSi samples with Lumogen Red and GN (Fig. 4C).

Excitation spectra for Lumogen Red in presence of GN demonstrate strong dependence of emission intensity on excitation energy. In the region of short wavelength of 230–300 nm GN only quench emission of the dye but in long wavelength region of 300–550 nm metallic nanoparticles provide significant enhancement of fluorescence, i.e. the highest gain by almost 2 times was obtained for 0.00004% of GN concentration. Since for all considered samples of Lumogen Red presence of GN in PSi provided reduction of excitation rates and small GN concentrations lead to emission enhancement we may conclude that GN provide significant increase of radiative decay rate in the dye that may exceed reduction of excitation rate [19].

Another well known perylene derivative dye is Lumogen Orange that we used in our experiments. Samples containing dye Lumogen Orange with concentration 2.8×10^{-5} M/l were prepared using diffusion method since the dye is not soluable in oligomer RTV141A. UV-vis spectra of PSi samples of Lumogen Orange are presented in Fig. 5A. Addition of GN results in gradual increase of absorption intenisty in the whole measuring spectrum region preserving the shape of spectrum. Thus the GN provide increase of excitation rates.

A

excitation wavelength — 485 nm

B

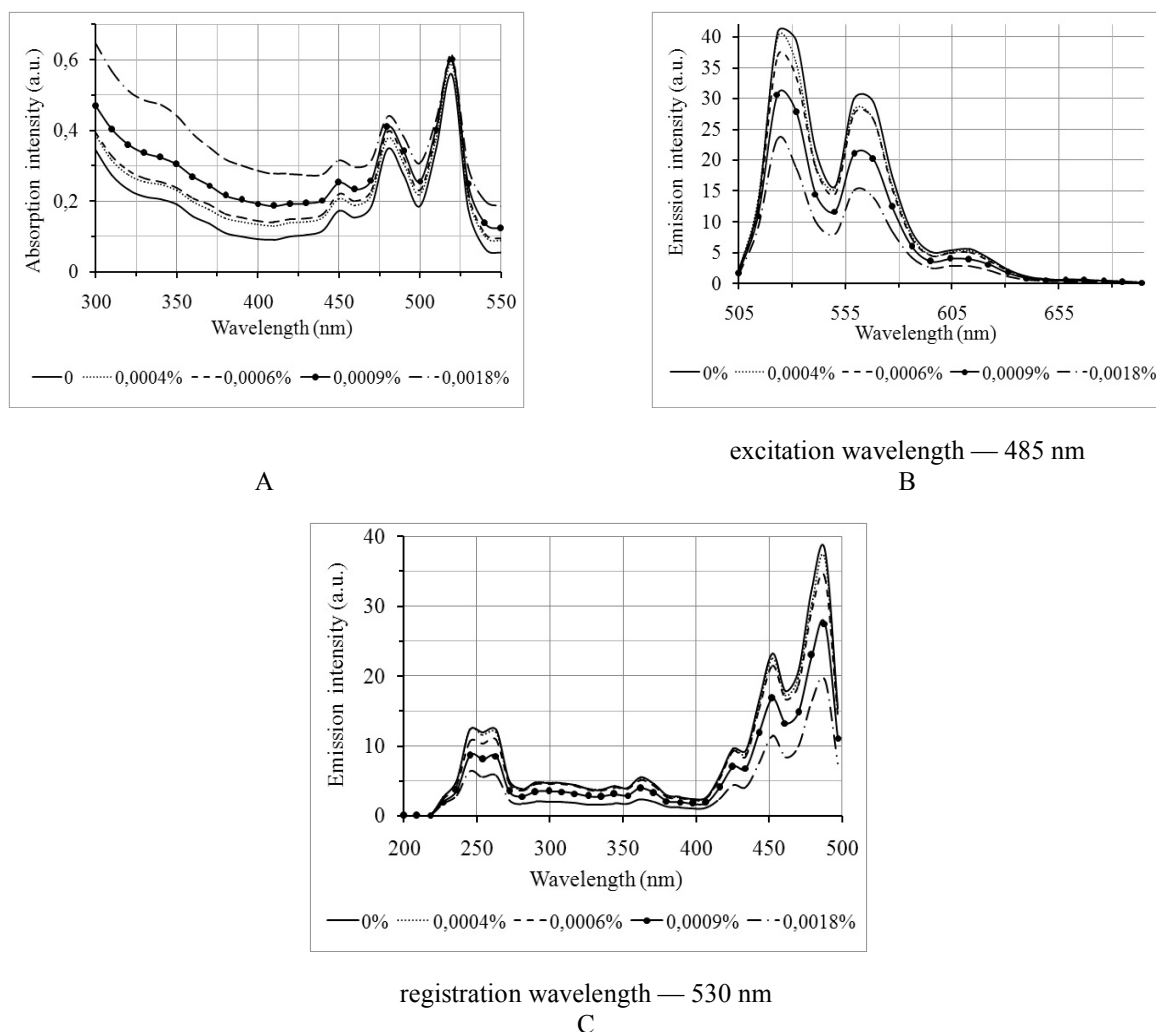registration wavelength — 530 nm

C

Figure 5. UV-vis spectra (A), fluorescence spectra (B) and excitation spectra (C) of dye Lumogen Orange in PSi for different GN concentrations (see inset). Dye concentration in PSi was $C=2.8 \times 10^{-5}$ M/l

Measured fluorescence spectraof PSi samples containing Lumogen Orange (Fig. 5B) demonstrate that addition of GN results in fluorescence quenching. Since the exctitaion rate is increased by GN we may suggest that nonradiative decay rate and nonradiative energy transfer are also increased even stronger so that they overwhelmed increase of excitation rate. The excitation spectra of Perylene Orange samples (Fig. 5C) demonstrate that presence of GN results only in quenching of the dye fluorescence independently on excitation energies in the region 230–500 nm. The higher the concentration, i.e. the shorter the distance between metalic nanoparticles and the dye molecules, the higher the probability of non-radiative decay processes.

Our results for 4 dyes demonstrate that dye I and III as well as Lumogen Red (small concentrations of GN) may provide fluorescence enhancement upon addition of GN and in case of Lumogen Orange presence of GN leads to quenching of the emission. High concentrations of GN in PSi matrix result in quenching of emission of Lumogen Red molecule. The enhancement of fluorescence for Lumogen Red depends on excitation wavelength.

In all considered results the increase of fluorescence intensity was estimated on the basis of value of maximal intensity of fluorescence at the constant wavelength for all samples of the same dye. Moreover the technical parameters of the measurements of fluorescence spectra (excitation wavelength, dye concentration in a sample, measuring wavelength region, sensitivity of the detector) were the same for all samples and that excludes the effect of background noise on estimation of increase of intensity.

In all cases the samples were totally transparent peaces of PSi of the same shape and thickness with uniform coloration of the whole volume and absence of any turbidity or non-dissolved particles.

The distinction of behavior of the dye Lumogen Orange from other three dyes cannot be related only to method of introduction of dyes into PSi by diffusion since the dye I was also introduced by this method and demonstrated similar results as dye III. We believe that distinctions of the behavior are due to spatial structure of Lumogen Orange.

The obtained results are very interesting for future development of LSC technique which are transparent polymer matrices doped by fluorophores. Intensity of emission of fluorophores determines the efficiency of LSC. Therefore one of the main ways toward the increase of LSC efficiency is increase of emission intensity of fluorophore. In our case the PSi matrix was doped by perylene derivative dyes demonstrating intensive emission in visible spectral range and the way of increase of their emission by addition of GN which is a significant step toward solution of a problem of increasing of efficacy of solar cells.

3.2 Quantum chemical calculations.

In this section we consider simplistic theoretical model of effect of GN on luminescent properties of dye III molecule. The luminescence intensity depends on many parameters which could not be included in theoretical considerations. One of the problems encountered by theorists is the shape and size of GN required for the realistic model. In the literature the clusters of different types and sizes were considered from couple of atoms up to few thousands [20–22]. Another issue is the orientaion of GN relative to the organic dye molecule. Also a method of evaluation of plasmonic effect on luminescent properties of the dye molecule is another barrier toward consideration interaction of metal nanoparticle with the dye. Some approaches to resolving these issues were suggested by authors [20–22].

Here we present simplistic model based on the assumption that GN may increase absorption rate of dye molecule [23]. This approach may not be considered as a comprehensive model but rather as a source of additional data helping clarify effect of metal nanoparticles on the dye molecule.

In our model we have considered GN effect on dye III molecule using the quantum chemical calculations.For the dye III molecule the optimized structure was calculated (Fig. 6) in DFT approximation using B3LYP [24, 25] standard functional. For gold atoms LanL2 effective core potential with DZ basis set [26] were used and for other atoms 6–31G(d) basis set was used. All calculations were performed using GAUSSIAN09 Rev. C01 program package [27]. It should be noted that calculated vibration frequencies for this structure do not demonstrate imaginary numbers therefore this obtained structure corresponds to global minimum. Figure 6 shows that the molecule has almost planar perylene core and twisted side substituent rings.In this respect dye III molecule structure resembles Lumogen Red structure [28].
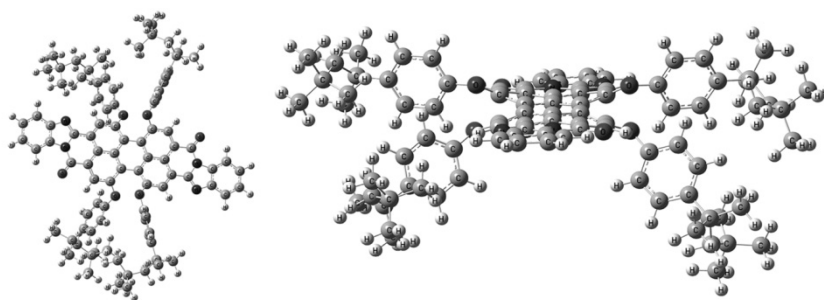
Figure 6. Optimized structure of the dye III molecule

For obtained optimized structure of dye III UV-vis spectrum was calculated using TDDFT [29–31] method (Fig. 7 and Table 1). All visualized spectra were obtained with 0.33 eV half-width and Gaussian type of function for describing broadening. Data presented in Figure 7 and table 1 demonstrate the presence of very intensive transition at 637 nm and less intensive transition at 449 nm. The comparison of experimental and theoretical UV-vis spectra shows good agreement thus proving the correctness of the obtained structure of the molecule. In Table 1 data on molecular orbitals (MO) corresponding to intensive transitions are presented. According to these data intensive transition at the wavelength of 637 nm corresponds to electron transition from HOMO to LUMO which are delocalized over the whole perylene core. The second intensive transition at wavelength of 449 nm corresponds to transition from HOMO – 3 to LUMO, where HOMO – 3 is partially localized on perylene core and partially on side substituent rings.
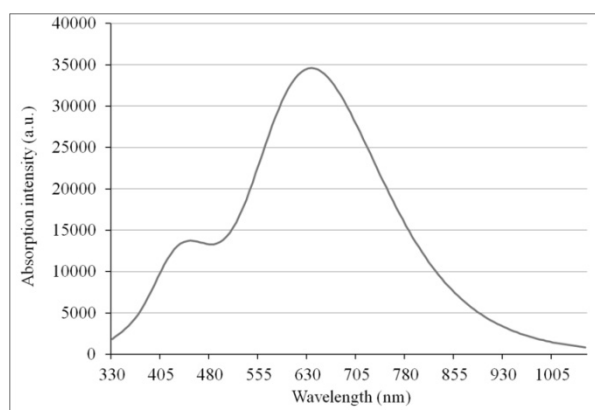

Figure 7. Calculated UV-vis spectrum of the dye III molecule

T a b l e 1

Intensive transitions of calculated UV-vis spectrum of dye III molecule

Transition #	Transition wavelength (nm)	Oscillator strength	MO of transitions
1	637	0.8456	HOMO→LUMO
3	467	0.0825	HOMO -2 → LUMO
4	449	0.1103	HOMO -3 → LUMO

Next we have considered models of complexes of the dye III molecule and gold. Experimental data indicate that addition of gold nanoparticles to polymer composition of the dye III may provide significant increase of luminescence intensity without changing the shape of spectrum as a result of SPR. One of the possible mechanism of luminescent intensity increasing under photo excitation is the increase of absorption intensity of the dye molecule in presence of GN [23]. It is also known that metallic nanoparticles usually have smaller sizes comparing to semiconducting nanocrystals and particularly gold atoms form Au_{25} cluster, i.e. contain odd number of atoms and may have unpaired electron [32]. Therefore we have considered a model with two separated gold atom where each atom represents gold cluster.

Model of complex of dye molecule and two gold atoms one of which is located over perylene plane and another one symmetrically under this plane (structure I) is shown in Figure 8 where dye structure was not re-

optimized in presence of gold atoms. For the structure I the UV-vis spectra were calculated for the cases of D = 4 and 5 Å, where D is a distance between gold atoms and perylene core plane. Results of calculation of electronic spectra of structure I are presented in Table 2. These data indicate that location of gold atoms over perylene plane at the distance of 4 Å leads to significant change of UV-vis spectrum. Particularly new intensive band appears in long wavelength region and the most intensive band at 637 nm has lower oscillator strength in comparison with the dye molecule without gold atoms. Analysis of MO participating in long wavelength transition shows that this new transition relates only to gold atoms while the most intensive transition corresponds to the same MOs as in case of single dye molecule. At the distance of 5 Å presence of gold atoms in structure I does not lead to significant changes in electronic spectrum of the dye and the MOs involved in the most intensive transition remains the same as in cases of D = 4 Å and the single dye molecule. The only change in this case is the decrease of oscillator strength of the most intensive transition at 638 nm although this reduction is less than for distance D = 4 Å. For D = 4 and 5 Å of structure I short wavelength transition also undergoes some reduction of oscillator strength comparing to the single dye molecule but the nature of MO does not change. Figure 9 shows visualized calculated UV-vis spectra of structure I in comparison with calculated electronic spectrum of the dye. Our results demonstrate that for structure I the presence of gold atoms leads to the decrease of absorption intensity which in turn may provide decrease of emission intensity of the dye. Besides the longer the distance between gold atoms and the dye the smaller decrease of oscillator strength. Such behavior could be explained by the fact that in case of structure I gold atom located directly over π MO of perylene core which relates to the formation of the most intensive transition introduce perturbation in this π MO.
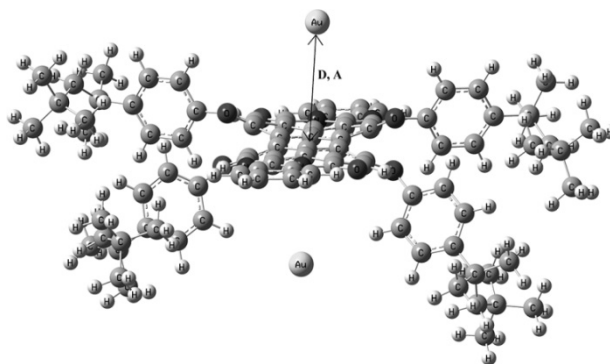

Figure 8. Cluster model of dye molecule and gold atoms located over and under perylene core of the dye (structure I), where D — distance between gold atom and perylene core plane

T a b l e 2

Intensive transitions in structure I

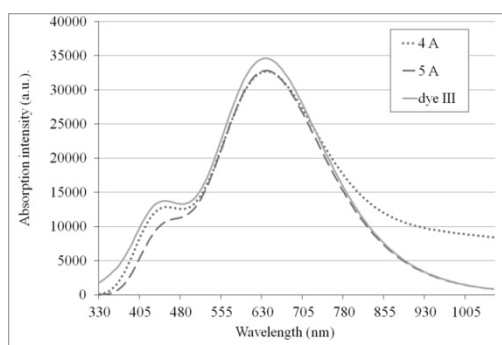| D, Å	Transition number	Wavelength of a transition (nm)	Oscillator strength	Transition MO
4	3	1045.93	0.1872	HOMO → LUMO
	7	637.87	0.7753	HOMO - 1 → LUMO + 1
	19	449.49	0.0981	HOMO - 4 → LUMO + 1
5	10	638.28	0.8022	HOMO - 1 → LUMO + 1
	24	448.36	0.0979	HOMO - 4 → LUMO + 1

Figure 9. Calculated UV-vis spectra of the dye and structure I

Next we have considered another model of gold atoms location relative to the dye molecule (Fig. 10) in which gold atoms were located in plane of the perylene core and coordinated with oxygen atoms of the carbonyl groups of the dye (structure II) where dye III structure was not re-optimized in presence of gold atoms. For this model the UV-is spectra were calculated and these data are presented in Table 3.
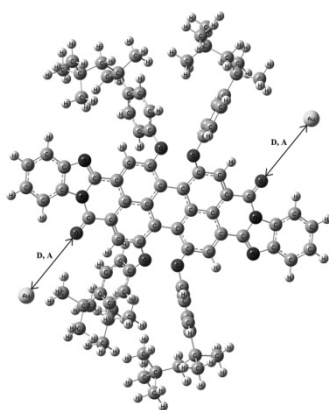

Figure 10. Structure II model

T a b l e 3

Calculated intensive transitions of UV-vis spectra of structure II model

D, Å	Transitions number	Transition energy (nm)	Oscillator strength	Transition MOs
2.5	6	687.18	0.8340	HOMO - 1 → LUMO + 1
	14	500.77	0.0994	HOMO - 4 → LUMO + 1
3	6	654.62	0.8562	HOMO - 1 → LUMO + 1
	18	466.77	0.1085	HOMO - 4 → LUMO + 1
3.5	6	644.15	0.8577	HOMO - 1 → LUMO + 1
	18	455.09	0.1031	HOMO - 4 → LUMO + 1
3.75	6	642.12	0.8471	HOMO - 1 → LUMO + 1
	19	452.85	0.1062	HOMO - 4 → LUMO + 1
4	7	640.90	0.8587	HOMO - 1 → LUMO + 1
	19	451.61	0.1046	HOMO - 4 → LUMO + 1
4.5	8	639.52	0.8587	HOMO - 1 → LUMO + 1
	22	450.22	0.1046	HOMO - 4 → LUMO + 1
5	9	638.64	0.8568	HOMO - 1 → LUMO + 1
	23	449.50	0.1059	HOMO - 4 → LUMO + 1

Results presented in Table 3 indicate that at small distances between gold atom and the oxygen atom of dye (2.5–3.75 Å) the basic absorption band shifts to long wavelength region but the nature of the transition does not change. At small distance of 2.5 Å the oscillator strength of the most intensive transition decreases compared to the single dye molecule. As the distance D increases (3, 3.5, 4, 4.5 and 5 Å) the band shifts to short wavelength region and the oscillator strength increases and becomes higher compared to the single dye molecule. Only in case of D = 3.75 Å oscillator strength becomes smaller than in case of neighboring values of D, i.e. violating the tendency.

It should be noted that at D = 4.5 and 5 Å wavelength of the most intensive transition has almost the same value as in case of the single dye molecule. The calculated electronic spectra of the dye and structure II model are shown in Figure 11.
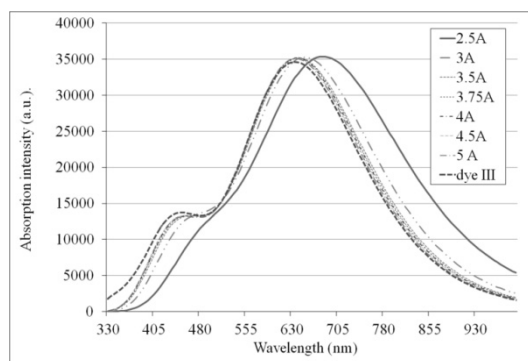

Figure 11. Calculated electronic spectra of structure II model in comparison
with the single dye molecule

Analysis of MOs related to intensive transition in structure II for D = 2.5 indicate that the intensive transitions have contribution from unoccupied orbital localized on perylene core and gold atom. For distances D = 3, 3.5, 3.75, 4, 4.5 and 5 Å the nature of MO contributing to intensive transitions coincides with character of MOs of the single dye molecule. Therefore starting from the distance of 3 Å and further the unoccupied MOs related to the intensive transitions do not have contribution from atomic orbitals of the gold atoms.

Thus on the basis of the obtained experimental results and quantum chemical calculations we may suggest that emission enhancement for the dye III molecule by GN is observed in case of their mutual location like in structure II model. On the contrary structure I model may lead to the quenching of the dye III emission.

4 Conclusions

The obtained experimental and theoretical data allow to make the following conclusions. Addition of GN of a certain concentrations into PSi matrices may lead to significant increase of fluorescence of the dyes I and III independent on the excitation wavelength. Such change of the emission intensity may correspond to gold atoms location like in structure II model in which the increase of absorption intensity occurs and this may provide increase of emission intensity of the dye III. Location of gold atoms like in structure I model, i.e. directly over perylene core π MO provides reduction of absorption probability of excitation radiation and thus may stimulate decrease of emission intensity respectively.

For the dye Lumogen Red some increase of fluorescence intensity may be provided at low GN concentrations and quenching of fluorescence was observed at relatively high GN concentrations. Increase of radiative decay rate of the Lumogen Red in presence of GN (low concentrations) overwhelms decrease of excitation rate.

Lumogen Orange upon addition of GN always exhibit only emission quenching although excitation rate increases. The phenomenon of selective emission enhancement effect of GN on these perylene derivative dyes needs further investigation.

Acknowledgement

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Полисилоксан матрицасындағы перилен негізді бояғыштардың алтын нанобөлшектері қатысындағы люминесценция

Құрамында 1,6,7,12-тетрахлороперилен-3,4,9,10-тетрадикарбоксидиангидрид (Dye I) пен 3,4:9,10-бис(1,2-бензимидазол)-1,6,7,12-тетра(4-терт-октилфенокси) перилен (син/анти-изомерлері) (Dye III) бар перилен туындылары алтын нанобөлшектерінің әр түрлі концентрациясы бар полисилоксан үлгілерін дайындауда қолданылды. Dye I мен III бояғыштарының флуоресценциясы алтын нанобөлшектерін қосқанда қоздыру энергиясына тәуелсіз артатындығын көрсетті. Lumogen Red бояғышы қосылған полисилоксан композициясына алтын нанобөлшегінің аз мөлшерін қосқанда ғана флуоресценция қарқындылығы өседі, алайда GN концентрациясын одан әрі арттыру жарық шығаруға кері әсерін тигізеді. Lumogen Red бояғышының жарық шығару қарқындылығының артуы қоздыру жылдамдығының азаюынан туындайтын шығарудың баяулау жылдамдығының өсуімен түсіндірілуі мүмкін. Алтын нанобөлшегінің Lumogen Orange бояғышына әсері GN тіпті аз концентрациясын қосқанда флуоресценцияның сөнуінен байқалды. Dye III-ке арналған DFT жақындауда есептеулер жүргізу шығару қарқындылығын жоғарылату үшін алтын нанобөлшектері перилен негізінің жазықтығында орналасқан деп болжайды.

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Люминесценция перилен производных красителей в полисилоксановой матрице в присутствии наночастиц золота

Перилен производные, включая 1,6,7,12-тетрахлороперилен-3,4,9,10-тетрадикарбоксидиангидрид (Dye I) и 3,4:9,10-бис(1,2-бензимидазол)-1,6,7,12-тетра(4-терт-октилфенокси) перилен (син/анти-изомеры) (Dye III), были использованы для приготовления полисилоксановых образцов (PSi), содержащих различные концентрации наночастиц золота (GN). Dye I и III демонстрируют значительное усиление флуоресценции при добавлении GN независимо от энергии возбуждения. Для PSi композиции с красителем Lumogen Red наблюдалось некоторое увеличение интенсивности флуоресценции при добавлении небольшой концентрации GN, однако дальнейшее увеличение концентрации GN приводило к тушению свечения. Увеличение интенсивности свечения красителя Lumogen Red возможно связано с увеличением скорости затухания свечения, так как скорость возбуждения уменьшается. Влияние GN на краситель Lumogen Orange выражалось тушением флуоресценции даже при малых концентрациях GN. Расчеты в приближении DFT для dye III предполагают расположение GN в плоскости периленовой основы для усиления интенсивности свечения.