

## Research Article

# Influence of Gold Nanoparticles on the Luminescence of an Acrylated Isocyanonaphthalene Derivative

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Dodecanethiol-functionalized gold nanoparticles were incorporated into the polymer matrix of diurethane-methacrylate monomer mixture in the presence of SiO<sub>2</sub> nanoparticles (8 wt %) and a new reactive organic luminescent material ACAIN (1-N-(2-acryloyloxy-3-chloroprop-1-yl)-amino-5-isocyanonaphthalene, 1 wt %). This way, a new, probably multifunctional, polymer nanocomposite was obtained. It was shown that the addition of SiO<sub>2</sub> nanoparticles enhances the fluorescent intensity of ACAIN by 1.5 times in the 450-550 nm spectral range. Furthermore, an additional fluorescence enhancement up to 4.5 times was observed when Au nanoparticles were added to this nanocomposite in a rather low (0.12 wt %) concentration.

## 1. Introduction

It is known that the luminescence of organic molecules in the presence of metal nanoparticles can be enhanced or just decreased, in dependence of different factors [1]. The presence of electromagnetic, plasmon field emitted by the proper excited metal nanoparticle can enhance the luminescence of an organic molecule [2]. At the same time the luminescence of the molecule, directly connected to the metal surface, can be essentially decreased because of the resonant transfer of excitation energy to the metal or due to the dissociation of excitons at the interface [3]. In a number of reports the enhancement of luminescence in  $\pi$ -conjugated polymers is related to the changes of polymer structure due to the introduction of metallic nanoparticles [4-6].

It is known that  $\pi$ -conjugated organic systems have been used as optoelectronic and sensing materials due to their characteristic efficient light emission or absorption and p-type charge transport. Hybrid nanostructures of  $\pi$ -conjugated organic systems with nanoscale metals offer surface plasmon- (SP-) enhanced luminescence, which can be applied to organic-based optoelectronics, photonics, and sensing.

The most popular route of metal (for example, Ag) nanoparticle introduction into the polymer matrix consists of the preparation of nanoparticles directly by a certain reduction process. For example, Ag nanoparticles (Ag NPs) can be pre-prepared by sodium citrate reduction and incorporated into agarose by mixing to form an Ag-containing agarose film (Ag@agarose), which yielded a maximum 8.5-fold increase in the fluorescence [7]. However, in a number of applications the selected form and dimensions of the nanoparticles are important, primarily for the determined plasmon resonance peak in the optical excitation and/or absorption spectra. The possibility of the direct introduction of pre-prepared gold nanoparticles to acrylate nanocomposites was shown in our previous paper [8]. Moreover, we recently developed a new reactive solvatochromic dye: 1-N-(2-acryloyloxy-3-chloroprop-1-yl)-amino-5-isocyanonaphthalene (ACAIN), the complexation of which can be used for the selective detection and quantification of silver(I) ions from aqueous media [9]. In addition, ACAIN was found to be a vital cell stain, which could selectively label the tonoplast in plant cells [10]. We assume that the combination of our multifunctional solvatochromic dye with the Au NP containing polymer matrix can be important for sensor applications, since organic

TABLE I: Compositions of the Au-SiO<sub>2</sub>-ACAIN monomer composites.

Sample No	Monomers	SiO <sub>2</sub> NPs [wt %]	Au NPs [wt %]	Initiator [wt %]	ACAIN [wt %]
1	UDMA/IDA=3/7	--	--	0.5 In2	1
2	UDMA/IDA=3/7	8	--	0.5 In2	1
3	UDMA/IDA=3/7	8	0.12	0.5 In2	1
4	UDMA/IDA=3/7	8	-	0.5 In2	-
5	UDMA/IDA=3/7	8	0.12	0.5 In2	-

luminescent materials, which change the characteristics of luminescent spectra under the influence of certain compounds or ions, enable the mass production of cheap sensing elements with the necessary forms and dimensions. Therefore, the increase of luminescence intensity of the markers in the polymeric material with increased stability is an important issue from the practical point of view. Our aim was to enhance the fluorescence of the multifunctional ACAIN and at the same time incorporate it to a polymer matrix, so that it could be used as a starting material for solid state sensors. The introduction of SiO<sub>2</sub> NPs to the polymer should prevent the leaching of luminescent components from the composite. In this paper we present the results on the preparation of an acrylate composite with ACAIN and SiO<sub>2</sub>, as well as Au nanoparticles. The influence of Au nanoparticles on the luminescence of this composite film was investigated.

## 2. Experimental

**2.1. Materials.** The following materials and chemicals were used in this work: diurethane dimethacrylate, mixture of isomers (436909 Aldrich, UDMA); isodecyl acrylate (408956 Aldrich, IDA); initiator: 2,2-dimethoxy-2-phenylacetophenone (19611-8 Aldrich, In2); dodecanethiol functionalized gold nanoparticles with average size 5 nm (Nanoprobes, No3014, AuNP) SiO<sub>2</sub> nanoparticles with size 7 nm (Aldrich No. 066K0110, SiO<sub>2</sub>NP); ACAIN, which is an organic material with the structure shown in Figure 1.

ACAIN was prepared in a two-step reaction according to scheme in Figure 2.

The detailed description of the synthesis and detailed optical characterization of 1-(3-chloro-2-hydroxyprop-1-yl)-amino-5-isocyanonaphthalene (CHAIN) and 1-N-(2-acryloyloxy-3-chloroprop-1-yl)-amino-5-isocyanonaphthalene (ACAIN) can be found in [9]. The compound is a yellow powder at room temperature.

**2.2. Preparation of the Au-SiO<sub>2</sub>-ACAIN-Monomer Mixtures and the Polymer Nanocomposite Films.** The compositions of the Au-SiO<sub>2</sub>-ACAIN monomer mixtures are presented in Table I and the preparation procedure is as follows: silicon oxide nanoparticles were added to the above-mentioned monomers and homogeneous solution was prepared by sonication. After homogenization the proper amount of ACAIN powder was mixed in and the solution of Au NP in toluene and initiator (0.5 wt % In2) were added to this solution and

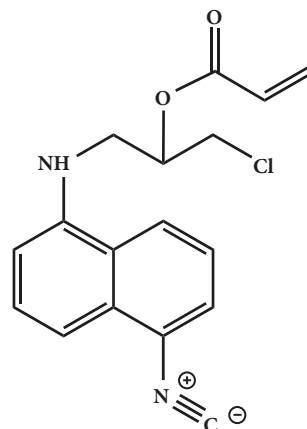


FIGURE 1: The molecular structure of 1-N-(2-acryloyloxy-3-chloroprop-1-yl)-amino-5-isocyanonaphthalene (ACAIN).

carefully mixed. Next the solvent, toluene, was evaporated until constant weight of the nanocomposite.

**Preparation of the Polymer Nanocomposite Films.** Preparation of the polymer nanocomposite films consists of the UV-curing of the monomer solutions between glass and polyester film to prevent the inhibiting effect of oxygen. The UV light source was a mercury lamp OSRAM, HQV 125 W. 20-30  $\mu$ m thick nanocomposite samples were formed on a glass substrate in the gap between the glass and a polyester film, as shown in Figure 3(a). The polyester film was removed after the UV-curing. The SEM picture of the cross-section of the sample is presented in Figure 3(b).

**2.3. Experimental Measurements.** Optical transmission spectra of the obtained polymer nanocomposites were recorded on a Shimadzu 1800 UV-vis spectrometer. Luminescence spectra were investigated by the scanning laser microscope Zeiss LSM-710 with pumping light wavelength at 405 nm (excitation) and 3 nm spectral steps. The structure of the nanocomposites containing Au NPs was characterized by TEM (JEM-2000FXII).

## 3. Results and Discussion

For practical applications the uniform distribution of the Au NPs in the polymer matrix is an important issue. Therefore, using transmission electron microscopy first we showed

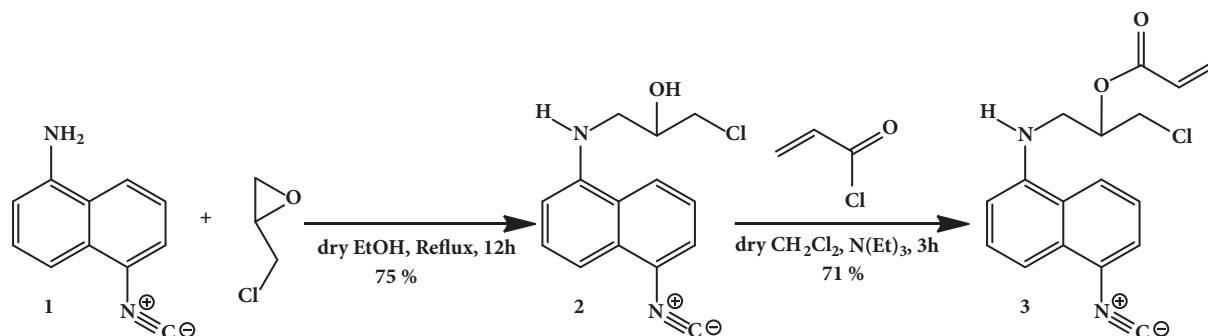


FIGURE 2: Synthesis of 1-(3-chloro-2-hydroxyprop-1-yl)-amino-5-isocyanonaphthalene (2, CHAIN) and 1-(2-acryloyloxy-3-chloro-prop-1-yl)-amino-5-isocyanonaphthalene (3, ACAIN).

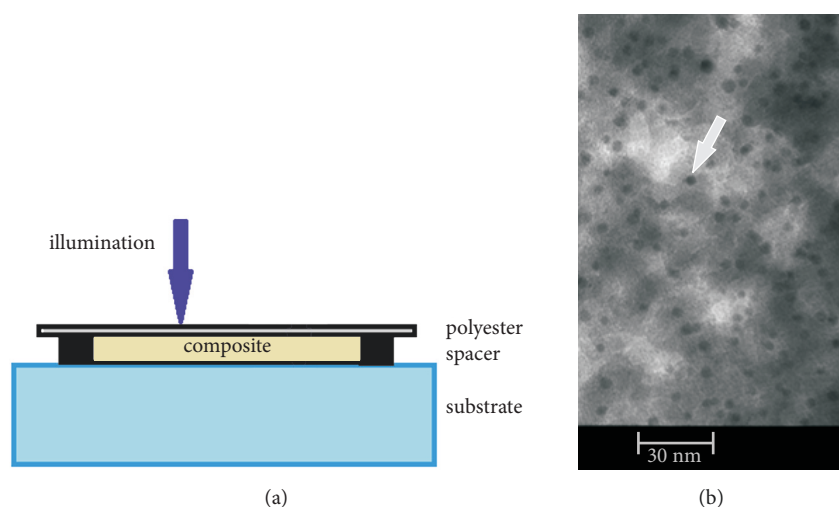


FIGURE 3: (a) Scheme of sample preparation. The polyester film is removed after polymerization. (b) TEM picture of Au NPs (the white arrow selects one) in the polymer matrix, Sample 3.

directly that the Au NPs are well distributed in the matrix and do not agglomerate (see Figure 3(b)). The absence of agglomeration was further supported by the presence of the plasmon resonance absorption peak near  $\sim 540$  nm (see Figure 4), corresponding to the dimensions of the Au NPs ( $\sim 5$  nm).

Since ACAIN contains a reactive acrylate functional group, we assumed its complete incorporation in the polymer matrix during the photopolymerization process. The uniform fluorescent color of the polymer films backed this assumption. Optical absorption spectra of pure acrylate composites with 1 wt % of ACAIN and with the addition of two types of nanoparticles (Au NPs and  $\text{SiO}_2$  nanoparticles) were measured (Figure 4). The ACAIN absorption maximum for all composites, shown in Table 1, is located near 350 nm (Figure 4). The introduction of 8 wt % of  $\text{SiO}_2$  nanoparticles and 0.12 wt % of Au nanoparticles results in the increase of the absorption maximum and its small, about 10 nm shift towards shorter wavelengths. These phenomena may be caused by the formation of a complex between the  $\text{SiO}_2$  NPs and ACAIN, which similarly to other cases [11, 12] could also prevent the possible leach out of the luminescent component. It should

also be noted that the addition of the NPs does not change the absorption maximum, essentially.

That is why in our experiments the luminescence was excited at the longwave-side of this maximum, at 405 nm. It is important to note that the introduction of Au NPs results in the appearance of an absorption peak with a maximum at  $\sim 540$  nm, which is related to the resonant absorption of the localized plasmons in the Au NPs.

The photoluminescence spectra of the above-mentioned composites are presented in Figure 5. It was established that the pure polymer matrix (composite 4) and the polymer composite with Au and  $\text{SiO}_2$  NPs (composite 5) were not luminescent, while the introduction of ACAIN stimulated a strong luminescence signal. The last spectrum has wide asymmetrical band shapes with small maxima features at 460 and 490 nm for the ACAIN polymer composite without and with  $\text{SiO}_2$  nanoparticles, respectively. These spectra have similar shapes as is characteristic for naphthalene derivatives, for example, described in [13]; however the maxima are essentially shifted to the red spectral range, which can be explained by the presence of the  $\text{N}\equiv\text{C}$  group in the ACAIN structure. It was established, as presented in Figure 5, that the introduction

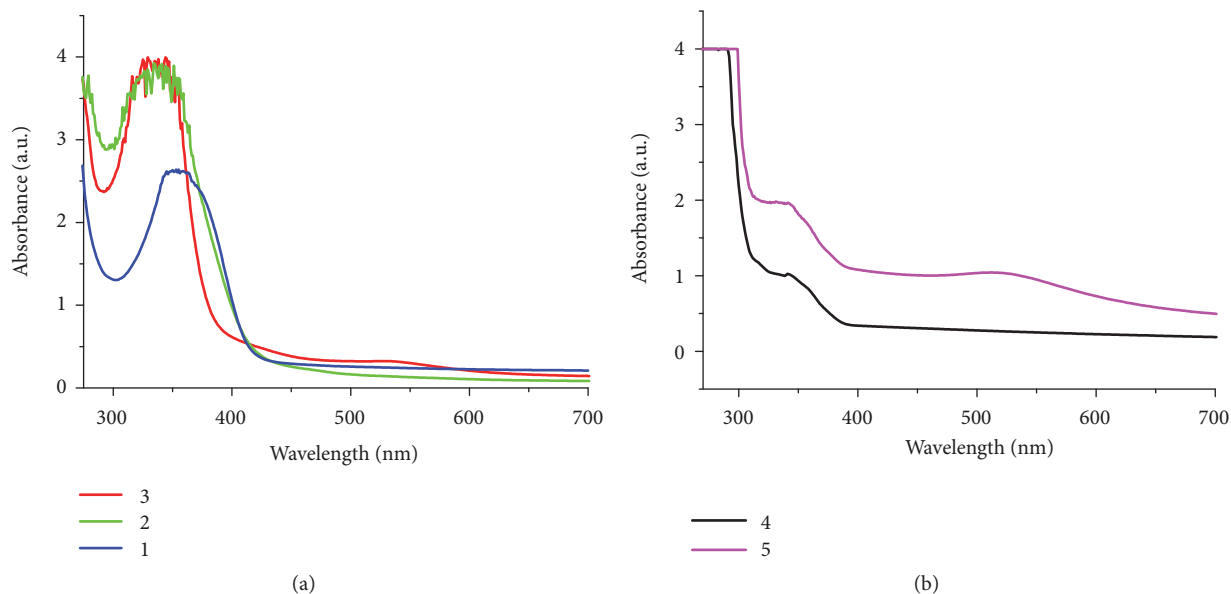


FIGURE 4: Optical absorption spectra of the ACAIN-containing (compositions 1-3) and polymer films without ACAIN (compositions 4,5).

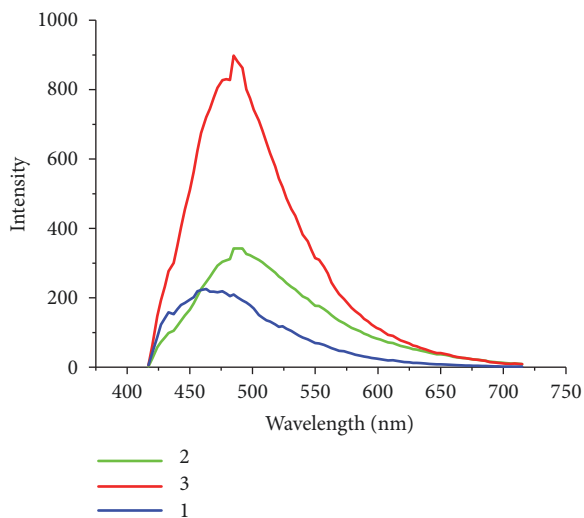


FIGURE 5: Luminescence spectra of the ACAIN-containing polymer films, compositions 1, 2, and 3.

of the SiO<sub>2</sub> nanoparticles to the UDMA/IDA/ACAIN composite increased the luminescence intensity by 1.5 times, and the addition of Au NPs/SiO<sub>2</sub> results in a 4.5-time increase in the intensity of luminescence. Besides the positive role of SiO<sub>2</sub> NPs described in refs. [11, 12] and the similar influence on ACAIN molecules in our materials, the essential role of Au NPs can be attributed to the generation of plasmon fields, which are localized near the Au NPs, causing an efficient interaction with the luminescent molecules. Both phenomena may cause the observed shift of the ACAIN luminescence maximum towards longer wavelengths in comparison with the empty polymer matrix only.

It is quite possible that in our case a donor-acceptor type complex formation occurs between ACAIN and the Au NPs, since the gold nanoparticles possess positive charge at the surface and the isocyanonaphthalene acrylate derivatives are considerably dipolar owing to the presence of the electron donating amino and the electron withdrawing isocyano groups, as it is seen in the ACAIN structure (Figure 1). The possibility of such complex formation was shown in our previous paper [14]. Under the influence of 450-550 nm luminescence, the localized plasmon can be excited at the short wavelength wing of the resonant peak and enhance the luminescence of the organic derivative, although with much less efficiency than in the resonance case. The effect is due to the known localized plasmon (LP) coupling and the local near-field enhancement of optical transitions. Tailoring Au NP size and concentration in such nanocomposites is expected to be used for the design and development of high-performance luminescent materials and functional components. In this case the application of preformed particles, as proposed in this paper, is preferable.

The enhancement of luminescence can be better at double-wavelength excitation, which includes the resonant excitation of localized plasmons in the given type of Au NPs. But in our case an interesting mechanism of luminescence enhancement may be proposed: self-excitation with positive feedback. In this mechanism the luminescence excites plasmon resonance, which in turn enhances the luminescence. Further investigations are in progress in this attractive direction.

#### 4. Summary

Polymer nanocomposites were fabricated by direct introduction of preformed SiO<sub>2</sub> and Au NPs with concentrations 8 wt % and 0.12 wt %, respectively, into the mixture of

acrylate monomers, which contain also a new luminescent isocyanonaphthalene based material, ACAIN. Resonant plasmon absorption was observed in these nanocomposites; i.e., gold nanoparticles were separated and localized plasmon fields can be generated by illumination. The luminescence of ACAIN was essentially enhanced to 4.5 times of the original in such nanocomposites, as a result of a plasmon-assisted process, which can also be explained by a self-exciting process with a positive feedback.

## Data Availability

The original data used to support the findings of this study are available from the corresponding and/or first author at burunj@list.ru, upon request.

## Conflicts of Interest

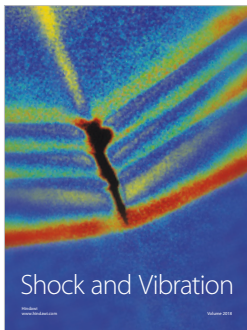
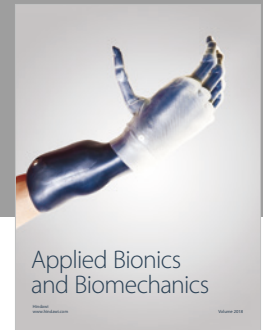
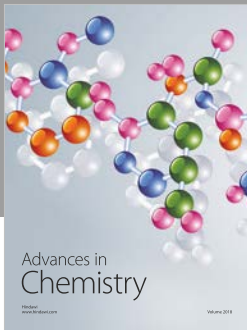
The authors declare that they have no conflicts of interest.

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## References

- [1] O. G. Tovmachenko, C. Graf, D. J. Van Den Heuvel, A. Van Blaaderen, and H. C. Gerritsen, "Fluorescence enhancement by metal-core/silica-shell nanoparticles," *Advanced Materials*, vol. 18, no. 1, pp. 91–95, 2006.
- [2] J. B. Khurgin and G. Sun, "Enhancement of optical properties of nanoscaled objects by metal nanoparticles," *Journal of the Optical Society of America B: Optical Physics*, vol. 26, no. 12, p. B83, 2009.
- [3] E. Dulkeith, A. C. Mortcani, T. Niedereichholz et al., "Fluorescence quenching of dye molecules near gold nanoparticles: radiative and nonradiative effects," *Physical Review Letters*, vol. 89, no. 20, Article ID 203002, 2002.
- [4] P. G. Nicholson, V. Ruiz, J. V. Macpherson, and P. R. Unwin, "Hybrid nanostructures using p-conjugated polymers and nanoscale metals: synthesis, characteristics, and optoelectronic applications," *Chemical Communications*, vol. 8, p. 1052, 2005.
- [5] D. H. Park, M. S. Kima, and J. Jinsoo, "Hybrid nanostructures using  $\pi$ -conjugated polymers and nanoscale metals: Synthesis, characteristics, and optoelectronic applications," *Chemical Society Reviews*, vol. 39, pp. 2439–2452, 2010.
- [6] B. K. Kuila, A. Garai, and A. K. Nandi, "Synthesis, optical, and electrical characterization of organically soluble silver nanoparticles and their poly(3-hexylthiophene) nanocomposites: Enhanced luminescence property in the nanocomposite thin films," *Chemistry of Materials*, vol. 19, no. 22, pp. 5443–5452, 2007.
- [7] X. Wang, F. He, X. Zhu, F. Tang, and L. Li, "Hybrid silver nanoparticle/conjugated polyelectrolyte nanocomposites exhibiting controllable metal-enhanced fluorescence," *Scientific Reports*, vol. 4, article no. 4406, 2014.
- [8] J. Burunkova, S. Kokenyesi, I. Csarnovics, A. Bonyár, M. Veres, and A. Csik, "Influence of gold nanoparticles on the photopolymerization processes and structure in acrylate nanocomposites," *European Polymer Journal*, vol. 64, pp. 189–195, 2015.
- [9] M. Nagy, D. Rácz, Z. L. Nagy et al., "An acrylated isocyanonaphthalene based solvatochromic click reagent: optical and biolabeling properties and quantum chemical modeling," *Dyes and Pigments*, vol. 133, pp. 445–457, 2016.
- [10] M. Nagy, S. Kéki, D. Rácz et al., "Novel fluorochromes label tonoplast in living plant cells and reveal changes in vacuolar organization after treatment with protein phosphatase inhibitors," *Protoplasma*, vol. 255, no. 3, pp. 829–839, 2018.
- [11] S. Santra, K. Wang, R. Tapeç, and W. Tan, "Development of novel dye-doped silica nanoparticles for biomarker application," *Journal of Biomedical Optics*, vol. 6, no. 2, pp. 160–166, 2001.
- [12] G. Canton, R. Riccò, F. Marinello, S. Carmignato, and F. Enrichi, "Modified Stöber synthesis of highly luminescent dye-doped silica nanoparticles," *Journal of Nanoparticle Research*, vol. 13, no. 9, pp. 4349–4356, 2011.
- [13] F. Qu, J. Liu, H. Yan, L. Peng, and H. Li, "Synthesis of organic nanoparticles of naphthalene-thiourea-thiadiazole-linked molecule as highly selective fluorescent and colorimetric sensor for Ag(I)," *Tetrahedron Letters*, vol. 49, no. 52, pp. 7438–7441, 2008.
- [14] J. Burunkova, M.-J. Ohoueu, I. Csarnovics, M. Veres, A. Bonyár, and S. Kokenyesi, "Peculiarities of interaction of gold nanoparticles with photoinitiators in polymer nanocomposites for holographic recording," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 359, pp. 111–120, 2018.



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