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Radiation Measurements

Multicolor photon emission from organic thin films on different substrates

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HIGHLIGHTS

- Novel organic thin films on specific substrates show multicolor photon emission.
- Using porous silicon as a substrate allows to observe blue, green and red emission simultaneously.
- Contribution of color components can be tuned by adjusting the excitation wavelength.

ARTICLE INFO

ABSTRACT

Thin films of 1-pentyl-2$^{/}$,3$^{/}$-difluoro-3$^{///}$-methyl-4$^{////}$-octyl-p-quinquephenyl and 9,10-Bis (4-pentylphenylethynyl)anthracene organic molecules were grown on optical glass, silicon and porous silicon substrates. First optical and luminescent properties of such hybrid composites are thoroughly studied using spectroscopic techniques. The strong decrease of aggregation in thin films of 1-pentyl-2$^{/}$,3$^{/}$-difluoro-3$^{///}$-methyl-4$^{////}$-octyl-p-quinquephenyl on porous silicon was observed. The possibility of simultaneous red, green and blue tunable photon emission from organic film/porous silicon hybrid structure is demonstrated.

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1. Introduction

Composite materials comprising organic and inorganic components are widely used in various electronic and optical systems (Kukhta et al., 2015). Combining the specific properties of the composite components one can enhance the desired characteristics of the material or design the structure in which a new effect occurs (Aksimentyeva et al., 2014, 2013). There are two types of such materials (i) interpenetrated and (ii) layered.

Luminescent organic thin films deposited on inorganic substrate can serve as an example of composite materials of the second type.

These materials have a great potential for their application usage in lightweight illumination devices or in the design of small-sized RGB emitting elements in electroluminescent displays (Sebastian et al., 2013). They are formed when a layer of optically active organic molecules is deposited onto dielectric or semiconducting substrate. An essential effect of substrate properties on morphology as well as on optical and luminescent properties of organic films was already noticed (Kukhta et al., 2009). Among different nano-structured semiconductors that can be considered as prospective substrate material, porous silicon (PS) is of particular interest. Visible luminescence from PS at room temperature confirmed by Canham (Canham, 1990) extends the application of PS in opto-electronics. Depending on molecular structure, an energy or charge transfer can be observed between organic and inorganic layers. The passivation of porous silicon surface with an organic layer allows

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not only to tailor optical and luminescent properties of such hybrid structure but also to decrease the degradation processes intensity and to protect the porous layer from ambient conditions influence (Nguyen et al., 2000; Olenych et al., 2012; Olenych, 2011). In particular, in (Nguyen et al., 2000) the authors combine the properties of polymer and porous silicon to expand the emission range and report 522 nm 564 nm and 620 nm bands. In (Olenych et al., 2012) it is demonstrated that the transmission of the passivation layer can be tuned and in (Olenych, 2011) the effect of passivation on the stability of porous Si luminescence is discussed. In the present work, an attempt to benefit from all these effect is discussed. The results of spectroscopic investigation of luminescent layered organic-inorganic composite thin films are reported with an emphasis on multicolor emission from PS/organic layer hybrid structures.

2. Experimental

For the purpose of experiment 1-pentyl-2$^{/}$,3$^{/}$-difluoro-3$^{///}$-methyl-4$^{////}$-octyl-p-quinquephenyl (M1) and 9,10-Bis (4-pentylphenylethynyl)anthracene (M2) organic molecules were thermally deposited in 10^{-4} Torr vacuum using VUP-5M machine (Ukraine). This deposition technique and instrumentation was earlier used to fabricate nanostructured metallic films with random structure (Bolesta et al., 2014; Karbovnyk et al., 2015). Both molecules are highly luminescent liquid crystalline compounds (Gimenez et al., 2004) capable to be deposited by thermal evaporation from solid and by spin coating from solutions. The thermal stability under evaporation is high (Kukhta et al., 2007). M1 has been obtained as described in (Sasnouski et al., 2012); M2 has been synthesized under conditions of Suzuki reaction. Both molecules were synthesized at the Institute of Applied Physical Problems. Chemical structure of M1 and M2 is shown in Fig. 1.

Optical glass, polished silicon and PS covered plates were used as substrate materials for film deposition. Each of the above mentioned organic analytes was deposited on every of the three substrates separately. In addition, simultaneous deposition of M1 and M2 on the selected substrates was performed (50% of M1 and 50% of M2 was weighted and used for depositing). It has to be noted, that the deposition rate of M1 and M2 during simultaneous deposition is different, so the resulting film may contain unequal amount of M1 and M2. The average rate of deposition was about 10 nm per second. Average thickness of deposited films was interferometrically measured to be about 100 nm. Before deposition the substrates were carefully cleaned with ethanol.

PS layers on the single crystalline plate were fabricated by electrochemical etching of n-type 400 micrometer thick silicon plate with volume resistivity of 4.5 Ohm·cm in HF acid based electrolyte (volume ratio HF: $C_2H_5OH = 1: 1$). Anode current density was kept constant at 40 mA/cm^2 for the entire duration of anode etching (15 min). In order to ensure the presence of positive carriers in the near-surface n-Si layer (these carriers are necessary for anode reactions to occur and PS to be formed) the working surface was illuminated by 500 W incandescent light bulb in the process of etching. Under such conditions macro porous silicon layers are formed with average pore diameter within the range of 100–1000 nm. These layers exhibit intensive photoluminescence in visible range (Cullis et al., 1997; Bisi et al., 2000). PS allows efficient penetration of organic molecules into the pores and, consequently, enables the passivation of silicon nanocrystals surface.

Molecular structure of PS and PS/organic layer hybrid structures was investigated using Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded with AVATAR instrument from Thermo Scientific in the range of 400 … 4000 cm^{-1}. Infrared absorption bands were identified according to literature data (Borghesi et al., 1993; Fukuda et al., 1997; Niwano, 1999; Silverstein et al., 1991).

Luminescent properties were studied using CM2203 spectrofluorometer (Solar, Belarus). Optical absorption spectra of the films on glass substrate were measured in 250–1000 nm range. Optical absorption spectra of the solutions were in the same range using quartz cuvettes. Luminescence excitation spectra were measured in 250–350 nm range for 460 nm, 520 nm and 620 nm emission bands. Photoluminescence spectra were registered in 350–800 nm range using UV light excitation ($\lambda = 330$ nm) at ambient temperature.

3. Results and discussion

Absorption spectra of M1 and M2 organic films on optical glass differ in the visible range (Fig. 2, left). While M1 film is essentially transparent in the visible, M2 film exhibits sharp absorption band peaked at 506 nm and slightly less intensive but wider bands at 462 nm and 430 nm. In addition, in case of M2 there are two sharp absorption peaks on the background of the optical glass absorption edge (below 350 nm). As expected, (M1+M2) film shows similar to M2 absorption profile with depressed bands at approximately same positions. For comparison, right-hand side of Fig. 2 illustrates the absorption spectra of diluted (less than 10^{-6} M/l) chloroform (CHCl$_3$) solutions. Comparing thin film and solution spectra we can notice an essential bathochromic spectral shift which is typical for transitions from liquid to solid phase.

Luminescence from M1 and M2 chloroform solutions and organic films deposited on different substrates is presented in Fig. 3.

The intensity of luminescence is different for each used substrate. The strongest emission is observed for molecules deposited on optical glass. Luminescence of M1 solution shows typical structureless blue emission band of π-π transition at about 380 nm, while M1 films on glass and Si have two bands at about 385 nm and more intense band centered around 460 nm. This 460 nm band originates probably from molecular aggregation. The intensity of both bands decreases significantly when one replaces glass substrate with silicon. When porous silicon is used, the blue emission at 460 nm disappears completely and only red PS-related band appears at nearly 620 nm. The reason of the 460 nm band absence can be worth conditions for molecular aggregation or different way of molecule packing inside the pores.

The spectral behavior of M2 molecule luminescence is similar. Both in solution and thin films M2 shows π-π transition spectra with vibrational structure at 520 nm (film) 0-0 vibrational maximum. Also, we observed an additional less intensive wide band at about 600 nm, which can be attributed to aggregation. It can be noted that the observed aggregation is not as strong as compared with M1. The third wide band up to 750 nm and beyond originates from PS luminescence.

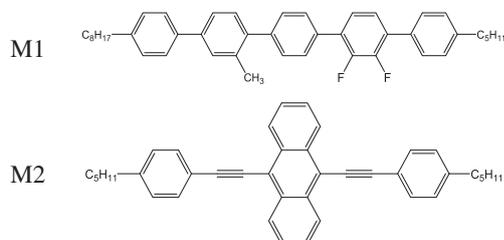No systematic luminescence intensity decay was observed in

Fig. 1. Chemical structure of 1-pentyl-2$^{/}$,3$^{/}$-difluoro-3$^{///}$-methyl-4$^{////}$-octyl-p-quinquephenyl (M1) and 9,10-Bis (4-pentylphenylethynyl)anthracene (M2).
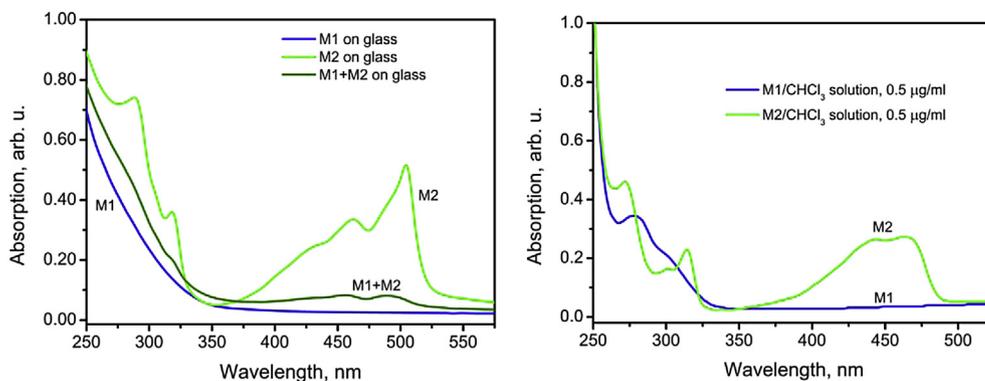
Fig. 2. Absorption spectra of organic molecules deposited on optical glass (left) and absorption spectra of M1 and M2 in chloroform solution (right).
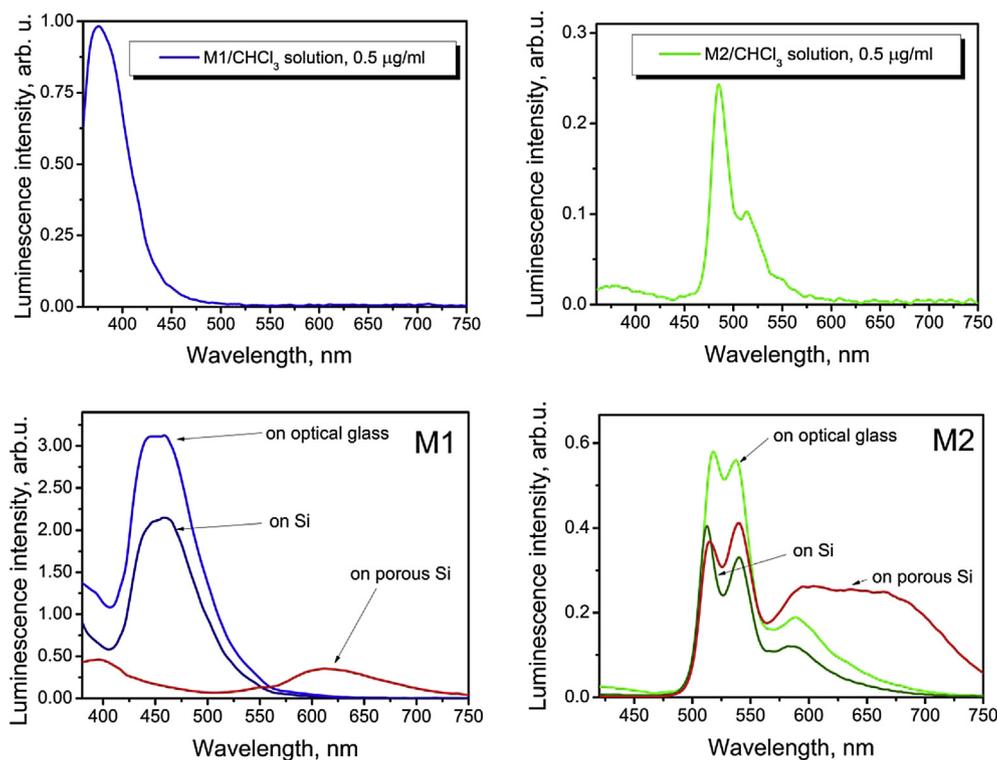

Fig. 3. Photoluminescence from M1 and M2 organic films on different substrates and for chloroform solutions of M1 and M2. Excitation wavelength is 330 nm. All intensities are normalized with respect to 376 nm peak height in M1/CHCl3 solution (shown in top left plot).

repeated measurements (one day and one week after sample preparation). The long-term stability of luminescence intensity will be the subject of forthcoming experiments.

To identify the components of PS-based hybrid structures luminescence we have examined FTIR spectra (Fig. 4).

The analysis of IR transmittance of PS indicated that most of the absorption bands are related to molecular complexes that include oxygen and hydrogen. Most prominent are IR bands in the 620–660 cm^{-1} range corresponding to bending Si–H_2 mode and the band peaked at 1100 cm^{-1} that can be related to valence Si–O–Si vibrations (Borghesi et al., 1993; Fukuda et al., 1997). The band at 460 cm^{-1} is usually ascribed to deformation vibrations of Si–O group (Niwano, 1999). Besides, we observed IR absorption within 860–1000 cm^{-1} range and between 2100 and 2200 cm^{-1}. These band are characteristic for hydrogen containing molecular complexes: O–SiH_x (x = 1,2) and Si–H, respectively. Bands in

3400–4000 cm^{-1} range are due to Si–OH groups and due to water molecules, adsorbed by PS (Olenych, 2011; Niwano, 1999).

For PS/organic film hybrid structures overall decrease in IR absorption was observed, probably due to increase of the thickness of the structure and additional absorption in deposited layer. Apart from that, several new bands appear due to the absorption by molecular complexes of the film and due to the interaction between these complexes and PS. In the 800–1000 cm^{-1} region, the series of band related to the vibrations of C–H bands was identified C–H (Silverstein et al., 1991). In the same region we observed the bands characteristic for halogen containing compounds, in particular, C–F complexes. In the wavenumber range of 2800–3000 cm^{-1} a few bands corresponding to stretching C–H_x bonds (x = 1,2,3) were detected. Broad band at 2100–2260 cm^{-1} is likely related to carbon complexes –C≡C–. The transformation of absorption band within 1070–1240 cm^{-1} can be due to C–O groups resulting from the
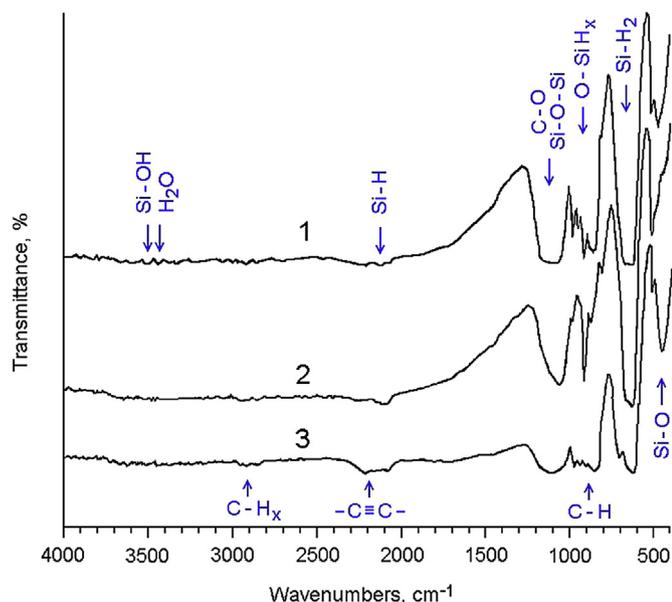
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Fig. 4. IR transmittance of PS substrate (1) and PS/M1 organic film hybrid structure (2) and PS/M2 organic film hybrid structure (3).

Fig. 6. Luminescence excitation spectra of porous silicon (620 nm band), M1 film (460 nm band) and M2 film (520 nm band).

passivation of PS surface by organic films.

Visible photoluminescence band of PS is a superposition of radiative processes resulting from the recombination of electron−hole pairs excited in silicon nanocrystals of different size. Electronic spectrum of such nanocrystals is modified due to quantum confinement effect. Therefore, photoluminescence band is broad and the peak position can be tailored either by changing the technological route of PS preparation or by the passivation with organic layers. Combining blue emission from M1 organic layer, yellow emission from M2 organic layer and intrinsic PS red luminescence it is possible to design the structure with custom emission properties. Examples of efficient combinations of blue and red an yellow/green and red emissions form M1 and M2 molecules and the PS substrate can be seen in Fig. 3 (red lines). We have also deposited M1 and M2 simultaneously on PS substrate, obtaining three-component multicolor emitting system. The respective spectrum is shown in Fig. 5.

The contribution of each emission component can be tuned, for instance, by adjusting excitation energy in the spectral range of 250
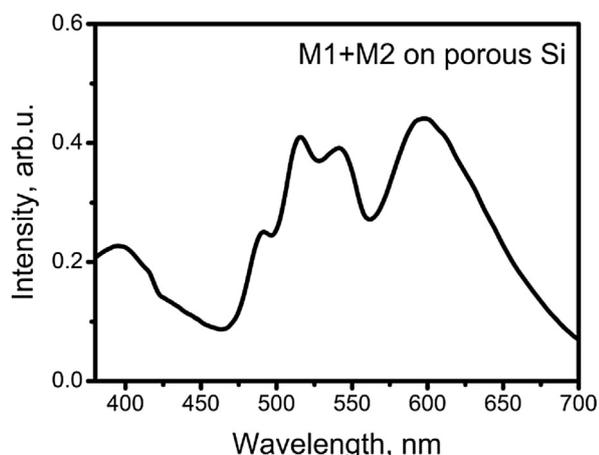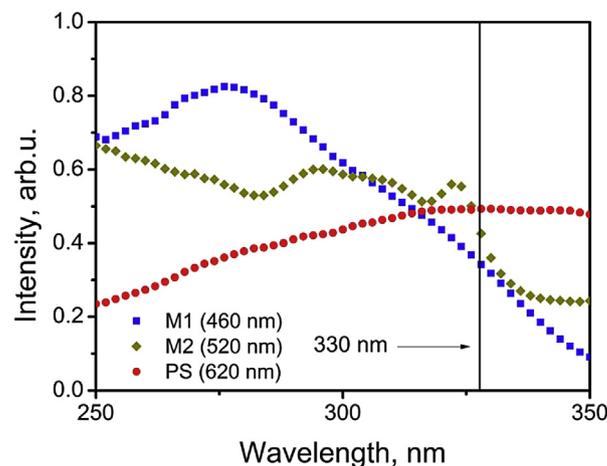
… 350 nm. As can be seen from luminescence excitation spectra in Fig. 6. 330 nm light effectively excites luminescence from PS and green emission from M2 layer, although it is not 100% efficient at exiting blue emission from M1.

Thus, going to higher energies of excitation source one is able to redistribute the intensities of red, blue and green components and tailor the resulting multicolor spectrum.

4. Conclusions

Novel thin organic films were fabricated by thermal vacuum deposition of luminescent liquid crystalline organic molecules on different substrates. It is demonstrated that combining specific substrate material with various organic molecules allows to observe multicolor emission, ultimately opening the way to designing a white light emitting structure. The possibility of tuning the multicolor light emission by changing the excitation energy is shown. The strong decrease of aggregation in thin films of 1-pentyl-$2',3'$-difluoro-$3'''$-methyl-$4''''$-octyl-p-quinquephenyl on porous silicon was observed.

Fig. 5. Emission from M1+M2 layer deposited on porous silicon substrate.

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