

Cascade three-component composition on polystyrene basis absorbing in visible range and emitting in near IR

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Design results have been presented for a three-component composition for solar energy conversion into the sensitivity range of Si and GaAs photocells based on polystyrene and polycyclic aromatic organic luminescent compounds. Two possible approaches to selection of concentrations of the components oriented to provide the maximum collection efficiency of the visible range solar radiation and the optimum conditions of the Foerster non-radiative energy transfer between the intermediate and final components of the cascade composition have been shown to give comparable results and thus do not form an alternative to one another.

Представлены результаты дизайна трехкомпонентной композиции для преобразования энергии солнечного излучения в интервал чувствительности Si и GaAs фотоэлементов на основе полистирола и ароматических полициклических органолюминофоров. Показано, что два возможных подхода к подбору концентраций компонентов, ориентированные на обеспечение максимально эффективного сбора излучения в видимом диапазоне и оптимальных условий Ферстеровского безызлучательного переноса энергии между промежуточными и конечными компонентами каскадной композиции, дают сравнимые результаты и, таким образом, не являются альтернативой друг другу.

The ever-increasing need for new energy sources capable to substitute for the exhausting hydrocarbon resources concentrates the attention of both applied and fundamental researchers on the solar power engineering development problems. Among the actual goals in this science field, there is the development of new light-resistant luminescent materials to convert the solar radiation into the near IR range (NIR) answering to the maximum photosensitivity of Si and GaAs semiconductors, that is, into

850 to 1000 nm range [1–3]. The use of organic luminescent materials (OLM) to design such devices is promising due to that OLM possess some unique parameters that are not provided by alternative inorganic materials. Among those parameters, the most important ones include: visible light absorption within a wide range (400 to 600 nm); minimum reabsorption; high quantum yield of fluorescence; high light and heat resistance; a sufficient compatibil-

ity with polymer materials used as matrices in solar light converters.

It is to note that most OLM do not show all the above-mentioned properties simultaneously; moreover, some of those are incompatible. The development of efficient IR OLM is a much more complex task as compared to UV and visible range luminophors, see, e.g., the review [4]. So, for example, materials either including a sufficiently long conjugation chains or showing a strong donor-acceptor interaction (right up to ionic type structures) are to be developed to provide an intense emission in the IR range. On the other hand, such materials are poorly soluble in organic polymers and show often a lowered light and heat resistance. The well-known cyanine structure OLM can be taken as an example that emit in the 800–1600 nm range but exhibiting a low light and heat resistance and poorly compatible with organic polymers.

Moreover, a specific feature of long-wavelength OLM is a low Stokes shift (typically 800 to 1200 cm^{-1}) that decreases as the emission wavelength is shifted towards IR region. As a result, the reabsorption increases, thus causing an efficiency of the devices including those materials. Besides, the narrow absorption bands of ionic dyes cannot cover the whole visible range, thus, the efficiency of solar radiation collection is deteriorated. That is why the most long-wavelength OLM cannot be used individually in the solar energy concentrators.

In our opinion, the development of a composition consisting of several OLM would be one of ways to solution of the above problem. Such an approach provides wide opportunities in the system designing and control of its optical characteristics. In this work, a possibility to provide such a cascade composition in polystyrene matrix is demonstrated taking as an example three dyes with intermolecular non-radiative transfer of the electron excitation energy,

where the dyes absorb the visible range light (400 to 650 nm) and re-emit it sequentially into the 714–850 nm region. To provide the light absorption in such a wide range and its re-emission into the IR region, functions of two light converting cascades are combined in the composition. The first cascade is a ternary one (dyes I + II + III) where the I compound absorbs the light within the about 400–500 nm region with its subsequent re-emission into IR region by the scheme $I \rightarrow II \rightarrow III$. The second cascade is a binary one (dyes II + III) where the II compound absorbs the light within the about 500–600 nm region with its subsequent re-emission into IR region by the scheme $II \rightarrow III$. The about 600 to 650 nm region is covered by the absorption spectrum of III that acts as a proper IR dye in the composition. In what follows, the principle of the composition design is described and its properties are presented.

The experimental samples in the form of thin (0.1 mm thick) polystyrene films containing the cascade compositions were prepared by evaporating 20 per cent toluene solutions of OLM in the required ratios on glass surfaces. The film thickness was set using a calibrated spacer. The films were dried in a special box at room temperature. To examine the optical characteristics, the films were taken off of the substrates.

The spectral characteristics of the initial OLM toluene solutions and the colored polystyrene films were determined using a HITACHI U2310 spectrophotometer and a HITACHIO F4010 spectrofluorimeter. The fluorescence quantum yields were evaluated versus the reference solution of quinine sulfate in 0.5 M aqueous sulfuric acid ($\phi = 0.55$ [5]). The spectral kinetics parameters were measured using a nanosecond pulse fluorometer operated in the photon counting mode. The instrument has been described in [6].

Table 1. Spectral characteristics of I–III dyes

Compound	ν_a	λ_a	ϵ_a	ν_f	λ_f	$\Delta\nu_{ST}$	ϕ	τ
I	21380	468	56400	18740	534	2640	0.62	1.37
II	17320	577	31200	16260	615	1060	0.44	4.45
III	15740	635	33300	14340	697	1400	0.26	4.96

Here, ν_a , ν_f are the absorption and fluorescence maxima positions, respectively, in the wave numbers scale (cm^{-1}); λ_a , λ_f , the same in the wavelength scale (nm); $\Delta\nu_{ST}$, the Stokes shift (cm^{-1}); ϵ_a , the molar extinction coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$); ϕ , the fluorescence quantum yield; τ , the fluorescence lifetime (ns).

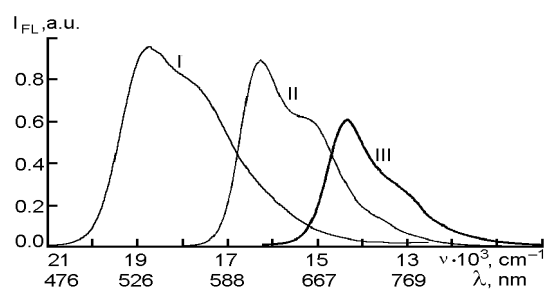


Fig. 1. Fluorescence spectra of dyes I–III normalized to the area under spectral curve according to their quantum yields.

The spectral and photophysical characteristics of fluorophors included in the proposed cascade composition are presented in Table 1 (as determined for liquid toluene solutions). The solvent used provides a maximum close approximation to physico-chemical properties of the solid solution based on polystyrene. Nevertheless, a small long-wavelength shift is possible when passing from toluene to polystyrene due to influence of the rigid polymer medium and changes in the fluorescent dye interaction with its nearest environment.

The longer-wavelength dyes II and III are seen to not exhibit very strong absorption in the middle part of the visible range, therefore, it is just the dye I that will contribute mainly to the light collection in this region. Fig. 1 shows the fluorescence spectra of three OLM proposed, the intensity ratio corresponding to that of their quantum yields.

A certain decrease of quantum yield is seen to occur as the absorption and emission bands are shifted towards long-wavelength region. This may be due to increase of the S_1-S_0 internal conversion efficiency resulting from energy convergence of the ground and excited state in the molecule. As a whole, the dyes proposed are rather efficient luminophors with spectral characteristics well matching to each other.

In Fig. 2, shown are the absorption and fluorescence spectra for pairs of dyes proposed by us for the cascade composition, between which the electron excitation energy transfer is possible. The spectra demonstrate a great overlap extent of the acceptor component absorption and the donor component emission in each pair. The great spectral overlap extent in the I–II and II–III pairs must provide a high energy transfer efficiency between the "neighboring" cascade components. Moreover, the spectral overlap between the "outermost" dyes I and

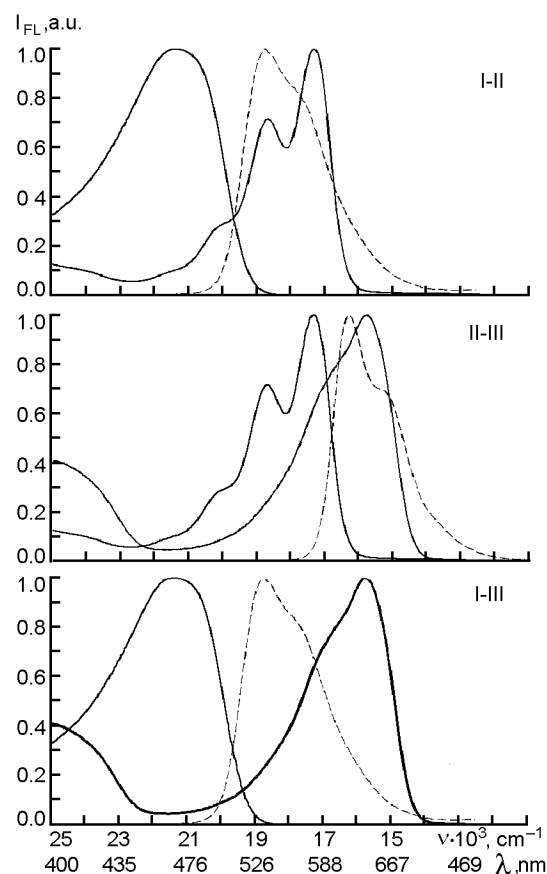


Fig. 2. Absorption and emission spectra overlap for pairs of dyes in the proposed cascade composition.

III. Thus, an additional transfer direction will take place in the proposed composition, thus favoring the improved efficiency of the whole cascade.

Two approaches that are not in general alternative ones can be used to formulate the cascade compositions. The component concentrations can be selected in order to provide the most complete and homogenous absorption in the visible range. In this case, the solar light will be collected at the maximum possible efficiency. The dye concentrations will be high enough and the energy transfer between the dyes will occur at a high probability. Another approach consists in selection of the dye concentrations providing a high efficiency of the electron excitation energy transfer between the individual components in the composition. Since, according to the Foerster theory, the energy transfer occurs over distances of 30 to 100 Å [7], this approach results inevitably in the use of high dye concentrations and thus in high optical density of the cascade in the absorption region covered therein. Besides of the Foerster non-radiative

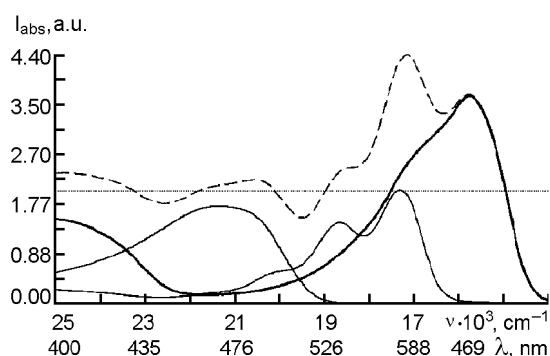


Fig. 3. Selection of the component concentration ratios basing on requirement of complete and homogeneous absorption within the visible region (concentrations: I, 0.1 %; II, 0.5 %; III, 0.4 %).

energy transfer, a partial realization of the radiative energy transfer mechanism is possible, where the light emitted by the short-wavelength components will be absorbed by the long-wavelength ones. The radiative energy transfer will occur at the distances between the donor and acceptor molecules exceeding those answering to the Foerster theory.

We attempted to design the cascade compositions in the frames of both approaches. Fig. 3 presents the absorption spectrum of the cascade proposed at the component concentration ratios providing the complete and as homogeneous as possible absorption within the visible region (400 to 650 nm) in toluene solution at the absorbing layer thickness of 1 mm (the optical density $D = 2$ answers to absorption of 99 % of radiation incident on the sample surface).

Basing on the ratio determined, we have prepared the polymer film samples and determined optical characteristics thereof under monochromatic and polychromatic excitation. In the last case, the solar radiation was modeled by the diffuse emission spectrum of a high pressure xenon lamp with UV and IR ranges cut off using a SZS-21 glass light filter. The emission of a polymer film sample with optimized content of dyes I–III is exemplified in Fig. 4.

The high energy transfer efficiency between the cascade components is evidenced by the low residual emission intensity of the shortest-wavelength dye and the intermediate one (I and II). In fact, the composition emission is presented mainly by the fluorescence of the most long-wavelength component thereof. Moreover, the relatively high content of the dye III in the composition provides an appreciable reabsorption of

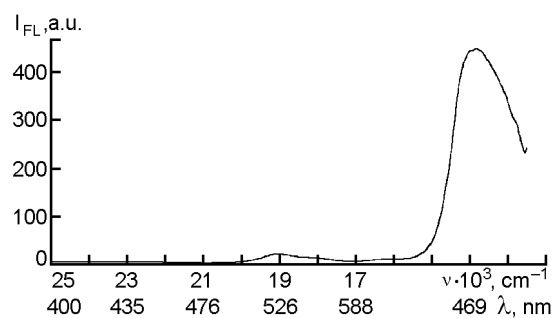


Fig. 4. Emission spectrum of the (I, 0.1 %; II, 0.5 %; III, 0.4 %) composition under polychromatic excitation.

its intrinsic emission. As a result, the emission maximum of the cascade composition is observed at a longer wavelength (723 nm) than the intrinsic emission of the NIR emitting luminophor in polystyrene (712 nm).

To reduce the reabsorption effect, we have used the second of the above-mentioned approaches to the cascade composition formulation. This approach consists in optimization of the concentration ratio to provide the maximum efficiency of the electron excitation energy transfer between the components. In this connection, the spectral overlap integrals for the proposed components were calculated in the frame of Foerster theory and then, basing on those integrals, the critical Foerster's transfer distances R_0 (where the transfer efficiency is comparable to the energy donor emission efficiency (2)).

$$J = \int_0^{\infty} F_d(\nu) \cdot \varepsilon_a(\nu) \cdot \nu^{-4} \cdot d\nu. \quad (1)$$

Here, $F_d(\nu)$ is the fluorescence spectrum in the wave number scale normalized to the unit area under spectral curve; $\varepsilon_a(\nu)$, the absorption spectrum (the intensity is expressed in extinction coefficient units); ν , the wave number (cm^{-1}). The integration is done with respect to wave number.

$$R_0^6 = \frac{9000 \cdot (\ln 10) \cdot k^2 \cdot \varphi_D J}{128 \cdot \pi^5 \cdot N \cdot n^4}. \quad (2)$$

Here, φ_D is the quantum yield of the energy donor fluorescence; N , Avogadro number; n , the medium refractive index; k^2 , the orientation factor taken as 2/3 for chaotic spatial orientation of the donor and acceptor.

The corresponding numerical results are shown in Table 2. In the last column, the critical transfer concentrations are pre-

Table 2. Characteristics of non-radiative energy transfer between the cascade components as estimated using the Foerster theory for toluene solutions

Dye pairs	$J, \text{mol}^{-1} \cdot \text{cm}^3$	$R_0, \text{\AA}$	$A_0, \text{mol/L}$
	Overlap integral of the donor and acceptor spectra	Critical Foerster radius	Critical acceptor concentration (75 % transfer)
I \rightarrow II	$1.70 \cdot 10^{-13}$	48.1	$4.02 \cdot 10^{-3}$
I \rightarrow III	$1.64 \cdot 10^{-13}$	47.8	$4.09 \cdot 10^{-3}$
II \rightarrow III	$3.56 \cdot 10^{-13}$	51.4	$3.29 \cdot 10^{-3}$

sented answering to the acceptor concentration providing the energy transfer efficiency equal to 75 % of the donor emission efficiency (3).

$$A_0 = \frac{3000}{2 \cdot \pi^{3/2} \cdot N \cdot R_0^3} \quad (3)$$

According to the results obtained, the concentrations of the composition components can be selected by solving the system of equations (4) where the dye ratios are selected to provide that the total concentration of each donor-acceptor pair is equal to the corresponding critical concentration A_0 .

$$\begin{aligned} C_I + C_{II} &= 3.41 \cdot 10^{-3}, \\ C_I + C_{III} &= 3.47 \cdot 10^{-3}, \\ C_{II} + C_{III} &= 2.88 \cdot 10^{-3}. \end{aligned} \quad (4)$$

The testing results of composition formulated in this fashion (0.15 % I + 0.16 % II + 0.12 % III) have shown that when the initially claimed result is attained, i.e. the reabsorption is reduced and the maximum emission wavelength of the sample is approached that of the NIR-emitting lumino-phor in diluted solution, the total composition efficiency must be somewhat reduced, since the residual emission of short-wavelength components is increased as compared to the composition tested before (see Fig. 4).

Therefore, the composition has been subjected to a further modification consisting in that the II and III concentrations were increased up to levels of corresponding critical transfer concentrations A_0 (Fig. 5), the short-wavelength component I concentration remaining unchanged.

Thus, we managed to bring the spectral parameters of this composition near to those of the cascade composition obtained under the first approach, while the content of the last emitting component was lowered, thus reducing its reabsorption.

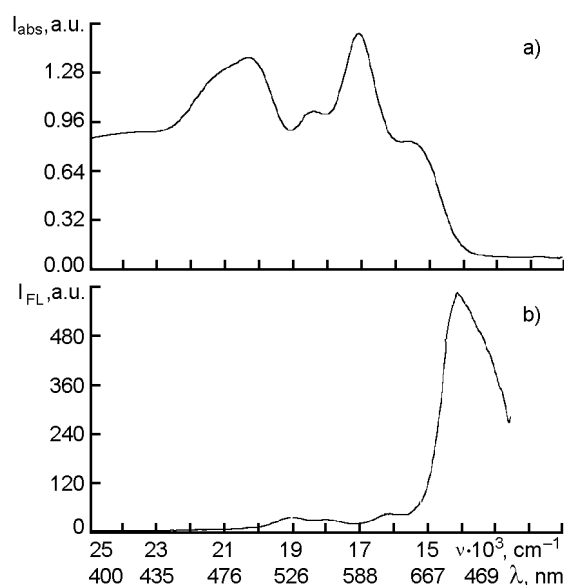


Fig. 5. Absorption and fluorescence spectra for a thin sample of modified composition (0.15 % I + 0.3 % II + 0.2 % III) under polychromatic excitation.

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**Каскадна трьохкомпонентна композиція
на полістирольній основі з поглинанням у видимому
та випромінюванням у ближньому ІЧ діапазонах**

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Представлено результати дизайну трьохкомпонентної композиції для конвертування енергії сонячного випромінювання в інтервал чутливості Si та GaAs фотоелементів на основі полістиролу та ароматичних поліциклічних органічних люмінофорів. Показано, що два підходи до добору концентрацій компонентів, орієнтовані на забезпечення максимально ефективного збирання випромінювання у видимому діапазоні і оптимальних умов Ферстерівського безвипромінювального переносу енергії між проміжними та кінцевими компонентами каскадної композиції, дають порівняні результати і, отже, не є альтернативою один одному.