Diflavonols as single emitters for polymer-based WOLEDs

V.V.Kosach¹, V.G.Pivovarenko², V.M.Yashchuk¹

¹Faculty of Physics, T.Shevchenko National University of Kyiv, 2 Glushkov Ave., 03022 Kyiv, Ukraine
²Faculty of Chemistry, T.Shevchenko National University of Kyiv, 12 L.Tolstoy Str., 01033 Kyiv, Ukraine

Received February 22, 2016

The spectral peculiarities of polymer/dye solid mixtures on the base of PPEKa polymer (polyethyleneoxide-carbazole) as matrix and DFOM (3,7-dihydroxy-2,8-diphenyl4H,6H-pyrene[3,2-g] chromene-4,6-diones) as emitter were investigated. Peculiarities intramolecular proton transfer after the excitation of molecule, incident to this material, allows one to create emitting layer with emission spectrum close to white light and using only one luminesphore. Spectral behavior of investigated compounds proves the presence of excitation energy transfer from the PPEKa matrix to the DFOM molecules, which is necessary for effective use of the excitation energy and forming luminescence curve needed. Luminescence of the investigated films demonstrates color characteristics CRI 54 and CIE (0.33, 0.42) which gives a possibility to consider such systems as promising in the context of developing White OLED emitters.

Keywords: WOLED, diflavonols, ESPT, organic light-emitting devices.

Исследованы спектральные особенности твердых смесей полимер/краситель на основе полимера ППЭК (полиэтиленоксициноваларбазол) в качестве матрицы и DFOM ((3,7-dihydroxy-2,8-diphenyl-4H,6H-pyrene[3,2-g] chromene-4,6-diones)) в качестве люминифора. Механизм внутримолекулярного переноса протона после возбуждения молекулы, свойственный этому материалу, позволяет получить излучающий слой со спектром излучения, близким к белому свету, используя при этом лишь один люминифор. Спектральное поведение исследованных систем позволяет предполагать присутствие в них переноса энергии электронного возбуждения от матрицы ППЭК к молекулам люминифора DFOM, что необходимо для эффективного использования энергии возбуждения и формирования заданного контура люминесценции. Луминесценция исследованных пленок продемонстрировала цветовые характеристики CRI 54 и CIE (0.33, 0.42), что позволяет рассматривать подобные системы, как перспективные при создании "белых" OLED-излучателей.

Використання діфлавонів в якості єдного випромінювача для полімерних "білих" OLED пристроїв. В.В.Косач, В.Г.Піроворенко, В.М.Ящук.

Досліджено спектральні особливості твердих сумішей полімер/барвник на основі полімера ППЭК (полиэтиленоксициноваларбазол) в якості матриці та сполуки DFOM (3,7-dihydroxy-2,8-diphenyl-4H,6H-pyrene[3,2-g] chromene-4,6-diones) в якості люминифора. Механізм внутрішньомолекулярного переносу протона після збудження молекули, властивий цьому матеріалу, дозволяє отримати випромінювач з ширі спектром випромінювання, близьким до білого світла, використовуючи лише один люминифор. Спектральна поведінка досліджених систем дозволяє припустити наявність у них перенесення енергії електронного збудження від матриці ППЭК до молекул барвника DFOM, що необхідно для ефективного використання енергії збудження та формування необхідного контуру люмінесценції. Люмінесценція досліджених плямок продемонструвала кольорові характеристики CRI 54 та CIE (0.33, 0.42), що дозволяє розглядати подібні системи, як перспективні у створенні "білих" OLED-випромінювачів.
1. Introduction

While in last two decades the OLED technology has impressively "grown up" and gained some success on electronics markets, the development of efficient White OLEDs (or WOLED) with good color characteristics remains an actual challenge. So it is still important to obtain new materials which would have a potential to improve the technology.

There are a number of problems in the WOLED development. If we use an organic matrix as light emitting layer with incorporated 2 or 3 molecular emitters, the following problems appear: (1) inhomogeneous distribution of emitting centers of different types in the matrix, which is related to different solubility in solutions for film casting (spin-coating technology) or different evaporating ability (evaporating technology), or other peculiarities of WOLED film preparation technologies; (2) the difference in energy transfer efficiency from the matrix to emitting centers of different types. These problems, from our point of view, could be overcome using single-molecular emitters possessing luminescent ability in a wide spectral range covering the entire visible region. In this context compounds with the intramolecular proton transfer represent a great potential because of their potential ability to form nearly "white" luminescence curve by themselves, with no additional luminophores [1]. One of the potentially useful classes of molecules of this kind are aminoxanthenes, which have been already well studied [2]. Another promising class of such type of compounds for WOLED is diflavanols. The photoinduced transfer of the proton that takes place in such molecules in some cases allows the emission spectrum to cover all the visible range of light spectrum. Thus, some simple single-layer polymer/dye systems could be made on the base of flavanol molecules with emission spectrum close to the white light.

2. Experimental

All measurements were performed at room temperature and ambient atmosphere. All solutions were prepared in dioxane as solvent, with concentration $c \sim 10^{-3}$ g/mL. Films were made from the solution by spin-coating on a glass substrate. For obtaining of PEPc + DFOM(3,7-dihydroxy-2,8-diphenyl-4H,6H-pyrazolo[3,2-g] chromene-4,6-dione) (DFOM) compounds (Fig. 1) solutions and their solid mixtures (films) with PEPc polymer as a matrix. DFOM molecule is related to the class of diflavanols in which the process of proton transfer after excitation of the molecule can take place [7–10]. Such proton transfer process is typically named as Excited-State Intramolecular Proton Transfer or ESIPT [7,9–11]. Such intramolecular proton transfer in diflavanols leads to three possible tautomeric forms of the diflavanol molecule: NN, NT and TT [12–14]. At present, it is believed that the diflavanols exist in the NN form in the ground state and in the NN* and NT* forms in the excited state [13, 15].

Both absorption and luminescence (Fig. 2) spectra of DFOM + PEPc solution ($m_{\% PEPc} \sim 1\%$) suggest the presence of two main optical centers: typical carbazole-like center with clearly structured absorption peaks on 295 nm, 330 nm, 346 nm and luminescence peaks at 351 nm and 367 nm. The second one is a typical flavonol-like optical center with a wide absorption peak near 363 nm and wide luminescence peak near 570 nm. Both centers take part in absorption and emission of light in the DFOM solutions.

In the luminescence of the PEPc + DFOM film, an additional comparable peak near 480 nm appears. Since PEPc has no sufficient fluorescence peaks in this spec-
Fig. 1. DFOM molecule [15].

Fig. 2. Absorption, fluorescence and fluorescence excitation spectra of DFOM + PEPCa solution (m_{PEPCa} - 1 %).

Fig. 3. Fluorescence, fluorescence excitation and absorption spectra (normalized) of PEPCa + DFOM film.

Fig. 4. Absorption, fluorescence and fluorescence excitation spectra (normalized) of PEPCa.

tml region, we consider both 479 nm and 555 nm peaks to be the result of different tautomeric DFOM forms emission [16]. It is worth to mention that fluorescence excitation spectra for all significant peaks of PEPCa + DFOM luminescence are almost identical to the absorption spectrum of pure PEPCa. These allow us to consider the presence of effective excitation energy transfer from PEPCa to DFOM molecules.

Color parameters CIE and CRI for the investigated PEPCa + DFOM film luminescence were estimated (for the λ_{ex} = 330 nm luminescence curve): CIE (0.33; 0.42) and CRI = 54. Such values are pretty close to color parameters of existing white light sources, and thus such films could be considered as potentially promising for the development of White OLEDs.

To examine the hypothesis of energy transfer from the luminescence data of the films studied, the luminescence excitation and absorption spectra of the matrix, dopant and resulting solid mixture should be compared. Absorption and luminescence excitation spectra of the solid mixture film (Fig. 3) in the 330-350 nm range are similar to the PEPCa film absorption spectrum (Fig. 4). This allows us to consider PEPCa molecules as main absorbing optical centers in the PEPCa + DFOM film. At the same time in the luminescence spectrum of the solid mixture all optical centers, i.e., PEPCa and DFOM in different forms, are presented with comparable intensities. From this data we can conclude that DFOM molecules in the mixed films emit light mainly due to excitation energy transfer from PEPCa to DFOM molecules.

4. Conclusions

In the present investigation the spectral properties of PEPCa + DFOM were studied. Analysis of the obtained spectral data al-
lows us to consider the presence of excitation energy transfer from the polymer matrix to luminophore in the investigated PEPc/DFOM films. Also it was shown that sufficient luminescence color characteristics (CRI 54 and CIE (0.33, 0.42)) of a single emitting layer could be obtained using DFOM molecule as emitter and PEPc polymer as matrix.

So, the results obtained demonstrate the possibility to develop white OLED with one type of light-emitting molecules, the excitation of which is realized by migration of the mobile electronic excitation through a suitable organic matrix. The coverage of the visible spectral region is provided by different tautomers that appear due to intramolecular proton transfer in excited states of flavonol molecules.

References