

# Hybrid bulk and planar heterojunctions with electroluminescent quantum dots CdZnSeS and poly(dioctylfluorene)

*O.O.Matvienko, O.S.Kryzhanovska, Yu.N.Savin, O.M.Vovk,  
N.V.Pogorelova\*, V.V.Vashchenko\**

Institute for Single Crystals, STC "Institute for Single Crystals"  
National Academy of Sciences of Ukraine,  
60 Lenin Ave., 61001 Kharkiv, Ukraine

\*SSI "Institute for Single Crystals", National Academy of Sciences of  
Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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Hybrid organic-quantum dot light emitting devices (QD-OLED) with bulk and planar heterojunctions based on poly(dioctylfluorene) and electroluminescent quantum dots CdZnSeS (QD) were obtained. The influence of QD concentration and the QD film morphology on the device electroluminescence was investigated. For QD-OLED with QD emissive bilayer, the device electroluminescent efficiency was higher compared to bulk heterojunction.

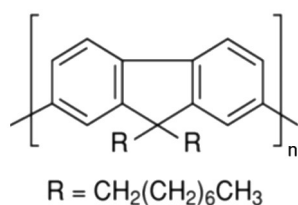
Получены гибридные органические светоизлучающие устройства (КТ-ОСИУ) с объемным и планарным гетеропереходами на основе поли(диоктилфлуорена) и электролюминесцентных квантовых точек CdZnSeS (КТ). Исследовано влияние концентрации КТ и морфологии слоя КТ на электролюминесценцию устройства. Эффективность электролюминесценции КТ-ОСИУ на основе эмиссионного бислоя из КТ выше по сравнению с КТ-ОСИУ на основе объемного гетероперехода.

## **1. Introduction**

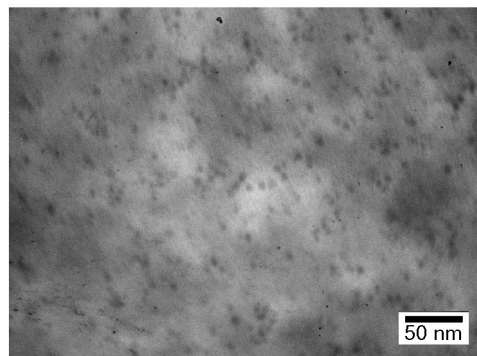
There has been an increasing interest in hybrid organic-inorganic materials based on electroluminescent nanocrystals (quantum dots, QD) and conjugated polymers. Such interest is motivated by a wide range of possible application, including organic light-emitting diodes (OLED) [1] and solar cells [2]. Large area devices can be made with conjugated polymers via easy processing from solution. Also a use of QD in LED structure (QD-OLED) is attracting increasing interest in an effort to obtain devices that combine the advantages of polymers with the unique emitting properties of QD [1].

Currently, wide variety of nanocomposites containing different QD has been applied and various multilayer schemes have been adopted to produce high-efficient de-

vices [1, 3–11]. Several kinds of QD-OLED devices can be discriminated: (1) the device with architecture based on a bulk heterojunction structure where charge photogeneration occurs at interfaces between electron donor (polymer) and acceptor (quantum dot) both mixed in the same active layer (polymer-QD blend), and (2) QD-OLED based on a planar heterojunction formed by using the QD as the luminescence layer, sandwiched between organic hole- and electron-transport layers. Despite the progress in performance of QD-OLED devices, the role of the QD in hybrid material has not been fully understood. Because monolayer character of QD layer in QD-OLED structures represent a major factor in device performance, it is important to have a complete picture how architectures of polymer-QD



a



b

Fig. 1. The molecular structure of PFO (a); TEM image of morphology of PFO/QD hybrid films at 75 wt.% concentration of quantum dots (b).

hybrid materials would influence on electroluminescent properties of QD-OLED.

Previous studies have already emphasized that integration of individual QD layer inside hybrid QD-OLED devices can be realized, besides by standard methods: spin-coating [3–10], dip-coating [11], contact printing [1] and Langmuir-Blodgett [1, 12]. The first two techniques introduce limitations such as solvent incompatibility with underlying polymeric conducting film. Exception is vertical phase segregation of spin-coated QD (aliphatic capping groups)-aromatic polymer blend into bilayer structure, where QD rise to the top [7, 13]. This paper deals with the influence of morphology of hybrid QD-polymer active layer and the QD-OLED architectures on their electroluminescent intensity and efficiency.

## 2. Experimental

The electroluminescent polymer used in the studied reported here was poly(dioctylfluorene) (PFO) with a molecular weight  $M_w = 58,200$  purchased from Sigma-Aldrich.

Monodisperse colloidal semiconductor CdZnSeS core-shell quantum dots with gradient structure, total diameter of 6 nm (size deviation ~10 %,  $\lambda_{Lum} = 530$  nm) passivity with organic ligands containing alkyl groups on the base of oleic acid with trioctylphosphine oxide and phosphonic acid (further CdZnSeS with such organic cover is designated as QD/TOPO) were synthesized by chemical colloidal organometallic method [6].

Hybrid polymer-QD light emitting materials were made by two different ways. By the first one to form the structure with a bulk heterojunction, thin hybrid films with a thickness 50–80 nm are prepared by spin-

coating method with different QD/PFO mass ratio. The QD concentration in the solution was changed in the range 17–80 wt. %. The second fabrication strategy employs the direct transfer of a QD monolayer on the top of predeposited by spin-coating PFO layer (50–80 nm) to form the structure with planar heterojunction.

The Langmuir films of self-assembled colloidal QD/TOPO were formed by spreading toluene solution of QD on the surface of doubly distilled water. After the solvent had completely evaporated, the QD layers were picked up to the hydrophobic PFO film or copper grid by Langmuir-Schaefer (LS) (horizontal lifting) deposition technique.

The morphology of nanohybrid PFO/QD and QD layers has been controlled by means of the transmission electron microscopy (TEM) with EM-125 microscope (Selmi, Ukraine) operated at 100 kV accelerating voltage.

The QD-OLED with total structure ITO/PEDOT:PSS/PFO+QD/Bu-PBD/Al (structure with bulk heterojunction) and ITO/PEDOT:PSS/PFO/QD/Bu-PBD/Al (structure with planar heterojunction) were fabricated. A hole injection polymer poly(3, 4-ethylenedioxythiophene)(poly(styrenesulfonate)) (PEDOT:PSS, Sigma-Aldrich) with thickness 40 nm and electron-conductor 2,4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (Bu-PBD, Sigma-Aldrich) with thickness 20–30 nm were spin coated. The luminescence spectra were recorded on SDL-2 spectrophotometer.

## 3. Results and discussion

Dispersion of QD in a polymer matrix is an important issue of any nanocomposite as QD have a tendency to phase segregate [7, 13]. TEM images on Fig. 1 show the uni-

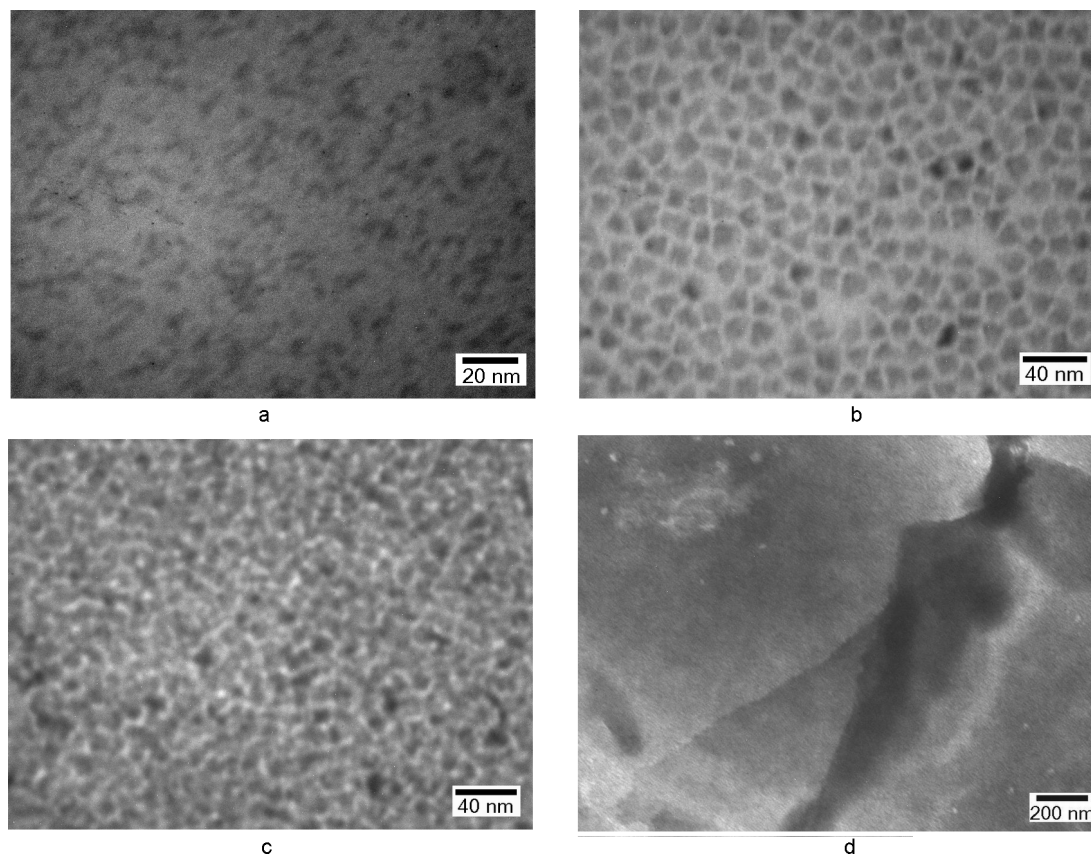


Fig. 2. TEM images of morphology of QD layer on PFO film transferred at (a)  $15 \text{ mN}\cdot\text{m}^{-1}$  surface pressure and  $2 \text{ mg/ml}$  QD concentration; (b)  $20\text{--}35 \text{ mN}\cdot\text{m}^{-1}$ ,  $2 \text{ mg/ml}$  (monolayer); (c)  $20\text{--}35 \text{ mN}\cdot\text{m}^{-1}$ ,  $3.8 \text{ mg/ml}$  (bilayer); (d)  $20\text{--}35 \text{ mN}\cdot\text{m}^{-1}$ ,  $5 \text{ mg/ml}$  (collapse of QD film).

form distribution of QD/TOPO in PFO films. Taking into account the surface passivation of QD by TOPO, we can assume that this QD/PFO homogeneous dispersion due to strong interaction between the aliphatic chains of TOPO and the aliphatic side arms of aromatic PFO (see Fig. 1, a).

The QD/TOPO monolayer is not formed in a single step by spin-coating of PFO/QD mixed solution. Because the large dipole moment of the phosphorous-oxygen bond permits TOPO-capped QD to form a stable monolayer at an air-water interface and the electrostatic interaction of the alkyl chain help prevent particle agglomeration, the alternative method for obtaining hybrid planar heterojunction QD-OLED is Langmuir-Schaefer (LS) techniques [12].

Fig. 2 shows the morphology of QD films on the water/air interface versus surface pressures. At low surface pressure ( $5\text{--}15 \text{ mN}\cdot\text{m}^{-1}$ ) and concentration of QD solution ( $2 \text{ mg/ml}$ ), QD/TOPO form a variety of isolated domain structures with  $15\text{--}50 \text{ nm}$  in diameter (Fig. 2a). At a surface pressure between  $20\text{--}35 \text{ mN}\cdot\text{m}^{-1}$  the formation of

monolayer is observed (Fig. 2b). The formed monolayer is unstable and has pores. Thus, for hybrid planar heterojunction QD-OLED the stable QD bilayer (Fig. 2c) as active layer was used, which was obtained on water/air interface at a surface pressure  $30 \text{ mN}\cdot\text{m}^{-1}$  and QD concentration  $3.8\text{--}4.0 \text{ mg/ml}$ . The QD film collapsed at a surface pressure of  $40\text{--}45 \text{ mN}\cdot\text{m}^{-1}$  and QD concentration more than  $4 \text{ mg/ml}$  (Fig. 2d). The obtained parameters of QD monolayer are in fair agreement with the surface pressure-area isotherms of QD/TOPO that were recently reported [12].

The study of the pressure isotherm of colloid quantum dots at air-water interface allowed forming homogeneous close-packed QD bilayer on the surface of a hole-conducting layer (PFO) by Langmuir-Schaefer technique. A series of experiments on transfer of multilayered QD films from a water surface on a PFO film surface is carried out. The obtained QD bilayer films were continuous and covered all surface of a PFO layer completely.

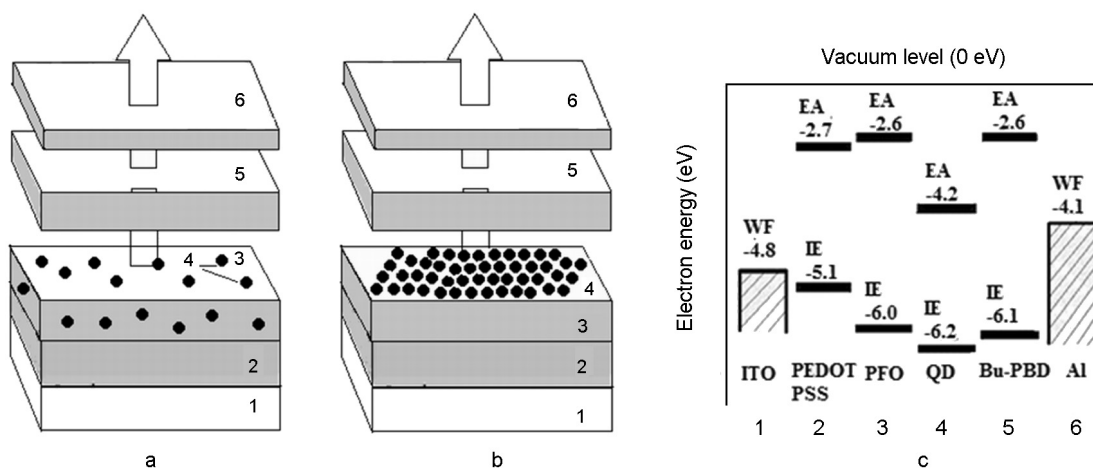


Fig. 3. Schematic of bulk (a) and planar (b) heterojunction and energy diagram of QD-OLED devices, where 1 — ITO anode; 2 — PEDOT:PSS; 3 — PFO; 4 — QD; 5 — Bu-PBD; 6 — Al-cathode.

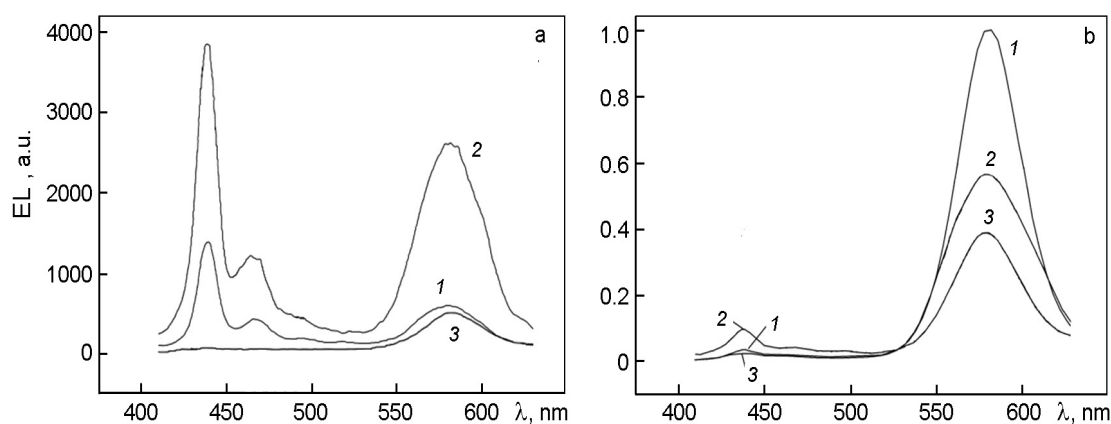


Fig. 4. EL spectra of (a) bulk heterojunction at 33 wt.% (1); 50 wt.% (2); 80 wt.% (3) QD concentration in active layer and (b) planar heterojunction with bilayer (1), monolayer (2) and collapsed layer of QD (3) as a active layer.

Fig. 3 show the electroluminescent devices with a two types of an architectures: ITO/PEDOT:PSS(40 nm)/PFO+QD(50 )/Bu-PBD(40 nm)/Al (a) and ITO/ PEDOT:PSS(40 nm) /PFO(50 nm)/QD/Bu-PBD(40 nm)/ Al (b), which contain an ITO layer as an anode, PEDOT:PSS as a hole transport layer, Bu-PBD as an electron transport layer, Al as a cathode, and energy band diagram associated with them.

Excitons formation takes place on the QD/PFO interface. Holes are injected from the ITO into the PFO matrix and are transported towards the QD, while electrons are injected from cathode and transported to the QD. The diagram (see Fig. 3c) shows that hole transport PEDOT:PSS and electron transport Bu-PBD layers decrease the corresponding potential barriers on ITO/PFO and QD/Al interfaces, thus, prob-

ability of injection of electrons from the cathode, and holes from ITO in an active layer increased. Exciton generation occurs via direct charge injection and Forster resonance energy transfer from polymer macromolecules to QD. Because a large surface area is set up to aid energy transport by blending the QD and polymer phases, in ITO/PEDOT:PSS/PFO+QD/Bu-PBD/Al electroluminescent structure the energy transfer from PFO to QD is responsible for nanoparticle EL and that direct electrical excitation is not predominant in these devices compared with the planar ITO/PEDOT:PSS/PFO/QD/Bu-PBD/Al QD-OLED structure.

The emissive spectra of diode with the bulk heterojunction reveals the band maximum at 420–440 nm, caused by the excimer luminescence of PFO macromolecules

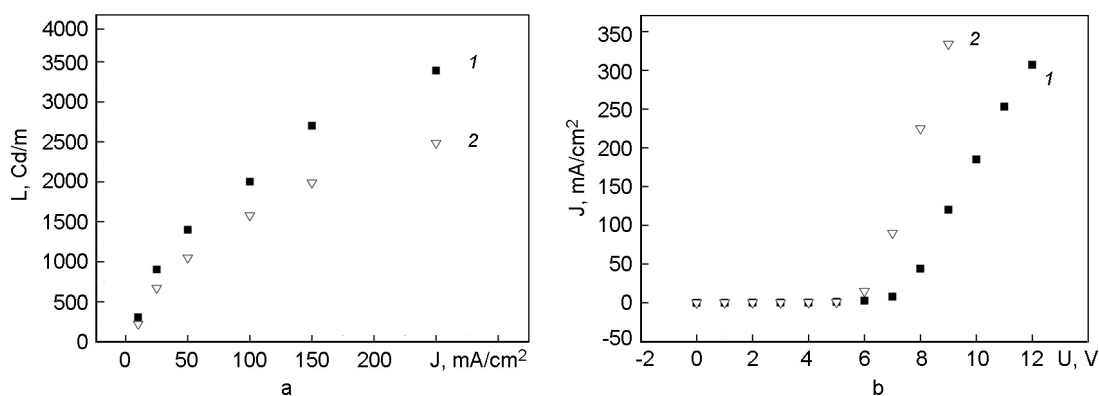


Fig. 5. Luminance vs the current density (a) and current-voltage characteristics (b) of the bulk heterojunction (1) and planar heterojunction (2).

and at 575 nm peak corresponding to the QD emission at incomplete energy transfer from a matrix to QD (Fig. 4a). In a range of QD concentration in polymer-QD films from 10 to 50 wt. % the EL intensity of PFO significantly decreases and the EL intensity of QD increases with increasing QD concentration due to energy transfer. In this configuration the QD act as luminescent centers and take a part in carrier transport process. The EL quenching was observed at the higher QD concentration due to disbalance of charge carriers in the active layer. By controlling the blend ratio, we could obtain a pure white color from the QD-OLED.

In the planar heterojunction (PFO/QD) device, the 420–440 nm peaks corresponding to the emission of PFO has a negligible intensity compared to that of the QD (see Fig. 4b). The highest EL efficiency and emissive intensity of QD-OLED are observed with QD concentration 4 mg/ml when QD bilayer film structure is formed. It was determined that QD monolayer transferred from a water surface to PFO films has a lot of defects and pores. This resulted to the decrease of the electroluminescent intensity and efficiency. In that planar heterojunction devices the QD are only the luminescence centers and don't participate in the charge transport. The thickness of QD layer increased with increase of QD concentration in nanocomposite. This causes reduction of efficiency of QD-LED device. The carrier number disbalance and reduction of EL intensity takes place, because low mobility of holes transported through a thick QD layer [14].

In Fig. 5 show current-voltage and the luminance characteristics for two types of QD-LED structures: with the emissive layer from QD, and the PFO/QD blend.

A maximum luminescence of  $1.5 \cdot 10^3$  Cd/m<sup>2</sup> and maximum current efficiency 0.9 Cd/A are obtained at 10 V in the bulk heterojunction. In the planar heterojunction, a luminance as high as  $2.2 \cdot 10^3$  Cd/m<sup>2</sup> with a maximum current efficiency 1.4 Cd/A is obtained.

#### 4. Conclusion

In conclusion, we have demonstrated the hybrid QD-LED structures with emissive layer on the base of bulk heterojunction (PFO/QD) and quantum dots layer. The emissive layer in the forms of QD bilayer structure provides higher QD-OLED efficiency compared with bulk structure, while the structures with bulk heterojunction allow changing the color coordinates by a variation of QD concentration in the polymeric matrix. Thus the morphology and structure of hybrid QD/polymer active layer are one of the most important factors defining EL efficiency of QD-OLED.

#### References

1. H.Haverinen, Acta Univ.Oul., Finland (2010).
2. N.Zhao, T.Osedach, L.Chang et al., *ACS Nano*, **4**, 3743 (2010).
3. P.Chin, R.Hikmet, R.Jenssen, *J.Appl.Phys.*, **104**, 013108 (2008).
4. J.Zhao, J.Zhang, C.Jiang et al., *J.Appl.Phys.*, **96**, 3206 (2004).
5. B.O.Dabbousi, M.G.Bawendi, O.Onitsuka et al., *Appl.Phys.Lett.*, **66**, 1316 (1995).
6. L.Yan, J.Zhang, Y.Cui, Y.Qiao, *Appl.Phys.Lett.*, **91**, 243114 (2007).
7. S.Coe, W.Woo, M.Bawendi, V.Bulovic, *Nature*, **420**, 800 (2002).
8. B.Torris, A.Hache, S.Gauvin, *Organ. Electron.*, **10**, 1454 (2009).

9. F.Teng, A.Tang, B.Feng et al., *Appl. Surf. Sci.*, **254**, 6341 (2008).
10. E.McCumiskey, N.Chandrasekhar, C.Taylor, *Nanotechnology*, **21**, 225703 (2010).
11. C.Lee, S.Nam, V.Kim et al., *Phys. Status Solidi B*, **246**, 803 (2009).
12. X.Ji, C.Wang, J.Xu et al., *Langmuir*, **21**, 5377 (2005).
13. O.Matvienko, Yu.Savin, O.Kryzhanovska et al., *Functional Materials*, **18**, 452 (2011).
14. K.Kohary, V.Burlakov, D.Pettifor, *J. Appl. Phys.*, **100**, 114315 (2006).

## **Гібридні об'ємний та планарний гетеропереходи з електролюмінесцентними квантовими точками CdZnSeS та полі(діоктилфлуореном)**

**О.О.Матвієнко, О.С.Крижановська, Ю.М.Савін, О.М.Вовк,  
Н.В.Погорелова, В.В.Ващенко**

Одержано гібридні органічні світловипромінюючі пристрої (КТ-ОСВП) з об'ємним та планарним гетеропереходами на основі полі(діоктилфлуорену) та електролюмінесцентних квантових точок CdZnSeS (КТ). Досліджено вплив концентрації КТ та морфології шару КТ на електролюмінесценцію пристрою. Ефективність електролюмінесценції КТ-ОСВП на основі емісійного бішару з КТ вище порівняно з КТ-ОСВП на основі об'ємного гетеропереходу.