

ELECTROLUMINESCENCE FROM OLED BASED ON DCM DERIVATIVE WITH CHEMICAL FORMULA $C_{25}H_{21}N_3O_3$

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The thin film of (E)-2-(2-(4-(dimethylamino)styryl)-6-((3-hydroxyphenoxy)methyl)-4H-pyran-4-ylidene)malononitrile (DCM derivative with molecular formula $C_{25}H_{21}N_3O_3$) has been synthesized by the method of thermal vacuum deposition. The optical properties of this thin film were studied. For the first time, OLED based on (E)-2-(2-(4-(dimethylamino)styryl)-6-((3-hydroxyphenoxy)methyl)-4H-pyran-4-ylidene)malononitrile was fabricated and characterized. The obtained results would be fruitful for designing highly-efficient organic light-emitting diodes with optimized parameters.

Keywords: Dicyanomethylenepyran Derivative, Tris-(8-hydroxyquinoline)aluminum, Photoluminescence, Electroluminescence, OLED.

1. Introduction.

The world has witnessed a revolution in display technology in the past two decades. In this period, the displays with bulky and heavy cathode ray tubes were transformed into ultra-slim organic light-emitting diode (OLED) display panels. Commercialization of any new technology requires a delicate balance between device efficiency and manufacturing cost. OLEDs are still costlier than the popular liquid crystal-based displays (LCDs) because of their higher production cost. However, OLEDs are gradually replacing LCDs [1].

One of the most widely studied organic compounds for manufacturing OLEDs are tris-(8-hydroxyquinoline)aluminum (Alq_3), dicyanomethylenepyran (DCM) and its derivatives [2–4]. Since the DCM compound itself has a very low luminescence intensity due to significant intermolecular interaction that quenches the luminescence, a "guest–host" system is used, for example, such as Alq_3 :DCM [5, 6]. For a high light output, the addition of 5–10 wt. % DCM to Alq_3 is chosen. Concentrations more than 10% leads to concentration quenching. To prevent the formation of aggregates and reduce intermolecular interaction based on the organic compound DCM, almost immediately after its discovery, work began on the synthesis of new compounds with a more dendritic (tree-like) structure of molecules [5, 6].

In the present study, we report the results of photoluminescence studies of (E)-2-(2-(4-(dimethylamino)styryl)-6-((3-hydroxyphenoxy)methyl)-4H-pyran-4-ylidene)malononitrile

(DCM-18) thin film and the results of manufacturing OLED device based on this compound. We could not find any literature data on such studies.

2. Experimental.

DCM-18, Alq₃ and Alq₃:DCM-18 (10 wt. %) organic films were thermally deposited in 10⁻⁴ Pa vacuum on optical glass substrates, transparent for wavelength above 300 nm or on transparent conductive indium-tin-oxide (ITO) glass (purchased from Sigma-Aldrich, surface resistivity – 70–100 ohm/sq) for OLED fabrication. Alq₃ powder (99.995% purity) was purchased from Sigma-Aldrich Corporation and purified by recrystallization. The DCM-18 powder was kindly provided for research by Leading Researcher, PhD Alexander Kukhta. Structures of the DCM and DCM-18 molecules are shown in Fig. 1. Thickness control during the process was provided by quartz crystal deposition rate controller.

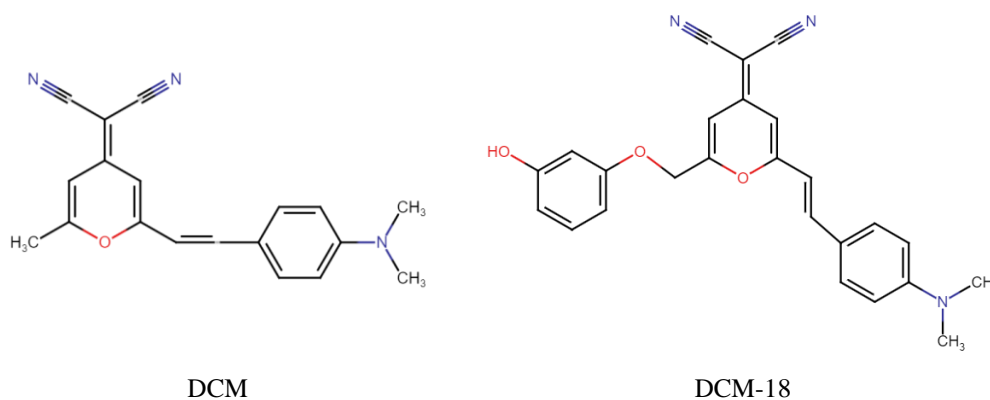


Fig. 1 Chemical structure of the DCM and DCM-18 molecules.

To produce OLED, the contact as the top electrode – cathode to the Alq₃ was formed using thermally evaporated Al [7]. The Al was evaporated through the shadow masks in a circular area of diameter ~ 3 mm. A liquid photo-positive resist based on o-naphto-chinon-diazide and novolack (a type of phenol-formaldehyde resin) "Positive 20" KONTAKT CHEMIE was used as the photoresist-insulator [8–10]. The schematic image of the OLED is shown in Fig. 2.

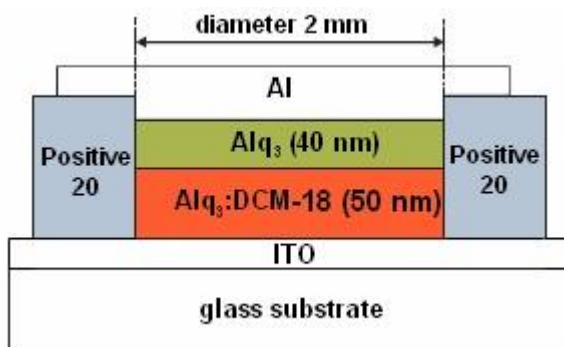


Fig. 2. Schematic structure of organic light emitting diodes based on Alq₃ and Alq₃:DCM-18 (10 wt. %) thin films.

To study absorption of light in the ultraviolet (UV) and visible (Vis) regions of the spectrum, we used a portable fiber optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Apeldoorn, Netherlands) with an input slit of 25 μm , a diffraction grating of 300 lines/mm and a resolution of 1.2 nm. Balanced compact deuterium-halogen light source Avantes AvaLight-DHc (200–2500 nm) was used. The detection of light in the spectrometer was carried out by a 2048 pixel CCD detector. The special software for automated computer control for this type of the spectrometer and spectra processing was used AvaSoft 8 (Apeldoorn, Netherlands).

The photoluminescence spectrum (PL) was measured using laboratory setup based on automated monochromator/spectrograph M266 (SolarLS JSC, Minsk, Belarus) connected with CCD camera, based on Hamamatsu S7030-1006S sensor. The sample was excited by GaN laser (405 nm) with pulse duration of less than 1 ns.

The electroluminescence (EL) spectra were measured using a portable fiber optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS with an input slit of 200 μm , a diffraction grating of 300 lines/mm and a resolution of 9 nm. The accumulation time was 200 msec.

3. Results and discussion.

Figure 3 shows the absorption spectrum obtained at room temperature of DCM-18 thin film deposited on the glass substrate. The DCM-18, like DCM dye, has very broad absorption in between 275 and 600 nm, with absorption bands where the longer-wavelength band is found to be more intense than the shorter-wavelength band [11]. The DCM-18 thin film shows two broad absorption peaks around 440 nm and 488 nm and a shoulder around 347 nm. DCM-type materials exhibit solvatochromic behavior. Our results are in agreement with the results for DCM dye given in [11].

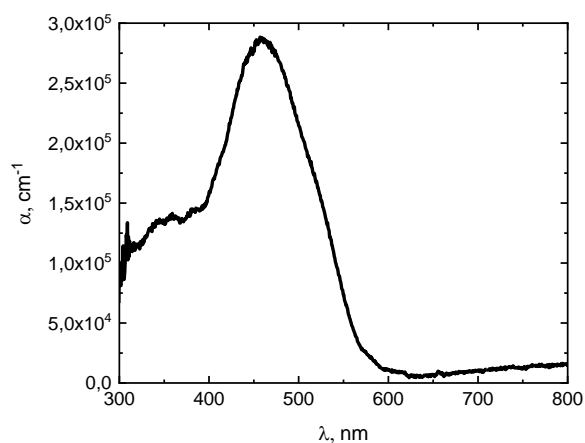


Fig. 3. UV-Vis absorption spectrum obtained at room temperature of DCM-18 thin film with the thickness 100 nm deposited on the glass substrate.

As can be seen from Fig. 4, the PL spectrum of the DCM-18 thin film, measured at room temperature, is exhibit three overlapping bands with the maxima at 570 nm, 635 nm and 665 nm in the visible region. The obtained spectrum is similar to the PL spectra of DCM and DCM derivatives films considered in our previous works [12–14]. Explanation of the nature of PL bands of DCM molecules in various solvents is very well described in [11]. According to [11],

the broad PL band of DCM molecules in solvents can be formed by emission from the locally excited state ($\lambda_{\text{max}} = 560\text{--}580\text{ nm}$), the state of intramolecular charge transfer emitting state ($\lambda_{\text{max}} = 610\text{ nm}$) and the twisted intramolecular charge transfer state ($\lambda_{\text{max}} = 630\text{ nm}$). Note that the PL bands of DCM films, compared with the PL bands of DCM solutions, are shifted to the red region of the light wavelength spectrum due to a stronger intermolecular interaction [13, 15, 16].

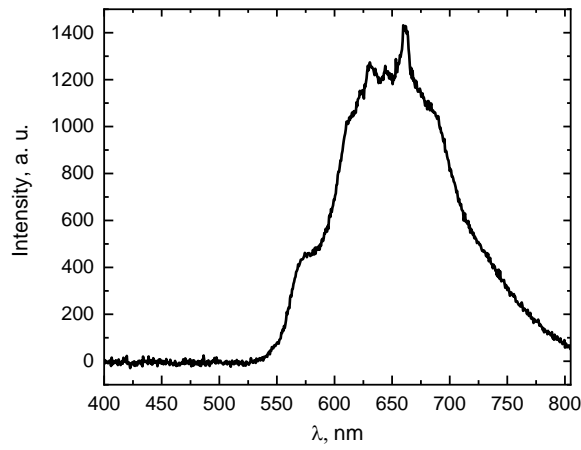


Fig. 4. PL spectrum of the DCM-18 thin film with the thickness 100 nm measured at room temperature.

The problem with weak photoluminescence of pure evaporated DCM-18 thin film has been overcome by preparing guest–host system. Which mean mixing the molecules (guests) with other matter (host). Tris-(8-hydroxyquinoline)aluminum (Alq_3) was used as host in most of the cases due to the compatibility of the energy levels [17–19].

Fig. 5 presents the EL spectrum of the our heterostructure with the configuration ITO/ Alq_3 :DCM-18 (10 wt. %)/ Alq_3 /Al. The emission intensities of the EL spectra increase with the increase in applied voltage. The wide band in the range from approximately 540 nm to 800 nm has a clear shoulder on the high-energy side. According to literature, normally, Alq_3 emits green light at $\sim 530\text{ nm}$ [20].

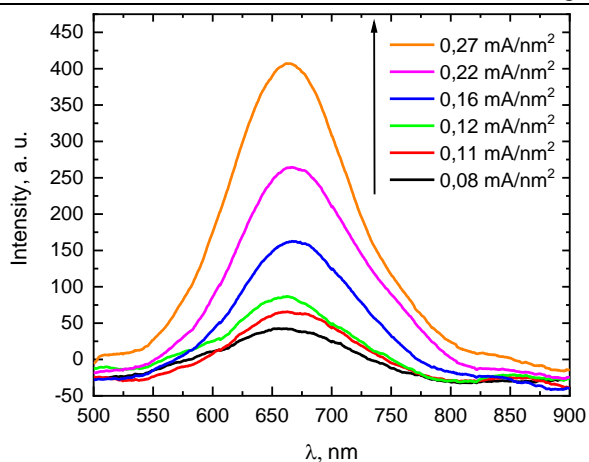


Fig. 5. Room temperature EL spectra of our OLED under different injected currents.

The electroluminescent emission of the ITO/Alq₃:DCM-18 (10 wt. %)/Alq₃/Al heterostructure (for current density 0.27 mA/cm²) has a CIE (x, y) color coordinates of (0.56, 0.32) (Fig. 6). That is, extra warm white light is emitted with an equivalent temperature $T = 2112$ K.

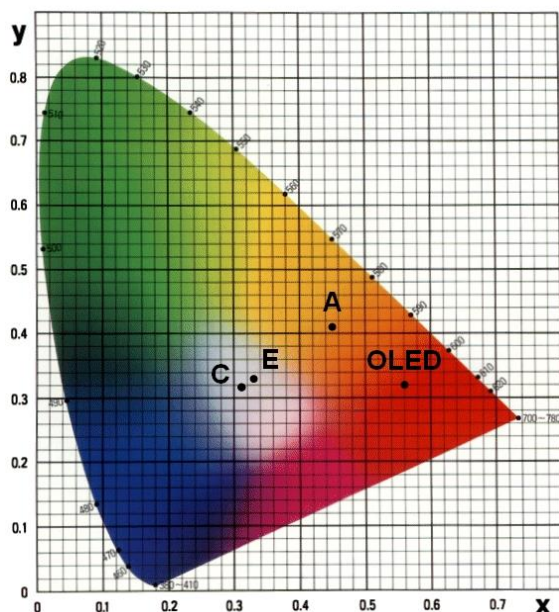


Fig. 6. Color coordinates measurement: OLED – our ITO/Alq₃:DCM-18 (10 wt. %)/Alq₃/Al heterostructure; A, C, E – the standard illuminants.

4. Conclusion.

In summary, thin film of (E)-2-(2-(4-(dimethylamino)styryl)-6-((3-hydroxyphenoxy)methyl)-4H-pyran-4-ylidene)malononitrile (DCM derivative with molecular formula C₂₅H₂₁N₃O₃) has been synthesized by the method of thermal vacuum deposition on to a glass substrate. For the first time, OLED based on (E)-2-(2-(4-(dimethylamino)styryl)-6-((3-

hydroxyphenoxy)methyl)-4H-pyran-4-ylidene)malononitrile was fabricated and characterized. The obtained results will be useful in the optimization and design of highly efficient OLEDs.

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REFERENCES

- [1] *Sarma M.* Exciplexes in OLEDs: Principles and promises / M. Sarma, L.-M. Chen, Y.-S. Chen, K.-T. Wong // *Materials Science & Engineering R.* – 2022. – V. 150. – P. 100689. <https://doi.org/10.1016/j.mser.2022.100689>
- [2] *Chen C.-T.* Evolution of Red Organic Light-Emitting Diodes: Materials and Devices / C.-T. Chen // *Chem. Commun.* – 2004. – V. 16. – P. 4389–4400. <https://doi.org/10.1021/cm049679m>
- [3] *Guo Z.* Dicyanomethylene-4H-pyran chromophores for OLED emitters, logic gates and optical chemosensors / Z. Guo, W. Zhu and H. Tian // *Chem. Commun.* – 2012. – V. 48. – P. 6073–6084. <https://doi.org/10.1039/c2cc31581e>
- [4] *Karbovnyk I.* Polarized photoluminescence of Alq3 thin films obtained by the method of oblique-angle deposition / I. Karbovnyk, B. Sadovyi, B. Turko, A. V. Kukhta, V. S. Vasil'yev, A. Horyn, Y. Kulyk, Y. Eliyashkevskiy, A. Kostruba, V. Savaryn, V. Stybel, S. Majevska // *Ukr. J. Phys. Opt.* – 2021. – V. 22. – P. 209–215. <https://doi.org/10.3116/16091833/22/4/209/2021>
- [5] *Tang C.* Electroluminescence of doped organic thin films / C. Tang, S. VanSlyke // *Journal of Applied Physics.* – 1989. – V. 65. – P. 3610–3616. <http://dx.doi.org/10.1063/1.343409>
- [6] *Yao Y.-S.* Starburst DCM-Type Red-Light-Emitting Materials for Electroluminescence / Y.-S. Yao, J. Xiao, X.-S. Wang, Z.-B. Deng, B.-W. Zhang // *Applications Advanced Functional Materials.* – 2006. – V. 16. – P. 709–718.
- [7] *Mori T.* Electroluminescence of organic light emitting diodes with alternately deposited dye-doped aluminium quinoline and diamine derivative / T. Mori, K. Obata, T. Mizutani // *J. Phys. D: Appl. Phys.* – 1999. – V. 32. – P. 1198–1203. <https://doi.org/10.1088/0022-3727/32/11/303>
- [8] *Kapustianyk V.* LEDs based on p-type ZnO nanowires synthesized by electrochemical deposition method / V. Kapustianyk, B. Turko, I. Luzinov, V. Rudyk, V. Tsybul'skyi, S. Malynych, Yu. Rudyk, M. Savchak // *Phys. Status Solidi C.* – 2014. – V. 11. – P. 1501–1504. <https://doi.org/10.1002/pssc.201300671>
- [9] *Turko B.* Electroluminescence from n-ZnO microdisks/p-GaN heterostructure / B. Turko, A. Nikolenko, B. Sadovyi, L. Toporovska, M. Rudko, V. Kapustianyk, V. Strelchuk, M. Panasyuk, R. Serkiz, P. Demchenko // *Optical and Quantum Electronics.* – 2019. – V. 51. – P. 135. <https://doi.org/10.1007/s11082-019-1853-5>
- [10] *Turko B. I.* Ultraviolet electroluminescence of LED devices based on n-ZnO nanorods grown by various methods and p-GaN films / B. I. Turko, A. S. Nikolenko, B. S. Sadovyi, L. R. Toporovska, M. S. Rudko, V. B. Kapustianyk, V. V. Strelchuk, R. Y. Serkiz, Y. O.

- Kulyk // J. of Physical Studies. – 2021. – V. 25. – P. 1701. <https://doi.org/10.30970/jps.25.1701>
- [11] Photophysical Properties of 4-(Dicyanomethylene)-2-Methyl-6-(4-Dimethylaminostyryl)-4H-Pyran (DCM) and Optical Sensing Applications. Chapter 1 in Book: Photophysics, Photochemical and Substitution Reactions – Recent Advances / ed. by S. Saha, R. K. Kanaparthi, T. Soldatovic. – Rijeka: IntechOpen CY, 2021. – 230 p. <https://doi.org/10.5772/intechopen.93149>
- [12] Karbovnyk I. Formation of oriented luminescent organic thin films on modified polymer substrate / I. Karbovnyk, B. Sadovyi, B. Turko, M. Sarzynski, A. Luchechko, I. N. Kukhta, H. Klym, A. Lugovskii // Applied Nanoscience. – 2019. – V. 10. – P. 2791–2796. <https://doi.org/10.1007/s13204-019-00969-8>
- [13] Kukhta A. V. Alignment of luminescent liquid crystalline molecules on modified PEDOT:PSS substrate / A. V. Kukhta, S. A. Maksimenko, K. M. Degtyarenko, T. N. Kopylova, B. Sadovyi, B. Turko, A. Luchechko, I. N. Kukhta, H. Klym, A. N. Lugovskii, I. Karbovnyk // Applied Nanoscience. – 2020. – V. 10. – P. 5063–5068. <https://doi.org/10.1007/s13204-020-01278-1>
- [14] Karbovnyk I. Polarized photoluminescence of thin films of dicyanomethylenepyran and its derivatives obtained by oblique deposition / I. Karbovnyk, B. Turko, V. Vasil'yev, A. Kukhta, O. Kushnir, H. Klym // Visnyk of the Lviv University. Series Physics. – 2021. – V. 58. – P. 50–60. (in Ukrainian) <https://doi.org/10.30970/vph.58.2021.50>
- [15] Vanjinathan M. Design, Synthesis, Photophysical, and Electrochemical Properties of DCM-Based Conjugated Polymers for Light-Emitting Devices / M. Vanjinathan, H.-C. Lin, A. S. Nasar // Journal of Polymer Science Part A: Polymer Chemistry. – 2012. – V. 50. – P. 3806–3818. <https://doi.org/10.1002/pola.26169>
- [16] Vembris A. Stimulated emission and optical properties of pyraniliden fragment containing compounds in PVK matrix / A. Vembris, E. Zarins, V. Kokars // Optics & Laser Technology. – 2017. – V. 95. – P. 74–80. <https://doi.org/10.1016/j.optlastec.2017.04.021>
- [17] Yokoyama S. Amplified Spontaneous Emission and Laser Emission from a High Optical-Gain Medium of Dye-doped Dendrimer / S. Yokoyama, T. Nakahama, S. Mashiko // Journal of Luminescence. – 2005. – V. 111. – P. 285–290. <https://doi.org/10.1016/j.jlumin.2004.10.008>
- [18] Zhong G. Y. In Situ Photoluminescence Investigation of Doped Alq / G. Y. Zhong, J. He, S. T. Zhang, Z. Xu, Z. H. Xiong, H. Z. Shi, X. M. Ding // Applied Physics Letters. – 2002. – V. 80. – P. 4846. <https://doi.org/10.1063/1.1489083>
- [19] Punke M. Coupling of Organic Semiconductor Amplified Spontaneous Emission Into Polymeric Single-Mode Waveguides Patterned by Deep-UV Irradiation / M. Punke, S. Mozer, M. Stroisch, M. P. Heinrich, U. Lemmer, P. Henzi, D. G. Rabus // IEEE Photonics Technology Letters. – 2007. – V. 19. – P. 61–63. <https://doi.org/10.1109/LPT.2006.889026>
- [20] Kaur A. Voltage tunable multicolor light emitting diodes based on a dye-doped polythiophene derivative / A. Kaur, M. J. Cazeca, S. K. Sengupta, J. Kumar, S. K. Tripathy // Synthetic Metals. – 2002. – V. 126. – P. 283–288. [https://doi.org/10.1016/S0379-6779\(01\)00570-7](https://doi.org/10.1016/S0379-6779(01)00570-7)

ЕЛЕКТРОЛЮМІНЕСЦЕНЦІЯ ОРГАНІЧНИХ СВІТЛОДІОДІВ НА ОСНОВІ ПОХІДНОЇ DCM З ХІМІЧНОЮ ФОРМУЛОЮ $C_{25}H_{21}N_3O_3$ **І. Карбовник¹, Б. Турко¹, В. Васильєв¹, Б. Садовий^{1,2}, О. Кушнір¹, Г. Клим³**

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Тонка плівка (Е)-2-(2-(4-(диметиламіно)стирил)-6-((3-гідроксифеноксі)метил)-4Н-піран-4-іліден)малононітрилу (похідна DCM з молекулярною формулою $C_{25}H_{21}N_3O_3$) синтезовано методом термовакuumного осадження. Досліджено оптичні властивості цієї тонкої плівки та фотолюмінесценція. Тонка плівка DCM-18 демонструє два широкі піки поглинання при 440 нм і 488 нм і плече при 347 нм. Матеріали типу DCM виявляють сольватохромну поведінку. Спектр фотолюмінесценції тонкої плівки DCM-18, виміряний при кімнатній температурі, демонструє три смуги, що перекриваються, з максимумами при 570 нм, 635 нм і 665 нм у видимій області.

Вперше було виготовлено та охарактеризовано OLED на основі (Е)-2-(2-(4-(диметиламіно)стирил)-6-((3-гідроксифеноксі)метил)-4Н-піран-4-іліден)малононітрилу. Сама сполука DCM-18 має дуже низьку інтенсивність свічення внаслідок значної міжмолекулярної взаємодії. Проблема зі слабкою фотолюмінесценцією чистої випареної тонкої плівки DCM-18 була подолана шляхом підготовки системи «гость-господар». Це означає змішування молекул (гостей) з іншою речовиною (хазяїном). Трис-(8-гідроксихінолін)алюміній (Alq_3) використовувався як господар через сумісність енергетичних рівнів. Отже, створена гетероструктура з конфігурацією ITO/ Alq_3 :DCM-18 (10 мас. %)/ Alq_3 /Al. Досліджено ектролюмінесцентні властивості отриманих зразків органічних світлодіодів за кімнатної температури залежно від струмів. Інтенсивність випромінювання спектрів електролюмінесценції зростає зі збільшенням прикладеної напруги. Широка смуга в діапазоні приблизно від 540 нм до 800 нм має чітке плече на боці високої енергії. Електролюмінесцентне випромінювання гетероструктури має координати кольору CIE (x, y) (0,56, 0,32), тобто надто тепле біле світло випромінюється з еквівалентною температурою 2112 К.

Отримані результати будуть корисними для розробки високоефективних органічних світлодіодів з оптимізованими параметрами.

Ключові слова: Похідні диціанометилпірану, трис-(8-гідроксихінолін)алюміній, фотолюмінесценція, електролюмінесценція, OLED.

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