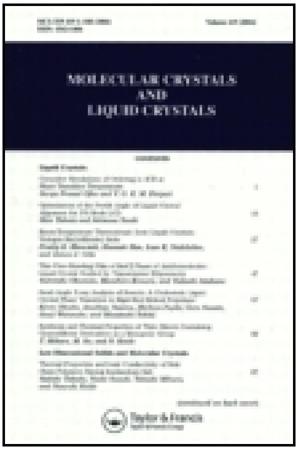


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Color Tuning in Oled Devices Based on New Perylene Derivatives

I. O. Balashova [a] , J. Y. Mayorova [a] , P. A. Troshin [a] , R. N. Lyubovskaya [a] , I. K. Yakushchenko [a] & M. G. Kaplunov [a]

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia

Version of record first published: 22 Sep 2010

To cite this article: I. O. Balashova, J. Y. Mayorova, P. A. Troshin, R. N. Lyubovskaya, I. K. Yakushchenko & M. G. Kaplunov (2007): Color Tuning in Oled Devices Based on New Perylene Derivatives, Molecular Crystals and Liquid Crystals, 467:1, 295-302

To link to this article: http://dx.doi.org/10.1080/15421400701224611

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 295–302, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701224611

Taylor & Francis
Taylor & Francis Group

Color Tuning in Oled Devices Based on New Perylene Derivatives

I. O. Balashova
J. Y. Mayorova
P. A. Troshin
R. N. Lyubovskaya
I. K. Yakushchenko
M. G. Kaplunov
Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow region, Russia

We have studied the spectral properties of a new perylene derivative – perylene 3,4,9,10-tetracarboxylic acid tetrabenzyl ester (TBEPTCA) individually and in blends with the zinc chelate complex bis(N-(2-oxybenzylidene)-4-tert- butylaniline) zinc (Zn(OBBA)$_2$). In the PL spectra of blends Zn(OBBA)$_2$:TBEPTCA, the maximum of the emission continuously shifts to longer wavelengths with increase in the ester content. We have also prepared the electroluminescent devices based on mixtures of perylene derivatives with Zn(OBBA)$_2$ and obtained the emission with an efficiency of about 1.1 cd/A.

Keywords: color tuning; electroluminescence; perylene derivatives

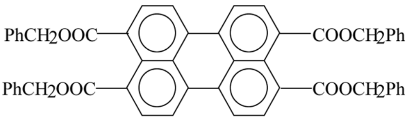
INTRODUCTION

Perylene dyes are of interest because of their high photostabilities and fluorescence quantum yields. Perylene derivatives are promising materials for different applications such as organic light-emitting diodes [1–4] and field effect transistors [5].

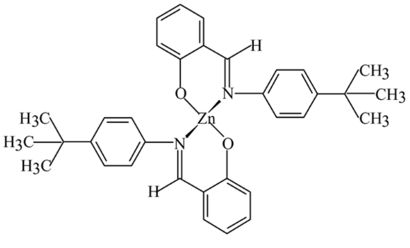
In this work, we report the properties of a new perylene derivative perylene 3,4,9,10-tetracarboxilic acid tetrabenzyl ester, TBEPTCA [6].

This work was supported by the RAS program "Fundamental Problems of Physics and Chemistry of Nano-Scale Systems and Materials."

Address correspondence to M. G. Kaplunov, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432, Russia. E-mail: kaplunov@icp.ac.ru



TBEPTCA



Zn(OBBA)$_2$

The light-emitting properties were studied for blends of TBEPTCA with the zinc chelate complex bis(*N*-(2-oxybenzylidene)-4-*tert*- butylaniline)zinc, Zn(OBBA)$_2$ which possesses good electron-conducting properties and is a good host matrix for organic dyes [7–9]. Mixing of perylene derivatives with Zn(OBBA)$_2$ gives a possibility to obtain different colors of light emission. The emission maximum continuously shifts to longer wavelengths with increase in the content of perylene derivative in the blend wit Zn complex.

We have also prepared the electroluminescent devices based on blends of perylene derivatives with Zn(OBBA)$_2$ and obtained the emission with an efficiency about 1.1 cd/A.

EXPERIMENTAL

Synthesis of TBEPTCA and Zn(OBBA)$_2$ is described elsewhere [6,9].

Spectral properties. The absorption spectra were measured in the region of 200–900 nm with a Specord M40 spectrophotometer. The photoluminescence spectra were measured with an Ocean Optics PC1000 plug-in spectrometer with the excitation from a light-emitting diode at 380 nm.

Preparation of Zn(OBBA)$_2$:TBEPTCA mixed films. Toluene solutions containing Zn(OBBA)$_2$ and TBEPTCA in proper ratios were poured on a glass substrate. Films were formed after drying the solvent at room temperature.

Preparation of the electroluminescence devices. The glass substrate coated with patterned indium-tin oxide (ITO) was covered with a poly(ethylenedioxythiophene)/polystyrene (PEDOT:PSS) hole-injecting layer [10]. PEDOT:PSS was a Bayer Baytron P aqueous solution used as-received. The Zn(OBBA)$_2$:TBEPTCA layer was spin-casted onto the PEDOT:PSS layer from a toluene solution containing Zn(OBBA)$_2$ and TBEPTCA in the 1:1 weight ratio. Finally, an aluminum cathode was evaporated on the top of the device. The technique of measuring the current-voltage and brightness-voltage curves is described elsewhere [9].

RESULTS AND DISCUSSION

Absorption and Photoluminescence Spectra of Solutions

The spectra of the solutions are shown in Figure 1. The absorption spectra are characterized by two main maxima in the region of 400–550 nm. A small Stokes shift between the absorption and PL bands is observed. In more polar solvents, the PL maxima are slightly shifted to the short wave region. Maxima of the absorption and PL bands are given in Table 1.

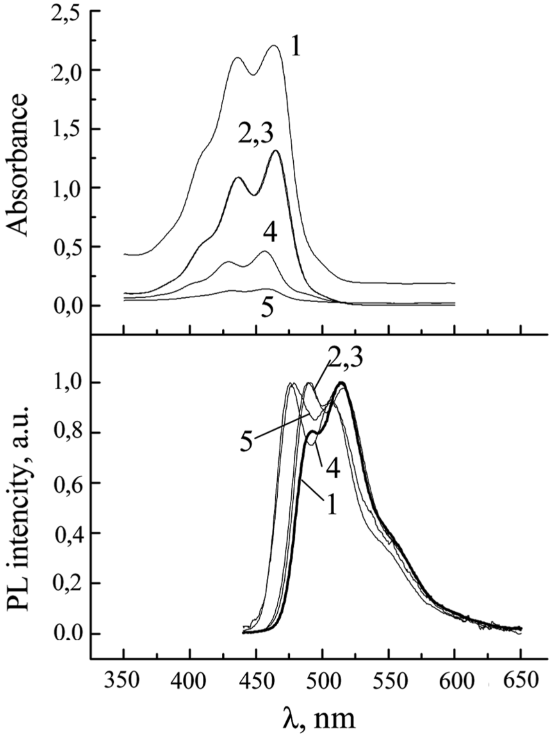


FIGURE 1 Absorption and PL spectra of TBEPTCA solutions in different solvents: 1–benzene, 2-chlorobenzene, 3-toluene, 4- acetonitrile, 5-ethanol. Concentrations are: 1–$1.9 \cdot 10^{-4}$, 2,3–$1.3 \cdot 10^{-4}$, 4–$4.5 \cdot 10^{-5}$, 5–$1.4 \cdot 10^{-5}$ M/l.

TABLE 1 Maxima of the Absorption and PL Bands (nm) in the Absorption and PL Spectra of the Perylene Derivatives in Different Solvents

Solvent	Absorption	PL
Benzene	436; 463	492; 515
Chlorobenzene	437; 465	491; 516
Toluene	436; 466	489; 514
Ethanol	432; 457	479; 507
Acetonitrile	429; 456	476; 507

Spectra of the Films of TBEPTCA and of the Mixtures of $Zn(OBBA)_2$:TBEPTCA

Films of TBEPTCA were obtained by casting from toluene solutions of the 15–20-g/L concentration. The absorption and PL spectra of the TBEPTCA film are shown in Figure 2 (100% curve). The position of the absorption band of the TBEPTCA film only slightly differs from that of the toluene solution. At the same time, the PL band is significantly shifted to the long-wave region relative to that of the solution and has a maximum of about 650 nm. The color of the PL is green for the solution and orange-red for the film. Such a shift of the PL band between the solution and the solid state was observed for some perylene derivatives and was attributed to the formation of oligomolecular aggregates [2]. The formation of molecular aggregates is characteristic of perylenes [11]. Taking into account that the shift of PL bands is much stronger than that of absorption bands in case of TBEPTCA, one may also suppose that the excimers of TBEPTCA molecules are formed.

In the electroluminescence devices, the light-emitting layer comprises a material with good electron transport properties. To change the color of the emission, mixtures of such electron-transporting materials with different organic dyes are used. In particular, a good electron-transporting material that can be used as a host matrix for the dye doping is $Zn(OBBA)_2$ [7–9]. In previous works, we have shown that the doping of $Zn(OBBA)_2$ with less than 1% of Nile red gives the change of the emission color from green to red due to the electronic excitation energy transfer from $Zn(OBBA)_2$ molecules to dye molecules [7,8].

In the present work, we have studied the effect of doping the electron-transporting material $Zn(OBBA)_2$ with perylene derivative TBEPTCA on the spectral properties of the latter. Films of mixtures of $Zn(OBBA)_2$ and TBEPTCA with TBEPTCA contents up to 50% were prepared by casting from toluene solutions containing $Zn(OBBA)_2$ and TBEPTCA in proper ratios.

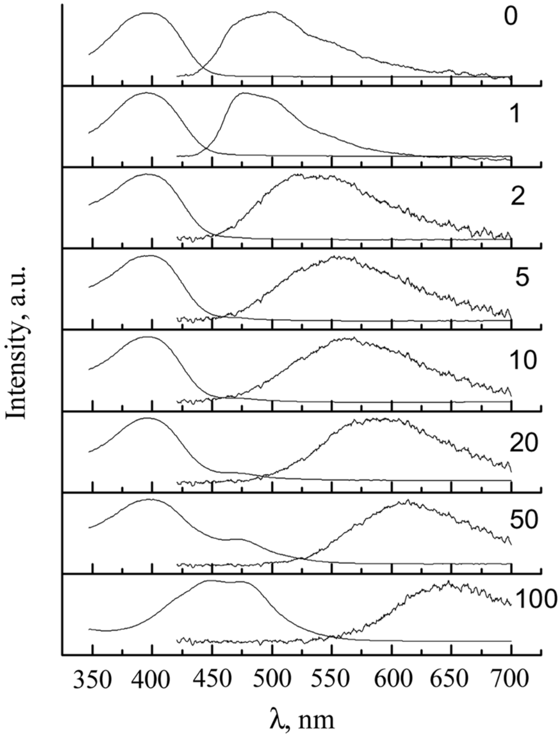


FIGURE 2 Absorption and PL spectra of mixed films Zn(OBBA)$_2$:TBEPTCA. Numbers next to curves represent the percentage of TBEPTCA. 0% corresponds to pure Zn(OBBA)$_2$ and 100% to pure TBEPTCA.

The absorption and PL spectra of the Zn(OBBA)$_2$:TBEPTCA films are shown in Figure 2. Maxima of the absorption and PL bands are given in Table 2.

In the spectra of pure Zn(OBBA)$_2$, the absorption band with the maximum at about 400 nm and the wide PL band in the region of 480–500 nm are observed. The absorption spectra of the Zn(OBBA)$_2$:TBEPTCA mixtures are superpositions of the spectra of the components. When TBEPTCA is added, the absorption band of Zn(OBBA)$_2$ at about 400 nm remains unchanged, while the absorption band of TBEPTCA at about 475 nm appears. The intensity of the 475-nm band increases with the TBEPTCA concentration, and this band becomes appreciable at concentrations of TBEPTCA of 20% and more.

Contrary to the absorption bands, the PL band in the spectra of the Zn(OBBA)$_2$:TBEPTCA mixtures is not a superposition of the PL bands

TABLE 2 Maxima of the Absorption and PL Bands (nm) in the Absorption and PL Spectra of the $Zn(OBBA)_2$:TBEPTCA Films

Film	Absorption	PL
$Zn(OBBA)_2$	400	480 (sh); 500
$Zn(OBBA)_2$:1% TBEPTCA	400	475; 500 (sh)
$Zn(OBBA)_2$:2% TBEPTCA	400	530
$Zn(OBBA)_2$:5% TBEPTCA	400	550
$Zn(OBBA)_2$:10% TBEPTCA	400	565
$Zn(OBBA)_2$:20% TBEPTCA	400; 475	590
$Zn(OBBA)_2$:50% TBEPTCA	400; 475	610
TBEPTCA	450; 475	650

of the components. In the PL spectra of the mixtures, only one band is observed, and its maximum shifts to the long-wave region with increase in the TBEPTCA concentration. For the film with TBEPTCA contents of 50%, the PL maximum shifts to 610 nm, which is not far from that of pure TBEPTCA (650 nm). The PL band of $Zn(OBBA)_2$ in the region of 480–500 nm completely disappears at concentrations of TBEPTCA more than 2–5%.

We may suppose that the absence of the $Zn(OBBA)_2$ PL band in the spectra of the mixtures is due to the electronic excitation energy transfer from $Zn(OBBA)_2$ molecules to TBEPTCA molecules analogously to the system $Zn(OBBA)_2$:Nile red [7,8].

The nature of the observed shift of the PL band is not clear now. The long-wave shift of the TBEPTCA PL band with the transition from solutions to solid films is probably due to some intermolecular interactions in the solid phase. The intermediate position of the PL band in the mixture films may be due, for example, to a change of the magnitude of such interaction arising from changes in the average distance between TBEPTCA molecules corresponding to variations of the TBEPTCA concentration in the $Zn(OBBA)_2$ matrix.

An alternative interpretation of the PL band shift may be related to possible polarization effects [12,13]. Such an effect was observed in the electroluminescence spectra of mixtures of aluminum (8-hydroxyquinoline) (Alq_3) and DCM2 dye [12]. For this system, a long-wave shift of the DCM2 luminescence band and the Alq_3 luminescence quenching with increase in the DCM2 concentration in the Alq_3 matrix were observed. This effect was attributed to the self-polarization of DCM2 molecules which contain polar CN groups [12]. The presence of polar CO groups in TBETBCA molecules suggests that TBEPTCA suspended in the solid matrix of $Zn(OBBA)_2$ may undergo an energy shift due to the self-polarization. That is, as the TBEPTCA concentration in the relatively

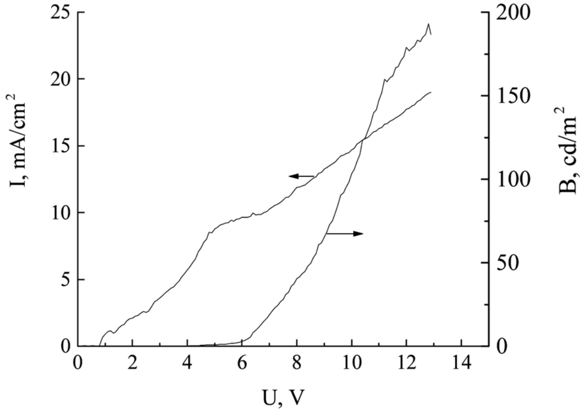


FIGURE 3 Current-voltage and brightness-voltage curves of the electroluminescence device ITO/PEDT:PSS/TBEPTCA:Zn(OBBA)$_2$(1:1)/Al.

non-polar Zn(OBBA)$_2$ is increased, the distance between the nearest neighbour, highly polar, TBEPTCA molecules decreases, thereby increasing the local polarization field. Shifts of the PL band for solutions of TBEPTCA in polar solvents could be an evidence in favor of polarization effects. However, such shifts for TBEPTCA (Table 1) are too low. For example, the shift of PL between benzene and ethanol solutions do not exceed 13 nm, contrary to the case of DCM2, where such a shift is 80 nm [12]. Therefore, the polarization mechanism of the PL shift for TBEPTCA seems less probable than the aggregation one.

Electroluminescence Device with TBEPTCA

We have prepared the electroluminescence device with TBEPTCA. The light-emitting layer in this device comprised a 1:1 mixture Zn(OBBA)$_2$: TBEPTCA. This material exhibits an orange-red emission color.

The current-voltage and brightness-voltage curves for the ITO/PEDOT:PSS/Zn(OBBA)$_2$:TBEPTCA(1:1)/Al device are shown in Figure 3. The emission arises at a voltage of about 5 V. A brightness of 200 cd/m^2 is attained at a voltage of about 13 V and a current of about 18 mA/cm^2, which means an efficiency of 1.1 cd/A.

REFERENCES

[1] Langhals, H., Ismael, R., & Yuruk, O. (2000). *Tetrahedron*, *56*, 5435.

[2] Hassheider, T., Benning, S. A., Kitzerow, H.-S., Achard, M.-F., & Bock, H. (2001). *Angew. Chem. Int. Ed.*, *40*, 2060.

[3] Cano, T. D., Hashimoto, K., Kageyama, H., De Saja, J. A., Aroca, R., Ohmori, Y., & Shirota, Y. (2006). *Appl. Phys. Lett.*, *88*, 071117.

[4] Chen, C.-Ti. (2004). *Chem. Mater.*, *16*, 4389.

[5] Rost, C., Karg, S., Riess, W., Loi, M. A., Murgia, M., & Muccini, M. (2004). *Synthetic Metals*, *146*, 237.

[6] Mayorova, J. Y., Troshin, P. A., Peregudov, A. S., Peregudova, S. M., Kaplunov, M. G., & Lyubovskaya, R. N. (2007). *Mendeleev Commun.*, *17*, 156.

[7] Pivovarov, A. P., Kaplunov, M. G., Efimov, O. N., Yakushchenko, I. K., & Belov, M. Yu. (2001). *Mol. Cryst. Liq. Cryst.*, *361*, 263.

[8] Pivovarov, A. P., Kaplunov, M. G., Yakushchenko, I. K., Belov, M. Yu., Nikolaeva, G. V., & Efimov, O. N. (2002). *Russ. Chem. Bull.*, *51*, 97.

[9] Kaplunov, M. G., Yakushchenko, I. K., Krasnikova, S. S., Shamaev, S. N., Pivovarov, A. P., & Efimov, O. N. (2004). *Russ. Chem. Bull.*, *53*, 2148.

[10] Elschner, A., Bruder, E. F., Heuer, H.-W., Jonas, F., Karbach, A., Kirchmeyer, S., Thurm, S., & Wehrmann, R. (2000). *Synthetic Metals*, *111–112*, 139.

[11] Balakrishnan, K., Datar, A., Naddo, T., Huang, J., Oitker, R., Yen, M., Zhao, J., & Zang, L. (2006). *J. Am. Chem. Soc.*, *128*, 7390.

[12] Bulovic, V., Shoustikov, A., Baldo, M. A., Bose, E., Kozlov, V. G., Thompson, M. E., & Forrest, S. R. (1998). *Chem. Phys. Lett.*, *287*, 455.

[13] Chew, S., Wang, P., Wong, O., Hong, Z., He, M., Zhang, R., Kwong, H., Tang, J., Sun, Sh., Lee, Ch. S., & Lee, Sh. T. (2006). *Synthetic Metals*, *156*, 185.