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Efficient “Warm-White” OLEDs Based on the Phosphorescent bis-Cyclometalated iridium(III) Complex

V. Cherpak,[†] P. Stakhira,[†] B. Minaev,[‡] G. Baryshnikov,[‡] E. Stromylo,[‡] I. Helzhynskyy,[†] M. Chapran,[†] D. Volyniuk,[§] D. Tomkutė-Lukšienė,^{||} T. Malinauskas,^{||} V. Getautis,^{||} A. Tomkeviciene,[§] J. Simokaitiene,[§] and J.V. Grazulevicius^{*,§}

[†]Lviv Polytechnic National University, S. Bandera 12, 79013 Lviv, Ukraine

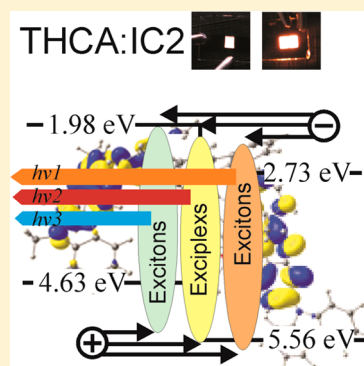
[‡]Bohdan Khmelnytsky National University, Shevchenko 81, 18031 Cherkassy, Ukraine

[§]Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT-50254 Kaunas, Lithuania

^{||}Department of Organic Chemistry, Kaunas University of Technology, Radvilenu Plentas 19, LT-50254 Kaunas, Lithuania

Supporting Information

ABSTRACT: The starburst carbazole derivative and phosphorescent bis-cyclometalated iridium(III) complex (IC2) were used for the preparation of multilayered “warm-white” organic light-emitting diodes (OLEDs), the emission spectra of which are modulated by the thickness of the phosphorescent layer. It was shown that the electroluminescence spectra of the fabricated devices are more extended into the visible region compared with the photoluminescence spectra of both component materials. The observed extension of the electroluminescence spectra can be assigned to the phosphorescent emission of the low-energy exciplex formed at the interface of the emissive layers. The quantum-chemical calculations performed by the DFT and (TD) DFT methods support the formation of the low-energy triplet exciplex at the interface of the IC2 layer and the neighboring layer of the starshaped carbazole-based compound, (4,4',4''-tris[3-methylphenyl(phenyl)amino]triphenylamine, tri(9-hexylcarbazol-3-yl)amine (THCA). Indeed, the triplet excited state of such bimolecular complex corresponds to intermolecular charge transfer between IC2 and THCA. The experimentally observed electrophosphorescence of these exciplexes is induced by strong spin–orbit coupling in the THCA:IC2 complexes due to the Ir(III) heavy atom effect. With dependence on the iridium(III)-complex film thickness (5–9 nm), the CIE coordinates changed from (0.41, 0.41) to (0.52, 0.47), corresponding to the warm white and orange color. The brightness of the fabricated OLEDs at the 15 V bias was in the range from 500 to 6000 cd/m².



INTRODUCTION

Though the modern systems of the OLED lighting¹ are less efficient than those based on the inorganic diodes in terms of the expiration time, still there is a number of competitive advantages of organic devices. Inorganic LED lighting is a point source, whereas the OLED is a planar one. In addition, the formfactor (mechanical flexibility and low weight) is a key point for the problems of new design. Finally, the “warm” color of OLED radiation is a priority factor for a comfortable human life.^{2,3} Thus, development of illumination systems on the basis of “warm-white” OLEDs represents an important and urgent task to fabricate the illuminants of sophisticated form with a big photoactive area.

A significant characteristic of OLED sources is the color temperature (CT) which is in the range of 2700–6500K for the inorganic white diodes and other energy-saving lamps. It is well-known that the light sources with the high CT parameter (near the 6000 K) increase the risk of cancer and inhibit secretion of oncostatic melatonin hormone,³ especially at night. Thus, the “warm white” (candle) light (CT = 2000–3000 K)

creates a comfortable and protecting atmosphere, which is the priority direction toward the goal of the fabrication of the new generation of night-light lamps.³ In this context, OLEDs represent the promising sources of the “warm white” light. The general trend for the design of such diodes is that they have to be constructed according the “host–guest” energy transfer principle.⁴ However, the homogeneous distribution of the guest molecules in the host retains the main problem in this field.⁵ An alternative way for the development of the “warm-white” OLEDs is based on the application of bifunctional molecules via attachment of carbazole-based fragments (acting as a host) to the phosphorescent core (acting as an emissive dopant).⁶ Such functionalization opens the new possibilities for the fabrication of the multilayer devices with a control of the functional layer thickness. From this point-of-view, the recently synthesized orange emitter, iridium(III)-bis{5-(9-carbazolyl)-2-

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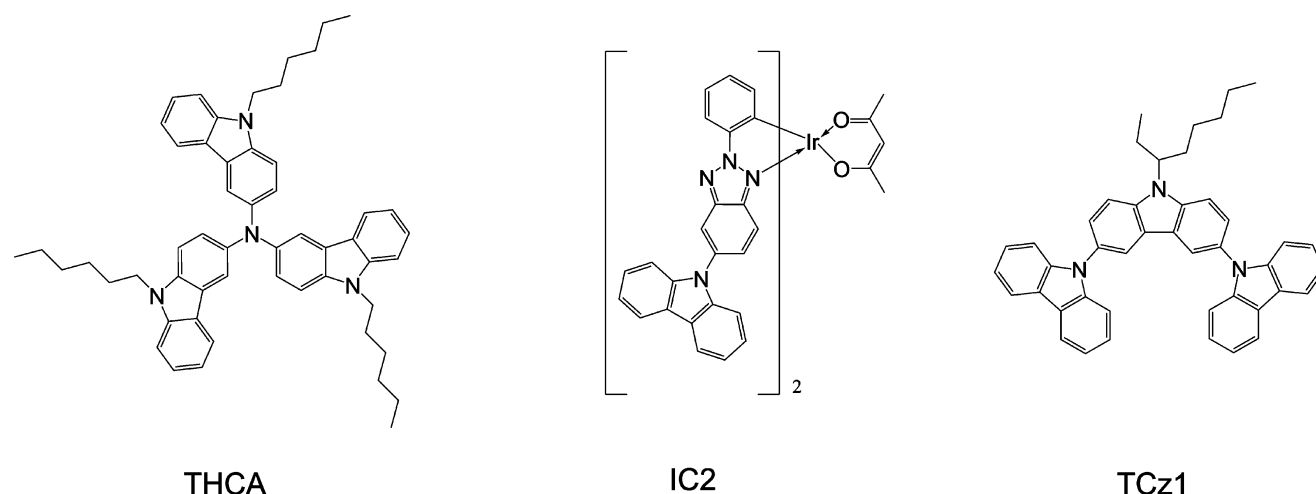


Figure 1. Chemical structures of THCA, IC2, and TCz1.

phenyl-1,2,3-benzotriazolato-N,C2'}acetyl-acetonate complex (IC2) (Figure 1) seems to be a promising candidate for the development of the "warm-white" OLEDs.⁷

Fabrication of OLEDs with the extended emissive spectral region and the minimal number of the functional layers is based on the idea that the auxiliary transport layers should be able to emit the visible light together with the propensity to form the exciplexes or the electroplexes at the interface.⁸ It was shown in the previous work that OLEDs based on the star-shaped compounds such as 4,4',4''-tris-3-methylphenyl(phenyl)amino triphenylamine, tri(9-hexylcarbazol-3-yl)amine (THCA) (Figure 1) possess the ability of the formation of the interface exciplexes.⁹ The exciplexes are formed by the charge transfer (CT) from the electron-donor molecule to the electron-acceptor molecule, producing the long-wavelength emission in the electroluminescence spectra.⁹

In the present work we report on the possible route to variation of the color (from the orange to the "warm white" light) of the exciplex-based OLEDs by controlling the thickness of the emissive layer by means of successive thermo-vacuum deposition of the blue-emitting THCA layer (the permanent thickness) and of the phosphorescent orange-emitting IC2 component (variable thickness).

EXPERIMENTAL METHODS

Five types of electroluminescent devices were fabricated by means of vacuum deposition of organic semiconductor layers and metal electrodes onto precleaned ITO-coated glass substrate under a vacuum of 10^{-5} Torr. The devices were fabricated by step-by-step deposition of different organic layers. THCA was used for the preparation of hole-transporting and a blue-light-emitting layer. IC2 was used as an orange phosphorescent light-emitting material. CuI and 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) (Figure 1) were used as hole and electron-transporting layers, respectively.^{10–12} TCz1 is a versatile compound previously shown to be useful as an effective electron-injection material,¹³ which helps to provide a stepwise electron transfer from the Ca:Al cathode to the emissive layer. The LUMO energy of TCz1 (−2.6 eV) is close to the work function of the Ca cathode (−2.9 eV).¹³ Since Ca is highly reactive and corrodes quickly in the ambient atmosphere, Ca layer topped with 200 nm aluminum (Al) layer was used as the cathode. The structures of the fabricated

devices were as follows: (A) ITO/CuI(8 nm)/THCA(40 nm)/IC2(9 nm)/TCz1(10 nm)/Ca(50 nm)Al(200 nm), (B) ITO/CuI(8 nm)/THCA(40 nm)/IC2(8 nm)/TCz1(10 nm)/Ca(50 nm)Al(200 nm), (C) ITO/CuI(8 nm)/THCA(40 nm)/IC2(7 nm)/TCz1(10 nm)/Ca(50 nm)Al(200 nm), (D) ITO/CuI(8 nm)/THCA(40 nm)/IC2(6 nm)/TCz1(10 nm)/Ca(50 nm)Al(200 nm), and (E) ITO/CuI(8 nm)/THCA(40 nm)/IC2(5 nm)/TCz1(10 nm)/Ca(50 nm)Al(200 nm).

The active area of the obtained devices was $3 \times 6 \text{ mm}^2$. The density–voltage and luminance–voltage characteristics were measured using a semiconductor parameter analyzer (HP 4145A) in air without passivation, immediately after the formation of the device. The brightness measurements were done using a calibrated photodiode.¹⁴ The electroluminescence spectra were recorded with an Ocean Optics USB2000 spectrometer.

The single layers of the THCA and IC2 were prepared by thermovacuum deposition, whereas the THCA:IC2 composite layer was prepared by casting onto clean quartz substrate from the THF solution of the mixture, consisting of 90% THCA and 10% IC2 (10 mg/mL). Fluorescence spectra and photoluminescence (PL) transients of the layers were recorded with the Edinburgh Instruments FLS980 spectrometer.

Computational Details. The ground singlet-state geometry optimization of THCA and IC2 was performed by the DFT/B3LYP^{15,16} method using GAUSSIAN 09.¹⁷ The 6-31G(d) basis set¹⁸ was used for THCA and for the C, O, N, and H atoms of the IC2 complex, whereas the effective core potential LanL2DZ¹⁹ basis set was applied to the iridium atom. The IR spectra of the studied molecules were also calculated. All the calculated vibrational frequencies were found to be real, which indicates the finding of a true total energy minimum on the potential energy hypersurface. The electronic absorption spectra and triplet excited-state energies of the studied compounds were calculated by the time-dependent (TD) DFT²⁰ method using the same B3LYP functional and basis sets with the polarized continuum model (PCM),²¹ incorporating t tetrahydrofuran (THF) and toluene as model solvents for THCA and IC2, respectively. The same THF and toluene were also used as the solvents for the experimental measurements of UV–vis spectra of THCA and IC2.^{7,9} With the aim to interpret the long-wavelength shoulder (~640 nm) in the electroluminescence spectra of the fabricated devices, we designed the series of THCA:IC2 (1:1) complexes, which are responsible for

the formation of exciplexes at the THCA and IC2 interface. The energies of the singlet and triplet vertical electronic excitations for the THCA:IC2 complexes were also calculated at the (TD) DFT level of theory.

RESULTS AND DISCUSSION

The electroluminescence spectra of the structures ITO/CuI/THCA/IC2/TCz1/Ca/Al shown in Figure 2 are characterized

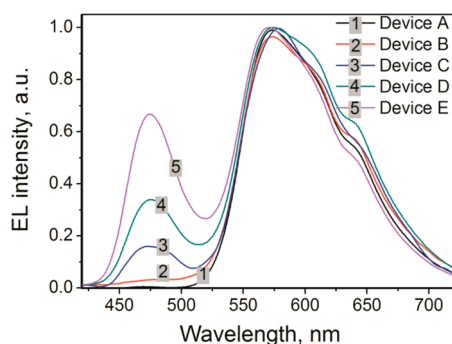


Figure 2. Electroluminescence spectra of the devices.

by four emission bands, the intensity of which correlates with the thickness the layer of IC2. One can stress that the TCz1 layer in the OLED structure provides exclusively the electron-transport function, which is approved by the absence of the short-wavelength emission bands (390 and 410 nm) being characteristic for the TCz1 species.¹¹

The first short-wavelength emission band with a maximum at 470 nm is characteristic of the pure THCA exciton radiation (Figure 3a, curve 1)⁹ of the fluorescence type, which is supported by the luminescence decay time measurements of the composite film (THCA/IC2) being in a nanosecond scale (Figure 3b, curve 1). The next two long-wavelength overlapped emission bands observed at 570 and 605 nm originate from the excited states of the IC2 complex⁷ of the triplet nature (Figure 3a, curve 2) (the luminescence decay time is in the microsecond range, Figure 3b, curve 2).

The lowest energy EL bands (640 nm) are shifted to the long-wavelength region compared with the photoluminescence spectra of vacuum-deposited films of THCA, IC2, and TCz1.¹¹ In addition, their intensity depends on the thickness of the IC2 layer. This observation most likely can be explained by the formation of the excited state complex (exciplex).²² The luminescence decay time of the composite film recorded at 640 nm is in the microsecond range (Figure 3b, curve 3) which indicates the phosphorescent nature of the exciplex.

This presumption is confirmed by appearance of the long-wavelength emission band (650 nm) in the photoluminescence spectra of spin-coated film of the blend: 80% THCA:20% IC2 (Figure 3a, curve 3). One can stress that because of the bulk interface character of the contacting molecules THCA and IC2, the exciplex band dominates here (Figure 3a, curve 3) in contrast to the EL spectra of OLEDs (Figure 2) with the almost planar interface. Moreover, the spectra of spin-coated film support the fact that the exciplex in the OLED structure is formed just at the THCA/IC2 interface, since the IC2/TCz1 interface is absent in this case. Appearance of exciplex-type emission can be explained by the presence of the energy barriers for both electron and hole charge carriers at the THCA/IC2 interface. One energy barrier of 0.93 eV is for

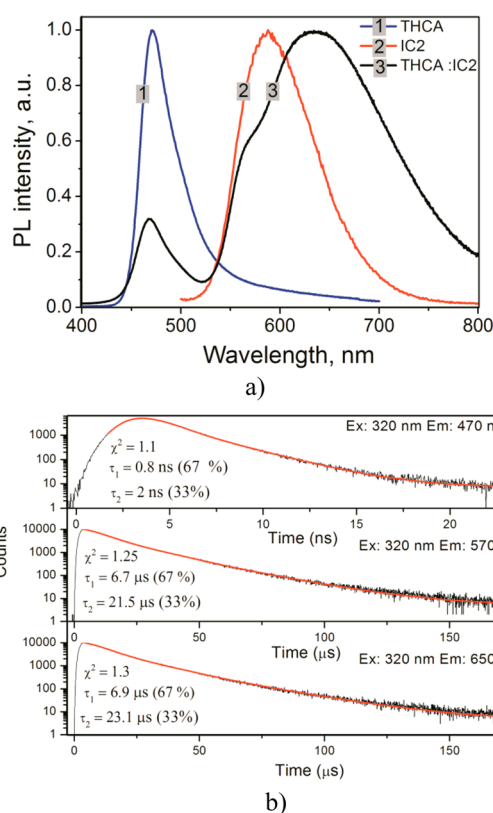


Figure 3. Normalized fluorescence spectra of the solid films of THCA and IC2 as well as of the spin-coated film of the molecular mixture of (a) 90% THCA and 10% IC2 and photoluminescence transients of spin-coated film of (b) the molecular mixture of 90% THCA and 10% IC2 measured at photoluminescence band maxima (470, 570, and 650 nm).

electron injection from the LUMO level of IC2 into the LUMO level of THCA (Figure 4). The second one of 0.75 eV

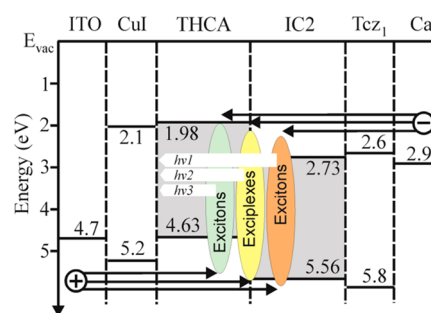


Figure 4. Energy-band diagrams of the device.^{6,8,10}

is for injection of holes from the HOMO level of (THCA) into the HOMO level of IC2 (Figure 4). When applying a direct bias (+ to ITO), electrons and holes accumulate at the interface THCA/IC2 due to high-energy barriers. As a result most likely implemented cross-interaction of electrons from the LUMO of IC2 and holes from the HOMO of THCA occurs with formation of exciplexes.⁹

Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x , y) of the devices were found to be from (0.41, 0.41) to (0.52, 0.47), corresponding to warm-white and orange, respectively (Figure 5, Table 1).

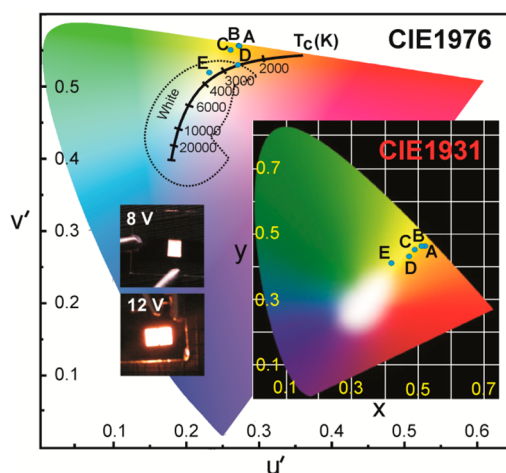


Figure 5. CIE1976 chromaticity diagram of devices A, B, C, D, and E. Inset: CIE1931 chromaticity diagram and photos of device E at 8 and 12 V. Color coordinates of devices are shown as the blue points.

The resultant devices exhibit color temperatures (T_C) of 2500–3600 K (Table 1) that are close to those of the fluorescent tubes (2500–3000 K). However, in contrast to these tubes, the emission spectra of the developed OLEDs do not contain the high-energy component, which is harmful for human beings.³

It is evident that the decrease of the thickness of the layer of IC2 leads to the increase of the electron transport into the fluorescent exciton-formation region in the THCA layer. It results in the increase of intensity of the high-energy component in the EL spectrum of the OLED (Figure 2, curve 5). The increase of the thickness of the layer of IC2 leads to the charge carriers balance redistribution in this layer and to the corresponding increase of the probability of the formation of triplet excitons (Figure 2, curve 1).

The brightness characteristics and current efficiency of the orange OLED (device A) exceed significantly the parameters of the “warm white” OLED (device E) (Figure 6, Table 1), which can be explained by the increase of the probability of the triplet–singlet transition. The correlation between the color chromaticity and the device efficiency is observed. It can be explained by the increasing contribution of the low-efficiency fluorescent component and by the decreasing contribution of the high-efficiency phosphorescent component in the EL spectra in the range from the devices A to E.

The efficiencies of the fabricated nondoped OLEDs are not very high compared with those of the doped phosphorescent OLEDs.²³ We suggest that the triplet–triplet annihilation is a key factor in this case, since we deal with the layered

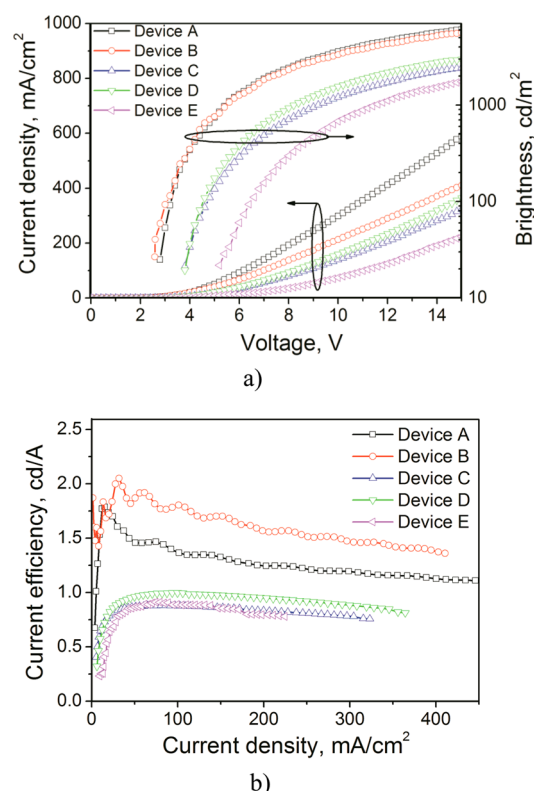


Figure 6. (a) Current density–voltage and luminance–voltage characteristics and (b) current efficiency–current density characteristics of the devices.

phosphorescent emitter.²⁴ There are several ways to improve luminance characteristics. The first way is the interfacial modifications and the introduction of the additional hole blocking layer in particular. The second way is the search for the promising bifunctional “self-host” Ir complexes or blue-emitting low-molecular-weight host materials that can form exciplexes with the phosphorescent emitters.

THEORETICAL INTERPRETATION

In the present paragraph we will discuss the electroluminescence spectra of the fabricated devices from the theoretical point-of-view. In the first stage, we have calculated the UV–visible spectra of THCA and IC2 to determine the nature of the long-wavelength absorption, including the complete assignment of the electronic absorption spectra. As one can see from Table 2, the first singlet excited state of the IC2 complex is calculated at 470 nm, which is in good agreement with the experimental observation. This S_1 state

Table 1. EL Characteristics of the Fabricated Devices

device	V_{on} at 25 Cd/m^2 (V)	max brightness at 15 V (cd/m^2)	at 100/1000 Cd/m^2					T_C (K)
			current efficiency (cd/A)	power efficiency (lm/W)	external quantum efficiency (%)	CIE 1931 UCS coordinates, (x, y) ^a	CIE 1976 UCS coordinates, (u, v) ^a	
A	2.85	6080	1.77/1.45	1.4/0.85	0.63/0.5	0.52; 0.47	0.27; 0.56	2500
B	2.63	5590	1.95/1.83	1.7/1.0	0.77/0.67	0.51; 0.47	0.27; 0.56	2500
C	3.88	2450	0.87/0.8	0.48/0.3	0.33/0.3	0.49; 0.45	0.26; 0.55	2700
D	3.88	2960	0.95/0.9	0.5/0.37	0.4/0.36	0.48; 0.42	0.27; 0.53	2700
E	5.32	1750	0.85/0.8	0.34/0.25	0.37/0.32	0.41; 0.41	0.23; 0.52	3600

^aCommission Internationale de L'Eclairage coordinates at the maximum brightness.

Table 2. Calculated Energy, Oscillator Strength and Orbital Assignment of the Selected $S \rightarrow T$ and $S \rightarrow S$ Transitions for the IC2 and THCA Molecules

compound	state	λ (nm)	λ_{exp} (nm)	f	assignment
IC2	T_1	526.1	–	0.0000	HOMO \rightarrow LUMO+1 (62%)
					HOMO–1 \rightarrow LUMO+1 (14%)
	T_2	514.8	–	0.0000	HOMO \rightarrow LUMO (48%)
					HOMO–1 \rightarrow LUMO (23%)
	S_1	470.2	460 ^a	0.2121	HOMO \rightarrow LUMO+1 (45%)
					HOMO \rightarrow LUMO (38%)
	S_2	462.6		0.0338	HOMO \rightarrow LUMO (45%)
					HOMO \rightarrow LUMO+1 (36%)
	S_3	426.9	433 ^a	0.2012	HOMO–1 \rightarrow LUMO (58%)
					HOMO–2 \rightarrow LUMO+1 (22%)
	S_{18}	328.4	326 ^a	0.3012	HOMO–8 \rightarrow LUMO (58%) HOMO–8 \rightarrow LUMO+1 (17%)
THCA	T_1	492.2	–	0.0000	HOMO \rightarrow LUMO (92%)
	T_2	444.4	–	0.0000	HOMO \rightarrow LUMO+2 (82%)
					HOMO–1 \rightarrow LUMO (6%)
	T_3	444.0	–	0.0000	HOMO \rightarrow LUMO+1 (82%)
					HOMO–2 \rightarrow LUMO (6%)
	S_1	422.2	423 ^b	0.0292	HOMO \rightarrow LUMO (99%)
	S_2	379.3	378 ^b	0.0325	HOMO \rightarrow LUMO+1 (98%)
	S_3	378.8		0.0326	HOMO \rightarrow LUMO+2 (98%)
	S_4	321.6	323 ^b	0.4292	HOMO \rightarrow LUMO+3 (94%)
	S_5	321.4		0.4404	HOMO \rightarrow LUMO+4 (94%)

^aFrom ref 6. ^bFrom ref 8.

(also like the nearby S_2 state) corresponds to the metal-to-ligand charge transfer (MLCT) character.^{25–37} As can be seen from Figure 7, the HOMO orbital of the IC2 complex is predominantly localized on the Ir atom (5d-function) and on the neighboring phenyl groups of both 5-(9-carbazolyl)-2-phenyl-1,2,3-benzotriazolol ligands (π -function). The LUMO and LUMO + 1 orbitals are almost degenerate (–2.10 and –2.09 eV, respectively) and can be assigned to the π -orbitals basically localized on both phenyl-benzotriazolyl fragments (the 5d-function on the Ir atom does not enter into LUMO relative to the HOMO orbital). The emissive degradation of the S_1 state is well-observed in the photoluminescence spectrum at ~560 nm with the quantum yield $\Phi = 0.41$ measured in toluene. However, the IC2 complex is able to produce the well-allowed phosphorescence, which is observed in the electroluminescence spectra of the fabricated devices with the emission maxima at 570 and 605 nm. These bands can be assigned to the 0–0 and 0–1 vibronic transitions from the T_1

state, which corresponds to the MLCT nature (Table 2, Figure 7) like the S_1 state. However, excited triplet state T_1 consists of the small contribution of the intraligand charge transfer configuration (Table 2). The spin–orbit coupling (SOC) induced mixing between T_1 and S_1 , S_3 states includes large 5d-orbital rotation (Table 2, Figure 7) and provides the short phosphorescence radiative lifetime.

We should mention that all neutral Ir(III) cyclometalated complexes with organic ligands demonstrate the strong SOC-induced mixing between few low-lying S and T states.^{25,26} It provides the nonzero intensity for the $T \rightarrow S_0$ transitions in such a way that a number of close-lying spin-sublevels of the T_1 , T_2 , and S_n states all produce contribution to the phosphorescence lifetime of the observed vibronic band. Comparison with the results of the low-temperature measurements^{27,28} where all spin-sublevels of emission can be resolved in time and frequency domains indicate that the most recent and sophisticated SOC calculations²⁶ can not explain the fine structure resolution. For example, the complexes of the HNT–7f type,²⁶ which include acac- and two (F4ppy) ligands (being similar to our IC2 complex) do not fit well to the experimental data. This means that the pseudo-Jahn–Teller effect in the close low-lying S and T states should be taken into account.²⁵ The vibronic perturbation should be very important for the proper interpretation of phosphorescence of the Ir(III) complexes.²⁹ Thus, the occurrence of the intense 0–1 vibronic band is very natural in this context.

The short-wavelength electroluminescence band (~470 nm for devices A–E) can be attributed to the fluorescence emission from the S_1 state of the THCA molecules. However, the corresponding $S_0 \rightarrow S_1$ transition is weakly allowed in the electric-dipole approximation (Table 2), which qualitatively indicates the comparatively low efficiency of the THCA fluorescence.

To demonstrate the nature of the long-wavelength shoulder (~640 nm) in the electroluminescence spectra of the fabricated devices, we have constructed the series of the most possible THCA:IC2 (1:1) complexes (Figure S1 of the Supporting Information), which are supposedly responsible for the formation of the exciplex-type phosphorescent emission. The THCA molecules are characterized by the high-lying HOMO levels in comparison with the IC2 complex. In this way, the HOMO orbital of the designed THCA:IC2 complexes corresponds to the π -orbital localized on the THCA host molecule (Figure 8). The LUMO and LUMO + 1 orbitals of the THCA:IC2 (Figure 8) are closing similar to those of the isolated IC2 complex. As a result, the low-lying excited triplet and singlet states appear in the electronic absorption spectra of the THCA:IC2 complexes. Among all the designed complexes, the aggregates 2 and 3 represent the most reliable disposition of THCA and IC2 components since their T_1 (Table 3) state most likely corresponds to the phosphorescent emission near 640 nm (taking into account the Stocks shift value).

As far as the exciplex emission band is concerned (Figure 2), we see from Table 3 that this new band in the blend layer of the OLED is determined by the HOMO \rightarrow LUMO + 1 transition in this associate.

Accounting for the above-mentioned LUMO + 1 in the IC2 and in the exciplex, one can easily analyze the SOC perturbation matrix elements,^{25,29,36} since the SOC mixing between the S_n and T_1 states of the exciplex is almost the same (by the orbital nature) like in the lowest triplet state of the IC2 species.

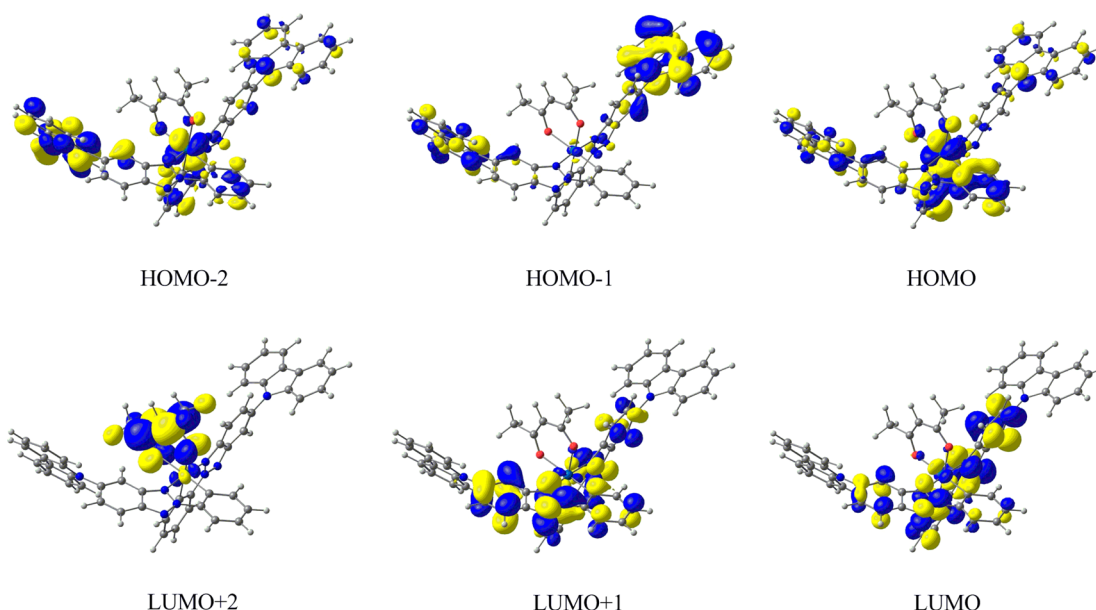


Figure 7. Selected molecular orbitals of the IC2 compound calculated with the B3LYP/6-31G(d)(C,N,O,H)/Lanl2DZ(Ir) method.

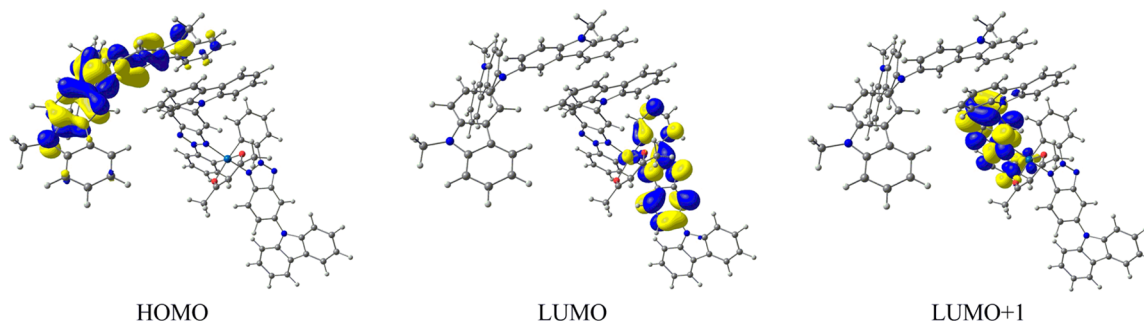


Figure 8. Frontier molecular orbitals of the THCA:IC2 aggregate 2 calculated with the B3LYP/6-31G(d)(C,N,O,H)/Lanl2DZ(Ir) method.

Table 3. Vertical Energies and Oscillator Strengths for the Low-Lying Excited Singlet and Triplet States of the THCA:IC2 (1:1) Complexes with the Different Disposition of THCA and IC2 Units

state	complex 1		complex 2		complex 3		complex 4		complex 5		assignment ^a
	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f	
T ₁	684	0	617	0	615	0	671	0	662	0	HOMO→LUMO+1
T ₂	644	0	597	0	605	0	651	0	648	0	HOMO→LUMO
S ₁	670	0.048	616	0.028	615	0.001	665	0.004	661	0.003	HOMO→LUMO+1
S ₂	644	0.000	597	0.000	605	0.000	651	0.000	640	0.006	HOMO→LUMO

^aFor complex 5, the assignment should be reversed for the T₁(S₁) and T₂(S₂) states.

It is large since the LUMO and LUMO + 1 include a large contribution of two different 5d-AOs at the Ir center (Figure 8).

It should be noted that the S₁, T₁ and S₂, T₂ states are almost degenerate, respectively, when the exchange between the HOMO and LUMO/LUMO + 1 orbitals is negligibly small. Indeed the S₁–T₁ (S₂–T₂) splitting proportionally increases with the rise of the oscillator strength for the S₀ → S₁ transition because of the exchange between the HOMO and LUMO/LUMO + 1 wave functions that directly correlates with the electric-dipole moment for the S₀ → S₁ vertical transition. In summary, we conclude that the formation of the THCA:IC2 aggregates at the interface of corresponding layers is favorable for the appearance of the corresponding exciplex states which

provide the extension of the long-wavelength band in the electroluminescence spectra of the devices A–E.

CONCLUSIONS

A series of multilayered OLEDs was fabricated, employing a phosphorescent 1,2,3-triazole-based iridium complex film vacuum deposition in the following device architecture: ITO/CuI(8 nm)/THCA(40 nm)/IC2(Xnm)/TCz1(10 nm)/Ca(50 nm)/Al(200 nm). The CIE chromaticity coordinates (x , y) of the devices were found to be from (0.41, 0.41) until (0.52, 0.47), corresponding to the warm white and orange color, respectively.

The spectral expansion of the EL devices was achieved by occurrence of the exciplex emission of the phosphorescent nature in the red range of the spectrum and by adding a blue

fluorescent component by the thickness modulation of the phosphorescent film. The quantum chemical modeling of the THCA:IC2 complexes allowed us to demonstrate the principal possibility of the exciplex states formation. Particularly, we demonstrated that the phosphorescence of the THCA:IC2 complexes corresponds to the intermolecular charge-transfer T_1 state and would be observed near the red spectral edge in good agreement with the experimental EL measurements. The $T_1 \rightarrow S_0$ radiative emission should be induced by the strong spin-orbit coupling between the low-lying T_1 and S_n excited states. Thus, the spin-forbidden $T_1 \rightarrow S_0$ emission becomes allowable both in IC2 species and in the THCA:IC2 exciplex due to the same effective SOC induced predominantly in the Ir atom.

We have shown that the spectrum of the device ITO/CuI(8 nm)/THCA(40 nm)/IC2(5 nm)/TCz1(10 nm)/Ca(50 nm)-Al(200 nm) is in the maximal vicinity to the white light and is psychologically friendly to use at night.^{2,3}

In this stage of the work, the luminance values were not high. The purpose of the present article was to demonstrate the possibility of fabrication of nondoped multilayered “warm-white” organic light-emitting diodes.

■ ASSOCIATED CONTENT

■ Supporting Information

Different structures of the THCA:IC2 (1:1) complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Juoas.Grazulevicius@ktu.lt. Tel: +37037300193.

Author Contributions

The manuscript was prepared with the contributions of all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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