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Mixing of Phosphorescent and Exciplex Emission in Efficient Organic Electroluminescent Devices

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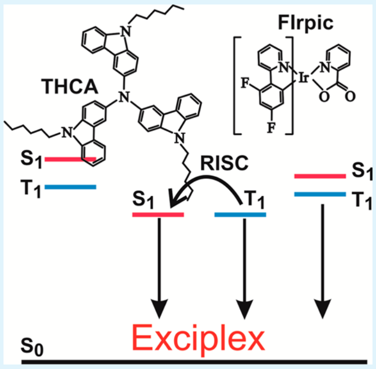
Ⓢ *Supporting Information*

ABSTRACT: We fabricated a yellow organic light-emitting diode (OLED) based on the star-shaped donor compound tri(9-hexylcarbazol-3-yl)amine, which provides formation of the interface exciplexes with the iridium(III) bis[4,6-difluorophenyl]-pyridinato-*N*,C2′]-picolinate (**FIrpic**). The exciplex emission is characterized by a broad band and provides a condition to realize the highly effective white OLED. It consists of a combination of the blue phosphorescent emission from the **FIrpic** complex and a broad efficient delayed fluorescence induced by thermal activation with additional direct phosphorescence from the triplet exciplex formed at the interface. The fabricated exciplex-type device exhibits a high brightness of 38 000 cd/m^2 and a high external quantum efficiency.



KEYWORDS: *organic light-emitting diode, thermally activated delayed fluorescence, reverse intersystem crossing, starshaped carbazole-based compound, blue iridium complex, density functional theory*

INTRODUCTION

The possibility of fabrication of the highly efficient OLEDs in which the intramolecular spin up-conversion from nonradiative triplet state to the radiative singlet state (thermally activated delayed fluorescence (TADF)) was recently demonstrated.[1−3] Both singlet and triplet excitons take part in generation of light emission in such devices, and internal efficiencies up to a point near 100% have been reported.[2] Realization of TADF is possible in the case of small energy difference between S_1 and T_1 states.[1] In this case the highest occupied molecular orbital (HOMO) should be distributed at the electron-donating units, whereas the lowest unoccupied molecular orbital (LUMO) should be distributed at the electron-accepting moieties.[1] However, there are many technological and chemical problems occurring upon realization of the TADF phenomenon in the single molecule. Therefore, a number of the TADF active compounds are limited.[1−4]

It was shown recently that exciplexes have small exchange energies since the compact electron densities from LUMO and HOMO of the charge-transfer complex are separated by a relatively long distance.[5−7] Taking into account the fact that the exciplex emission is characterized by a broad band this gives a possibility of realization of the highly cost-effective white organic light-emitting diodes (WOLEDs).[8−11] Among the known donor species capable of formation of exciplex exited states the star-shaped compounds 4,4′,4″-tris(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (m-MTDATA) and 4,4′,4″-tris(carbazol-9-yl)-triphenylamine (TCTA) can be used as the potential materials for the fabrication of high-efficiency OLEDs.[5,6,12−14] As acceptor materials both organic compounds and metalloorganic complexes (such as tris-(8-hydroxyquinoline) aluminum[10]), and in particular the phosphorescent complexes of platinum, iridium, and terbium ions are typically used.[9,15,16]m-MTDATA- and TCTA-based exciplex-type OLEDs are characterized by the high values of the external quantum efficiency (EQE) parameter. For example, the device based on the emission of exciplex of m-MTDATA and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) showed EQE of 5.4%,[5] the device based on the emission of exciplex of m-MTDATA and 2,8-bis(diphenylphosphoryl)-dibenzo-[b,d]thiophene (PPT) showed EQE of 10%,[6] OLED based on the exciplex emission of TCTA and 2,4,6-tris(3-(1*H*-

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pyrazol-1-yl)phenyl)-1,3,5-triazine (3P-T2T) exhibited EQE of 7.8%,[13] and OLED based on the exciplex emission of TCTA and bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine showed EQE of 3%.[14] The further progress and the achievement of the efficiencies comparable to those of the phosphorescent OLEDs can be realized by the search of appropriate donor and acceptor materials.[1]

In our previous works[10,11,17] we used for WOLED fabrication the star-shaped compounds, 4,4′,4″-tris[3-methylphenyl-(phenyl)amino] triphenylamine and tri(9-hexylcarbazol-3-yl)-amine (**THCA**), which possess the ability of the interface exciplex formation.

THCA forms a glass and is characterized by a nonplanar structure (the dihedral angle of each carbazole moiety in respect to its plane is roughly 47°).[10] The nonplanar structure decreases the probability of the exciplex formation, since the molecular planarity is one of the necessary conditions to enhance the molecular stacking.[18] On the other hand, the star-shaped structure of **THCA** provides a small exchange energy in the exciplex formed by donor and acceptor species (ΔE_{ST}) since the LUMO and HOMO of the formed charge-transfer complex are separated by a relatively long distance determined by nonplanarity of the species.[19] The commonly used exciplex-forming star-shaped compounds such as TCTA and m-MTDATA[5,6,12−14,19] have a planar structure that leads to the flat-on orientation of the molecules in solids,[20] which leads to appearance of excimer emission in the solid state.[12] It is known that the excimer emission usually overlaps with the exciplex emission in the mixed solids, which complicates, for example, the measurements of the exciplex fluorescence lifetimes.[12] In principle, the usage of the triplet excimer emission is useful for fabrication of highly efficient WOLED device,[18] but the long-lived triplet excimers may provide the nonradiative decay channels, and thus they can reduce the device efficiency and device lifetime.[21] TCTA has been used as a hole-transport layer for the iridium(III) bis-[4,6-difluorophenyl]-pyridinato-*N*,*C*2′]-picolinate (FIrpic) emitter without involvement of exciplex formation.[22,23]

We used FIrpic, which is a well-known blue-emitting phosphorescent material[22−24] as the second exciplex-forming emitter. Taking into account the fact that, between **THCA** and **FIrpic**, there are high-energy barriers for electron (0.92 eV) and for hole (1.17 eV) transfer (Figure 4), we could predict that the exciplex formation by the two compounds is possible.[11]

In the present work we present the experimental protocol for the fabrication of the double-layer exciplex-based OLED fabricated by means of the thermo-vacuum deposition containing both **THCA** and **FIrpic** emitters. A theoretical background of the OLED emission channels is also discussed. **THCA** (Figure 1) is used as an electron donor, and **FIrpic** (Figure 1) serves as an electron acceptor. We have achieved in this work an up-conversion from the nonradiative triplet state to the radiative singlet state due the exciplex formation between **THCA** and **FIrpic**.

EXPERIMENTAL METHODS

The electroluminescent device was fabricated as reported earlier[7] by means of vacuum deposition of organic semiconductor layers and metal electrodes onto precleaned indium tin oxide (ITO) coated glass substrate under vacuum of 1×10^{-5} Torr. The device was fabricated by step-by-step deposition of various functional layers. CuI[25,26] was used for the hole-transporting layer, and 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (**TCz1**) was used for the electron-transporting layer.[11,27,28] **TCz1** is characterized by good electron-injection properties,[11,27,28] and it was used as a host material for the **FIrpic** phosphor.[29] The Ca layer topped with aluminum (Al) layer was used as the cathode. The structure of the fabricated device was as follows: ITO/CuI(8 nm)/**THCA**(40 nm)/**FIrpic**(9 nm)/**TCz1**(10 nm)/Ca(50 nm)/Al(200 nm). The active area of the obtained device was 3 × 6 mm^2.

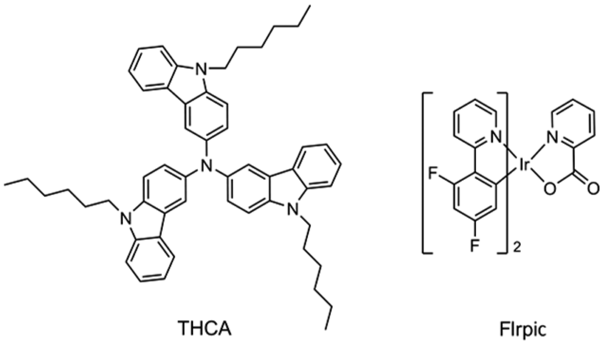


Figure 1. Chemical structures of **THCA** and **FIrpic**.

Characteristics of the current density−voltage and luminance−voltage dependences were measured with a semiconductor parameter analyzer (HP 4145A) using it in the air without passivation immediately after fabrication of the device. The measurement of brightness was performed using a calibrated photodiode.[17] Calibration of photodetector was carried out using a radiometer RTN 20 (accuracy ±2%). The photodiode was placed in front of OLED in a dark room, and the calibration was performed according to the method described earlier.[30] The external quantum efficiency (EQE) values were determined using the equations given in ref 31.

The OLED electroluminescence and photoluminescence (PL) spectra of the solid films were recorded with an Ocean Optics USB2000 spectrometer. For the spectral studies the single layers of **THCA** and **FIrpic** as well as the **THCA**/**FIrpic** composite layer were prepared by thermovacuum deposition onto clean quartz substrates. Luminescence spectra and luminescence decay curves of the layers were recorded with the Edinburgh Instruments FLS980 spectrometer at 77 K and room temperature using a low repetition rate μF920H Xenon Flashlamp as the excitation source. To separate the phosphorescence spectra of the studied **THCA** film, the emission was measured with a delay after the pulse was turned off (the delay time was set to be ca. 100 μs) at 77 K.

RESULTS AND DISCUSSION

The electroluminescence spectra of the device ITO/CuI/**THCA**/**FIrpic**/**TCz1**/Ca/Al shown in Figure 2 are charac-

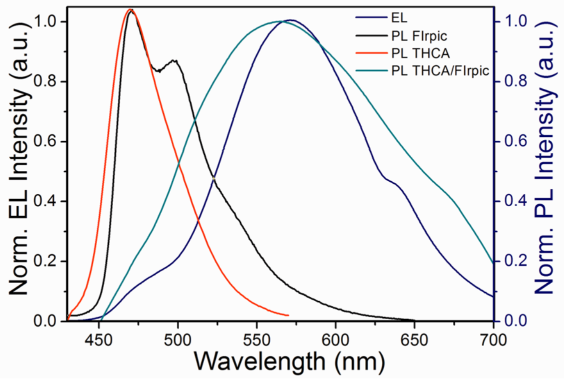


Figure 2. Electroluminescence spectrum of the device (blue) and the normalized photoluminescence spectra of the solid films of **THCA** and **FIrpic** as well as of the film of **THCA**/**FIrpic** (room temperature).

terized by three emission bands: a weak shoulder at 470 nm, which corresponds to the **FIrpic** triplet emission and intense exciplex band (570 nm) with a shoulder at 635 nm. As it was shown earlier[11,28] **TCz1** layer can provide 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**. It was shown that **TCz1** is an effective host material for **FIrpic**.[29]

Electroluminescence spectrum of the OLED is quite similar to the PL spectrum of the film of the molecular mixture **THCA**/**FIrpic**. Thus, the latter is responsible for the OLED emission. The PL spectrum is wider, and the lower-energy shoulder is shifted to 670 nm. We should note that the intensity maxima of PL bands of **THCA** and **FIrpic** coincide. As it follows from our TD DFT calculations they correspond to the singlet and triplet states emission, respectively.

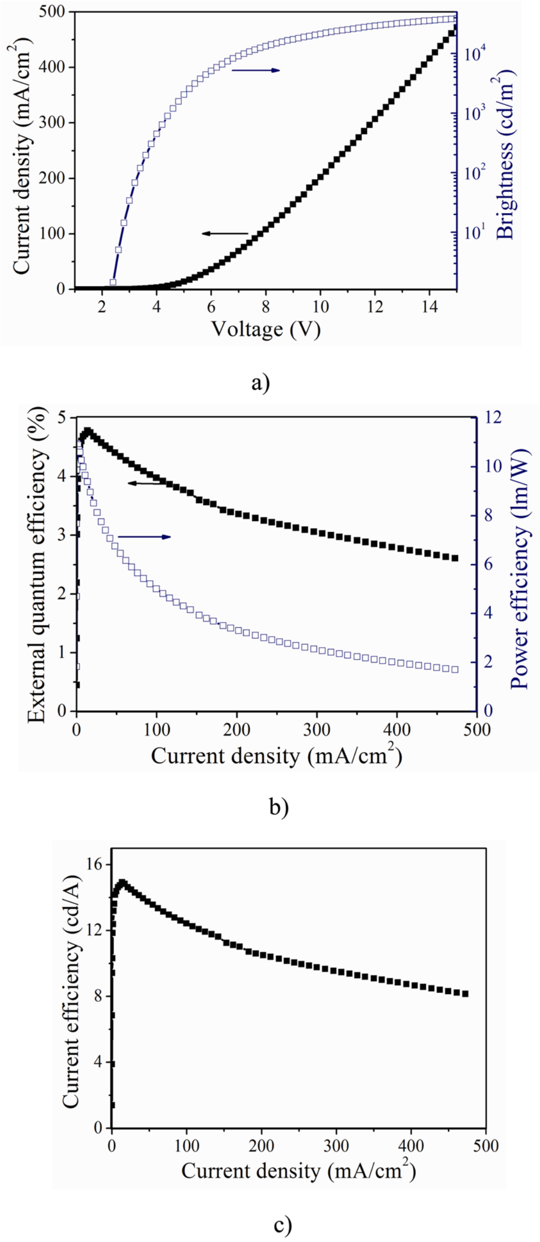
Figure 3 shows the current density−voltage characteristics and luminance−voltage characteristics of the electroluminescent device. OLED shows a low turn-on voltage (V_{on}) of 2.3 V for electroluminescence (at 2 cd/m^2). The low driving voltage achieved here can be attributed to the improved charge-carrier injection into the device due to the absence of energy barriers for holes and electrons between the electrodes and the emission layers (Figure 4).

The device exhibited high current efficiency values of 15 cd/A and maximum brightness of 38 000 cd/m^2 (at 15 V), as well as external quantum efficiency of ca. 5%. Chromaticity coordinates (x, y) of the device were found to be (0.44, 0.45).

The efficiency of the fabricated WOLED is lower than those of the other known exciplex-based OLEDs[6] and of the phosphorescent OLEDs.[29] We suggest that the triplet−triplet annihilation is a key factor predetermining the efficiency of the device, since we deal with the layered phosphorescent emitter.[32] There are several methods of the modification of the luminance characteristics and of changing the emission spectrum making it closer to the real white. One approach involves the interfacial modifications and introduction of additional hole injection layers in particular. Another approach involves the fabrication of coevaporated film and optimization of the thickness of the layer of **FIrpic** layer thickness. This approch we plan to use in our future study.

The electroluminescence spectrum of the device is shown in Figure 2 (blue line). The first short-wavelength emission broad band of this device at ca. 470 nm (shoulder in Figure 2) is characteristic for the pure **FIrpic** emission of the phosphorescent type.[29] This band cannot be assigned to the **THCA** fluorescence because of the microsecond decay time recorded for the 470 nm band maximum in the PL spectrum of **THCA**/**FIrpic** blend (Figure 5, Table 1). The strong emission band with a maximum at ∼470 nm is also observed well in the phosphorescence spectrum of the pure **FIrpic** compound at 77 K (Figure 6, red curve). This band is also clearly visible in the phosphorescence spectrum of the mixture **THCA**/**FIrpic** (Figure 6, black curve) but with the 5 times less intensity. Because of the bulk interface character of the contacting molecules of the mixture of **THCA** and **FIrpic** (interface between interacting molecules of **THCA** and **FIrpic** is more developed), the PL spectrum of the exciplex band is broader (Figures 2 and 6) compared to the EL spectrum of OLED (Figure 2) with almost planar interface **THCA**/**FIrpic** (interface is restricted in terms of intermolecular interaction).[34]

Two long-wavelength overlapped emission bands observed at 574 and 635 nm in the EL spectrum of the fabricated OLED (Figure 2, blue line) most likely can be explained by the formation of the excited-state complexes (exciplex) formed between **THCA** and **FIrpic**. This presumption is corroborated



a)

b)

c)

Figure 3. Current density−voltage and luminance−voltage characteristics (a), external quantum efficiency and current efficiency−current density characteristic (b and c) of the device.

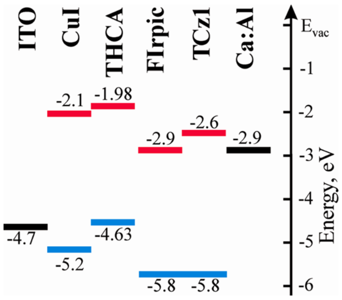


Figure 4. Energy-band diagrams of the device.[10,25,33]

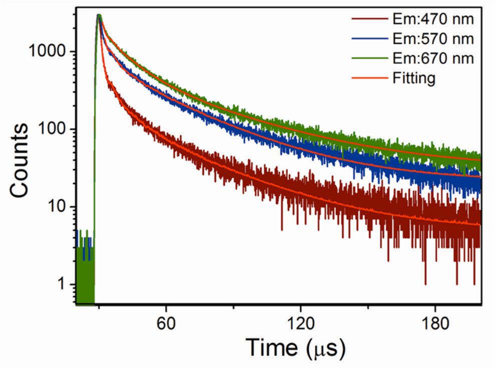


Figure 5. Normalized fluorescence decay curves of the solid films of **THCA/FIrpic** recorded at photoluminescence band maxima (470, 570, and 670 nm) at room temperature.

Table 1. Fitting Results of the Photoluminescence Transients of the Solid Films Prepared by Simultaneous Vacuum Deposition of THCA and FIrpic at 300 K

wavelength of PL spectra (nm)	470	570	670
PL lifetimes (τ) (μs)	0.2 (76%) 34.2 (24%)	0.2 (67%) 32 (33%)	0.2 (39%) 9.6 (21%) 40 (40%)
χ^2	1.097	1.260	1.014

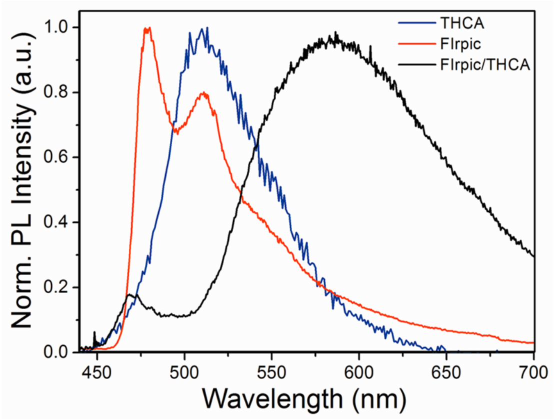


Figure 6. Normalized phosphorescence spectra of the solid films of **THCA**, **FIrpic**, and of the mixture **THCA/FIrpic** recorded at 77 K.

by the appearance of the long-wavelength emission bands (~570 and 670 nm) in the PL spectra of the film of the mixture **THCA/FIrpic** (Figure 2). Appearance of exciplex-type emission can be explained by the presence of the high-energy barriers for both electron and hole charge carriers at the **THCA/FIrpic** interface (Figure 4). One energy barrier of 0.92 eV is for electron injection from the LUMO level of **FIrpic** into the LUMO level of **THCA**; the second one of 1.17 eV is for the injection of holes from the HOMO level of (**THCA**) into the HOMO level of **FIrpic** (Figure 4). The luminescence decay time of the film of the blend **THCA/FIrpic** recorded at 570 and 670 nm is in the microsecond range (Figure 5, Table 1). This observation can be explained by the two possible phenomena: phosphorescence of the exciplex or by the TADF of the exciplex.[5,6] The last case seems to be much more likely and more efficient because of the high EL intensity observed at 574 nm, which can hardly be assigned totally to the triplet exciplex radiative emission (especially at the room temperature). The reason for the allowed exciplex phosphorescence is discussed below in addition to the TADF channel.

THEORETICAL INTERPRETATION

To explain the experimentally observed PL and EL spectra of **THCA**, **FIrpic**, and **THCA/FIrpic** blend we performed for them the quantum-chemical calculation by the density functional theory (DFT) method. Geometry optimization of the ground singlet state for **THCA** and **FIrpic** was performed first by the DFT computations using the B3LYP[35,36] hybrid functional and 6-31G(d)[37] basis set for the O, H, F, N, and C atoms and effective core potential Lanl2DZ basis set[38] for the Ir atom. Then a number of models for the **THCA/FIrpic** aggregates were simulated, and their absorption spectra were calculated by the time-dependent DFT (TD DFT)[39] approximation at the same B3LYP/6-31G(d)/Lanl2DZ method. All DFT and TD DFT calculations were carried out using the Gaussian09 software.[40]

Among the numerous **THCA/FIrpic** aggregates only three examples are presented in Figure 7. These systems were constructed by the following principles: **THCA** and **FIrpic** molecules should be overlapped by the carbazole/F2ppy or carbazole/piq plains; the distance between the overlapped plains should be approximately 3.5 Å.

The calculated energy diagram of the S_1 and T_1 state levels for the designed **THCA/FIrpic** exciplex models (Figure 7 a–c) is presented in Figure 8 comparing with the same energetic levels for the free molecules of **THCA** and **FIrpic**. As one can see from Figure 8 the calculated S_1 and T_1 energies agree qualitatively (by the levels of relative disposition) and even quantitatively with the experimental observations. Here we

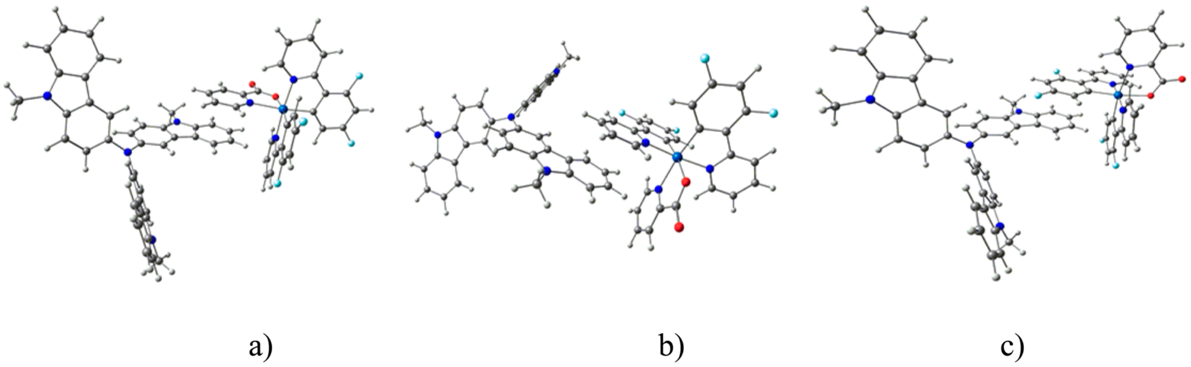


Figure 7. Different structures of the **THCA/FIrpic** (1:1) complexes (a–c).

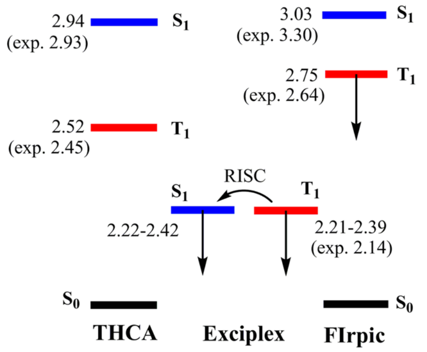


Figure 8. Energy diagram (values in eV) for the S_1 and T_1 states of **THCA**, **FIrpic** and their mixture (**THCA/FIrpic**), which is responsible for the exciplex emission.

should note that the experimental positions of the T_1 energy levels for **THCA**, **FIrpic**, and **THCA/FIrpic** were taken as the highest peaks in the corresponding phosphorescence spectra (Figure 6), whereas the S_1 energy levels for **THCA** and **FIrpic** were taken from the literature.[11,41] Figure 8 clearly demonstrates that both S_1 and T_1 states of the **THCA/FIrpic** aggregates are quasi-degenerate with a very small positive ΔE_{S-T} value equal to 35, 3.8, and 7.5 meV (Supporting Information, Table S1) for the complexes (a), (b), and (c), respectively (Figure 7). Thus, the T_1 state can be effectively populated by the reverse intersystem crossing (RISC) process through the thermally activated up-conversion mechanism at room temperature.[6,19] This evidence is in favor of the TADF nature of the long-wavelength intense exciplex emission in the PL spectrum of **THCA/FIrpic** blend and in the EL spectrum of the OLED device. At the same time the pure **FIrpic** triplet emission also contributes into the resulting device emission and provides the high-energy emissive shoulder at ~470 nm in the device EL spectra but with 5 times less intensity than that for the exciplex emission at 570 nm.

Analysis of spin−orbit coupling (SOC) matrix elements and $T_1 \rightarrow S_0$ intensity-borrowing schemes indicates that the exciplex phosphorescence transition moment has a large contribution from the SOC-induced mixing between the T_1 and S_3−S_8 states (Table S1). The corresponding SOC matrix elements include rotation of 5d orbitals at the iridium center, which creates a torque at the heavy atom (Ir).[42,43] Such SOC integral includes, for example, a single-electron matrix element between LUMO and LUMO+1 wave functions (Figure 9); see T_1 and S_4 configuration expansions in Table S1, for example. All these excited states are represented mainly by the exciplex configurations with charge transfer from **THCA** moiety (HOMO) to various empty orbitals at the **FIrpic** complex (LUMO and LUMO+n), which differ by rotation of 5d orbitals at the iridium ion.

Thus, the exciplex $T_1 \rightarrow S_0$ phosphorescence should be intense (like the **FIrpic** triplet emission[42,43]) because it is induced by strong SOC at the Ir center. In this way, we proposed that the TADF emission at ~570 nm can be mixed with the exciplex $T_1 \rightarrow S_0$ phosphorescence, both of which provide the high-emission intensity. The exciplex phosphorescence is predicted to be relatively intense because of effective SOC mixing between T_1 and S_n states. Thus, our exciplex-based OLED differs from the similar devices[19] that include only pure organic mixtures; the emission of those corresponds entirely to delayed fluorescence determined by the RISC processes.

CONCLUSIONS

We report a new approach for the fabrication of effective OLED being characterized by a broad electroluminescence, which consists of the combination of the blue phosphorescence emission from iridium complex and the wide highly efficient delayed fluorescence emission from exciplex formed at the interface of the star-shaped hole transporting compound and **FIrpic**.

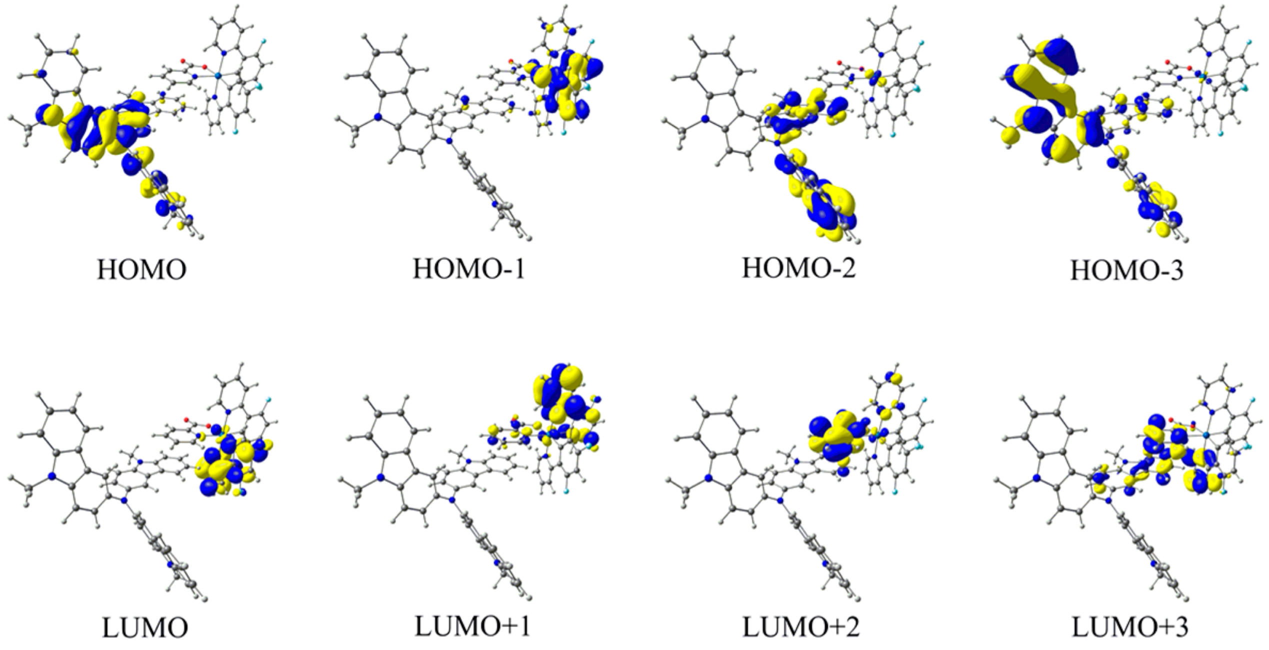


Figure 9. Energy schemes and molecular orbitals of the **THCA/FIrpic** aggregate (a) (Figure 7) calculated by the B3LYP/6-31G(d) (C,O,F,H,N)/Lanl2DZ(Ir) method.

The fabricated exciplex-type electroluminescent device exhibits a high current efficiency value of 15 cd/A, brightness of 38 000 cd/m^2, and the external quantum efficiency of ~5%. Chromaticity coordinates (x, y) of the device are found to be (0.44, 0.45).

The quasi-degenerate nature of the lowest excited T_1 and S_1 states of the exciplex explains the wide experimentally observed EL band; both states provide emission with slightly different lifetimes. The S_1 state could be populated by the thermal activation from the triplet exciplex produced by electron−hole recombination in the emission layer with the 3:1 ratio (T/S). The triplet exciplex provides its own radiative activity because of large spin−orbit coupling contribution at the metal center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Energies of the frontier molecular orbitals for the FIrpic molecule, vertical energies and oscillator strengths of THCA:FIrpic complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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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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