

Investigation of Flrpic in PhOLEDs via LC/MS technique

Research Article

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Abstract: The commercial breakthrough of phosphorescent organic white light sources is presently hampered due to the unavailability of a stable blue phosphorescent emitter material. Moreover, only few analytical investigations have been made regarding the chemical degradation of the phosphorescent emitter materials during the processing or the operation of the devices. Organic light emitting devices (OLEDs) containing phosphorescent metal complexes with iridium as central ion were investigated. Special attention was paid to the chemical degradation of the material. The devices were analyzed by means of high performance liquid chromatography coupled with mass spectrometry (HPLC/MS). Electron spray ionization (ESI) was employed as ionization source. Isomerization phenomena of the blue-green emitting heteroleptic iridium complex Flrpic could be observed after the device manufacture and after operation. These findings could give hints on the mechanisms that influence the lifetime of PhOLEDs based on Flrpic or similar blue emitters.

Keywords: Emitter • HPLC/MS • PhOLED

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1. Introduction

OLEDs have attracted a great deal of attention due to their potential application in full color displays or as new light sources [1-4]. Since the pioneering works of Tang and van Slyke in 1987 [5] research efforts concentrated on obtaining OLEDs which fulfill the requirements for industrial applications.

Since 1998, research efforts have focused on phosphorescent organic light emitting devices, the so-called PhOLEDs. Red [6], green [7] and blue phosphorescent emitter [8-10] combinations are needed to produce a full color display or a white light source. Today, stable red, green and blue-green

light emitting devices, which fulfill the application requirements, have been demonstrated. So far, stable OLEDs with deep blue phosphorescent emitters could not be realized.

Today, phosphorescent metal complexes containing iridium as central atom are playing the central role in the design of phosphorescent emitter materials. Due to the strong spin-orbit coupling induced by iridium these complexes have a phosphorescent emission at room temperature with a quantum efficiency that can approach unity [11].

In order to improve the lifetime stability of PhOLEDs, many analytical approaches are currently taken to elucidate the failure mechanisms.

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One approach is the investigation of topographic aspects which could influence the stability of the OLEDs. In this case spectroscopic methods such as scanning tunneling microscopy (STM) [12], transmission electron microscopy (TEM) [13], scanning electron microscopy (SEM) [14] and atomic force microscopy (AFM) [15] are used. Causes for device failures due to crystallization and inter diffusion of organic layers were reported by Adachi *et al.* [16] and Han *et al.* [17]. Beside morphology changes in OLEDs, molecular changes of the organic materials were investigated using mass spectrometric tools *e.g.*, secondary ion mass spectrometry [18]. In addition chemical and physical degradation phenomena are found to diminishing the OLED lifetime [19,20]. Studies of operation-induced chemical changes in OLED devices using green emitting material Ir(ppy)₃ *via* LC/UV have been published [21].

Very recently, isomerization of heteroleptic iridium complexes such as from (Ir(2-phenylpyridine)2(2-carboxy-4-dimethyl amino pyridine)) and iridium(III) bis(4,6-difluorophenyl)-pyridinato-N,C2')picolinate (Flrpic) during sublimation process was reported [22].

Via LDI/TOF/MS method, it was suggested that an oxidation of the ligand picolinate may lead to a degradation of the emitter molecule Flrpic [23]. Surprisingly no analytical approach such as liquid chromatography has been described investigating the composition of OLED materials containing, *e.g.*, Flrpic after the deposition process. On-line coupling of liquid chromatography with ion trap mass spectrometry is especially a result of the

breakthrough in interface technology, which becomes a technical tool in determining undefined substances. Beside APPI (atmospheric- pressure photo ionisation) and APCI (atmospheric- pressure chemical ionisation) ionisation technique, ESI (electron spray ionisation) is one of the common interface tool in the HPLC-MS.

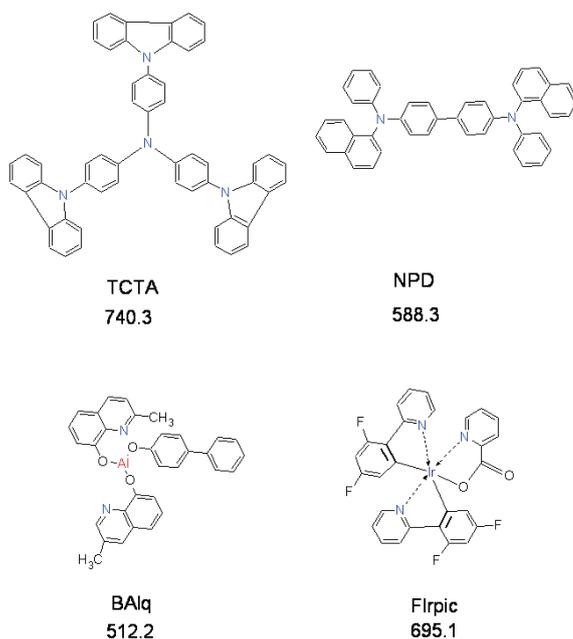
In this paper, the influence of the deposition process was investigated, in particular the chemical transformations of OLED materials during device manufacture. For the characterization of the device composition liquid chromatography in combination with an ion trap mass spectrometer was used. Ionization of the analytes was performed employing ESI source. This technique is capable of detecting analytes down to the ppb range. ESI/MS is widely used for the characterization of polar molecular compounds.

The LC/MS results reveal an unexpected transformation of the emitter Flrpic during the evaporation process. After vacuum deposition the formation of a new isomer of Flrpic was observed.

2. Experimental Part

2.1. Organic materials and devices

Pure sublimed organic materials 4,4',4''-tris (N-carbazolyl)-triphenylamine (TCTA), bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminium (BAIq), 4,4'-bis (N-(1-naphthyl)-N-phenyl-amino) biphenyl (α -NPD) and iridium(III)bis(4,6-difluorophenyl)-



Scheme 1. Chemical structures of the materials

pyridinato-N,C2')picolinate (Flrpic) were provided by Philips Research Aachen (Scheme 1).

Devices with following configuration (ITO / α -NPD (50 nm) / TCTA (10 nm) / 150 nm TCTA doped with 8% blue phosphorescent emitter Flrpic/ BALq (50 nm) / LiF (1 nm) / Al (100 nm)) on glass substrates were used for these investigations. The analyzed devices were also supplied by Philips Research Aachen and were stored in a dry, inert nitrogen atmosphere containing less than 0.1 ppm H₂O and O₂.

2.2. Sample preparation

The devices were aged in a glove box (<0.1 ppm H₂O and O₂). In order to analyze the failure of the blue phosphorescent devices, a forward bias current of 10 mA cm⁻² was applied. The devices were aged for 24 hours at constant current. Prior to the analysis, the organic layers had to be removed from the devices by means of liquid extraction. Due to its excellent dissolving properties dioxane (HPLC grade) was chosen as solvent. All extraction steps and processes were carried out under normal atmosphere and at ambient temperature. The organic extract was filtered through a nylon microdisc (4 μ m). The remaining solvent was evaporated to dryness under an N₂ stream. The crude extract was redissolved in 500 μ L dioxane (HPLC grade).

2.3. Instrument and LC/UV and LC/MS methods

Chromatographic separations were achieved using a LaChromElite HPLC System (VWR Hitachi) equipped with a LC-2100 Pump, an UV Detector L-2400, a LC-2300 column oven and a LC-2200 autosampler. In addition to the UV detection the HPLC was coupled with an ion trap mass spectrometer Esquire 4000 (Bruker Daltonics) equipped with an ESI ion source.

Prior to the measurement of the extracted samples, a HPLC method was determined to the expected substances Flrpic, α -NPD and TCTA.

Due to the high differences in the analytes polarities a conventional separation with only one column was inapplicable. Therefore several HPLC columns with different stationary phases were coupled to achieve a sufficient chromatographic separation. The analytical columns used in the resulting method were Chromolith Si (125 \times 4,6 mm; 5 μ m; Merck, Germany) coupled with Chromolith RP18e (125 \times 4,6 mm; 5 μ m; Merck, Germany) coupled with Purospher RP18e (125 \times 4,6 mm; 5 μ m; Merck, Germany). 100% acetonitrile (ACN) was used as mobile phase. The column oven temperature was set at 40°C + 1°C. Isocratic conditions were used for these experiments. The mobile phase flow rate was 0.3 mL min⁻¹ and the injection volume of samples was

10 μ L. All MS spectra were recorded in positive ion mode.

3. Results and Discussion

A challenging task in the HPLC method development was the chromatographic separation of the four analytes α -NPD, TCTA, Flrpic and BALq. A typical UV chromatogram at $\lambda = 259$ nm obtained by injection of a standard mixture containing α -NPD, TCTA, Flrpic and BALq is given in Fig. 1a. Three analytical columns (Chromolith Si, Chromolith RP18e, Purospher RP18e) were coupled.

However, only the hole transport material α -NPD, the host material TCTA and the phosphorescent emitter Flrpic could be separated. With this method aluminum (III) bis(2-methyl-8-quinolate)-4-phenylphenolate (BALq), which acts as hole blocking material but also as electron transport material, could not be separated from the injection peak. The developed method has been applied to study unstressed as well as stressed devices. The chromatograms are displayed in Figs. 1b,c.

Comparing the chromatograms of the unstressed device ITO/ 50 nm α -NPD / 10 nm TCTA / 150 nm TCTA +8% Flrpic / 50 nm BALq / 1nm LiF / 100 nm Al with the stressed ones, the responses of the host material TCTA as well as from α -NPD were slightly different. Considering the UV signal of the phosphorescent material Flrpic at a retention time of $t_r = 20$ min and $t_r = 22$ min ($\lambda = 259$ nm) two signals could be observed in the chromatogram of the unstressed device. Only one signal for Flrpic with an identical retention time of 20 min is obtained in the chromatogram of a standard mixture of the four analytes (Fig. 1a). Comparing the material composition of the electrically stressed device with the unstressed the additional signal at $t_r = 22$ min is detected with high intensity which is illustrated in the chromatogram (Fig. 1c). The formation of this compound with high intensity was observed after operation of the OLED. This could be verified by several repetitions of the experiment, which yielded the same results. These results show that thermal-evaporation rate of the materials influence the formation of the new isomer.

Unfortunately, UV detection only delivers little information regarding the chemical structure of the new compound (retention time $t_r = 22$ min), therefore the HPLC was coupled to an ion trap mass spectrometer.

An analytical MS method was developed and optimized for the four organic materials in question. In order to characterize the unknown peak at $t_r = 22$ min, observed *via* UV detection, ESI was used. For the host

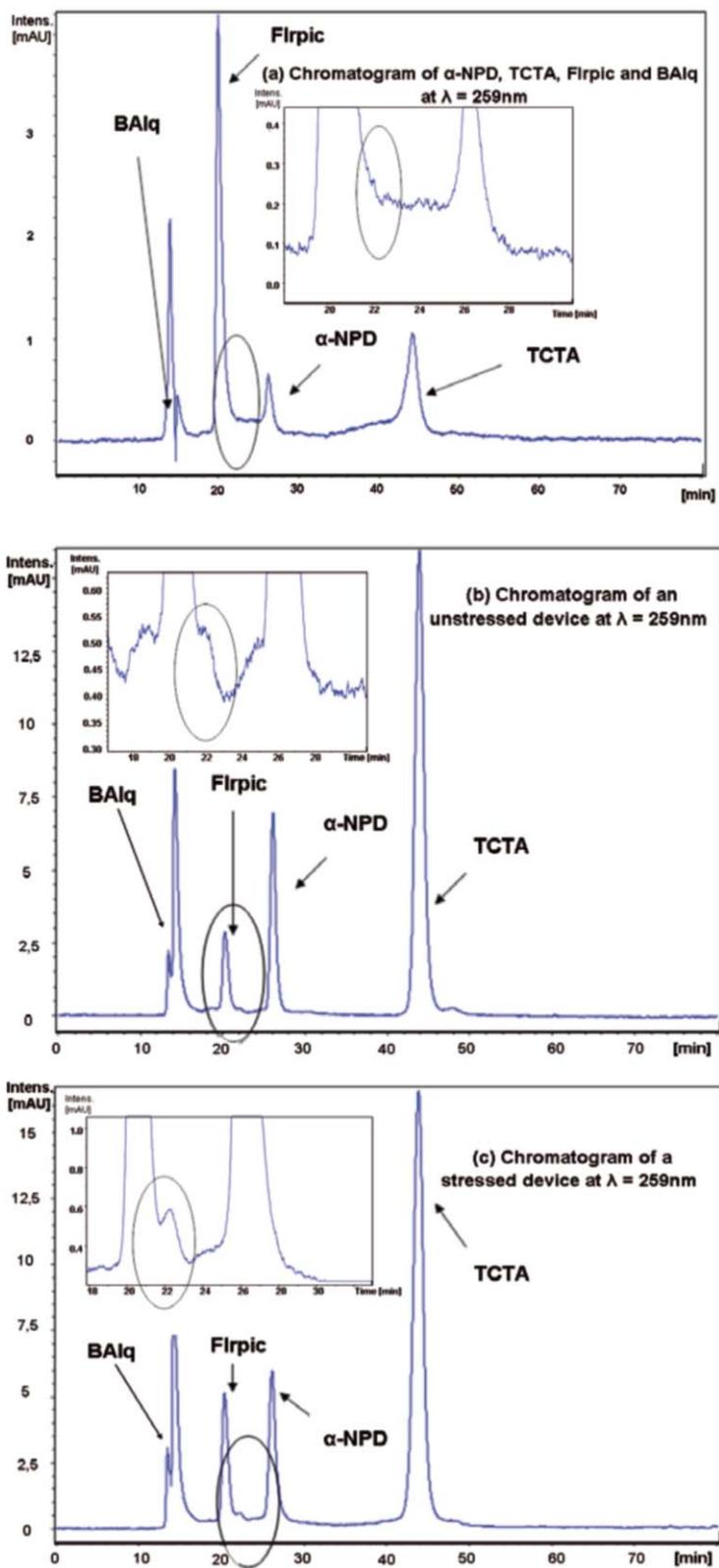


Figure 1. LC/UV chromatogram of (a) pure materials α -NPD, TCTA, Firpic and BAIq; (b) unstressed device and (c) stressed device at $\lambda = 259\text{ nm}$

material TCTA, the hole transport material α -NPD, the phosphorescent material Flrpic and the electron transport material BAQ the MS ionization conditions were optimized. An effective ionization of the different compounds was the primary objective. In order to investigate the most suitable ionization mode, positive and negative ion spectra were also acquired. The resultant spectra are strongly dependant on the polarity and structure of the materials.

In this paper, all MS spectra shown were acquired in positive mode. Furthermore two different modes were employed to gain a deeper understanding of the new molecule observed in the UV-chromatograms. The total ion current- (TIC) and extracted ion current (EIC) modes were used. TIC represents a measure of the overall intensity of all ions formed in a certain mass range in a certain time, whereas EIC describes the intensity of an ion with a defined m/z .

Fig. 2a displays the TIC chromatogram which was obtained by a standard mixture of the four analytes employing an ESI source.

Applying ESI as ionization technique, the phosphorescent emitter Flrpic can be ionized with sufficient intensities. The results of these ionization technique showed that the TIC ion abundance of the analyte α -NPD was extremely low. The TCTA signal for the injected mixture was not detectable using TIC mode. The corresponding TICs are displayed in Figs. 2b,c.

Surprisingly, the TIC chromatograms of the unstressed and aged devices deviate from a reference containing the pure analytes BAQ, TCTA, Flrpic and α -NPD (Fig. 2a).

Comparing Fig. 2a with Fig. 2b and Fig. 2c, huge differences could be observed in the region between the retention time of $t_R = 19$ min and $t_R = 24$ min. Employing the ESI ionization condition one intense signal at $t_R = 20$ min and a small distinctive signal at $t_R = 22$ min can be observed for the unstressed device. The peak at $t_R = 20$ min corresponds to Flrpic. The shoulder, which arises at $t_R = 22$ min, was detected in device extracts of unstressed and stressed devices. However, the comparison reveals that the shoulder peak at $t_R = 22$ min is much more intense in the case of stressed device. Regarding these results, the characterization of the unknown peak at $t_R = 22$ min can be performed in terms of background subtraction procedure and extracted ion chromatogram (EIC) profiles.

Prior to the analyses of the new signal, pure Flrpic was investigated employing the optimized ESI/MS method. The theoretical molecular weight of Flrpic is 694.6. Using ESI technique, the first observation was that the heteroleptic complex Flrpic can not be ionized as $(M+H)^+$ ion. The analysis of Flrpic with ESI MS showed

the formation of two different ions. Flrpic is ionized as an sodium adduct $(M+Na)^+$ and the cleavage of picolinic acid is taking place, resulting in the formation of a $(M\text{-picolinate})^+$ ion. The formation of the $(M\text{-picolinate})^+$ ion suggests that the picolinate ligand is weaker bonded to the iridium than the difluorophenylpyridine ligands. Both ions, $(M\text{-picolinate})^+$ and $(M+Na)^+$, are singly charged. The heteroleptic complex constitutes a special isotopic pattern (Fig. 4c), compared to the other organic molecules in the devices. Both peaks, $(M\text{-picolinate})^+$ corresponding to m/z 573.0 and $(M+Na)^+$ mass of m/z 718 have the same isotopic pattern (Figs. 4a,b). Both signal, m/z 573.0 as well as m/z 718, indicate iridium as a component.

For elucidation of the new shoulder peak at $t_R = 22$ min, which can be detected in stressed devices *via* UV detection and in unstressed as well as in aged devices *via* ESI ionization, EIC profiles of the blue emitter complex Flrpic were used in the subsequent analysis of the stressed and unstressed samples. EICs is especially useful to identify a target compound of known m/z but also to uncover the relationship of certain m/z values at different retention times, which may indicate impurities of the sample or different isomers.

Fig. 3a represents the corresponding EIC of the m/z 573 spectra of the reference standard mixture of the four analytes BAQ, TCTA, Flrpic and α -NPD. The m/z 573 trace shows the expected peak at $t_R = 20$ min which corresponds to the emitter Flrpic. EIC profiles of m/z 718 as well as m/z 573 show only one significant intense signal at $t_R = 20$ min. From these data it could be excluded that impurities of Flrpic have led to the peak at $t_R = 22$ min. In contrast to the standard mixture, extracts from the devices deliver two signals, at different retention times ($t_R = 20$ min and $t_R = 22$ min) using EIC mode when recording the masses with m/z 718 $(M+Na)^+$ and m/z 573 $(M\text{-picolinate})^+$ (Fig. 3b). These findings were also detected for the extracts of 24 h aged device which is illustrated in Fig. 3c. Surprisingly, both EIC spectra of unstressed and stressed devices show the same curve progression as the TIC mode of the device extracts. For the stressed devices, the shoulder peak at $t_R = 22$ min was more intense than in extracts from the unstressed device.

For both peaks, $t_R = 20$ min and $t_R = 22$ min, identical mass spectra were observed. As shown in Figs. 4a,b the corresponding mass spectra of the peaks at $t_R = 20$ min and $t_R = 22$ min both possess identical mass spectra.

In view of the results above, it is important to point out that Flrpic tends to isomerize during the evaporation process. The new isomer ($t_R = 22$ min) was formed during the evaporation and operated process and it was detected in higher amounts in stressed device which results from the operating process.

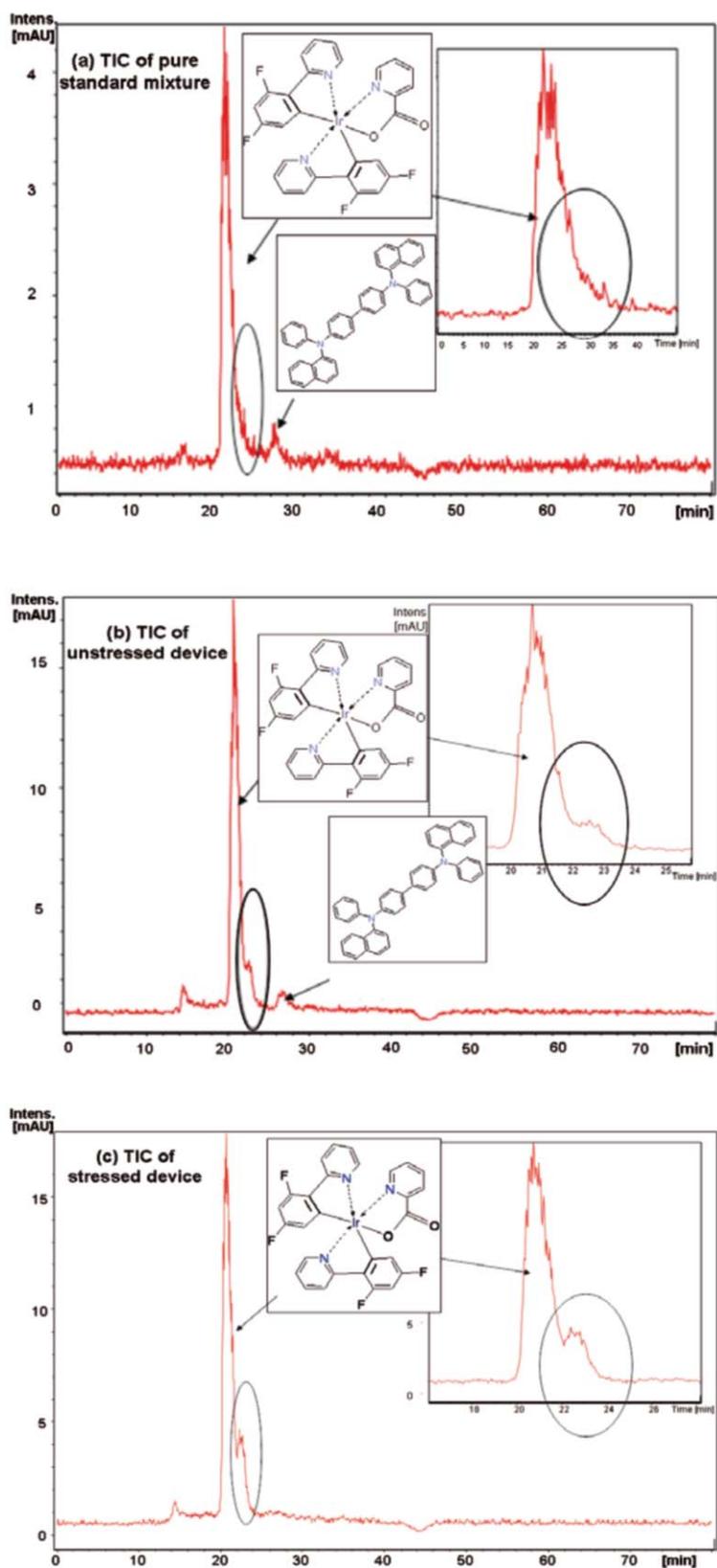


Figure 2. TIC chromatogram of (a) pure materials α -NPD, TCTA, Firpic and BAIq; (b) unstressed device and (c) stressed device

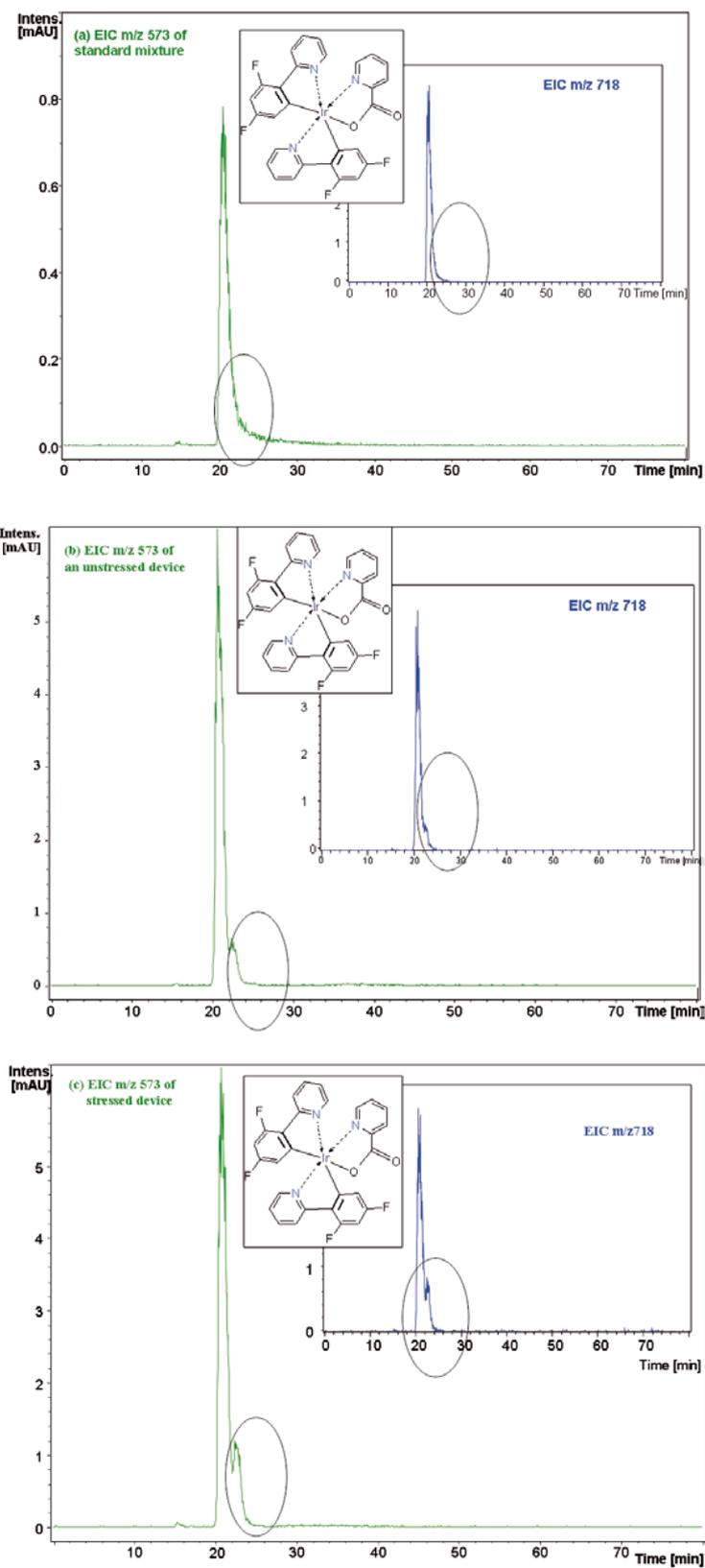


Figure 3. EIC chromatograms of (a) pure materials α -NPD, TCTA, Flrpic and BALq; (b) unstressed device and (c) stressed device

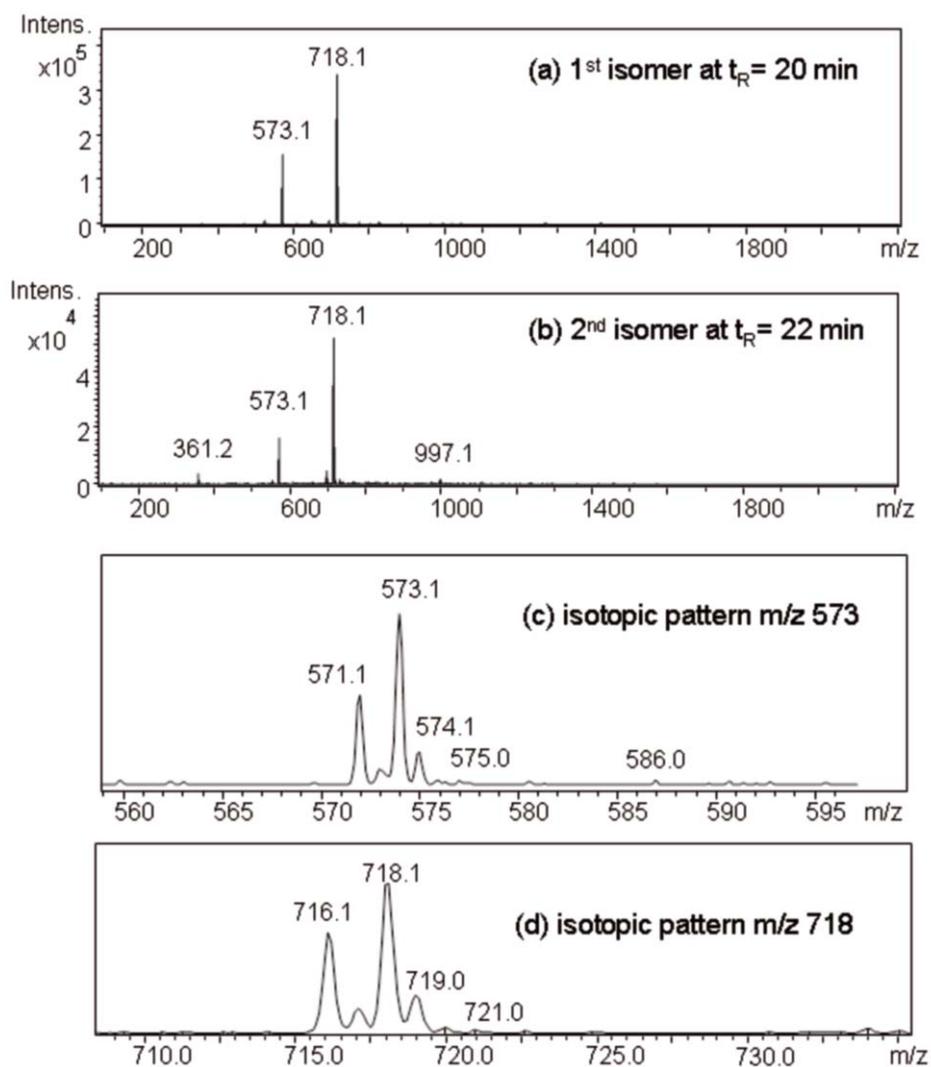


Figure 4. MS spectra of (a) 1st isomer peak at $t_R = 20$ min; (b) 2nd isomer peak at $t_R = 22$ min; (c+d) isotopic pattern of the characteristic signals with 718 m/z and 573 m/z

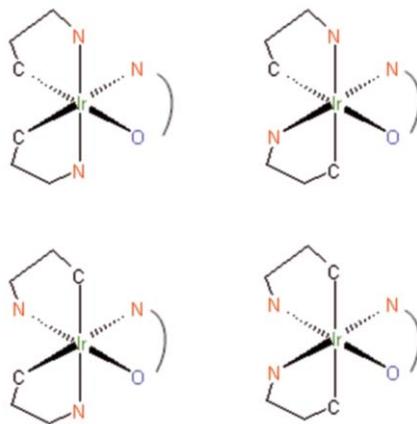


Figure 5. Chemical structures of the (iridium (III) bis[(4,6-fluorophenyl)-pyridinato-N,C²]picolinate) isomers

Neglecting the delta configurations theoretically four different stereochemical isomers, of the heteroleptic complex could exist, depending on their thermodynamic and kinetic properties. Chemical structures of the possible theoretical isomers of the blue phosphorescent complex Flrpic are given in Fig. 5.

First of all, on-column ligand exchange kinetics can be excluded which might be a scenario from the experimental technique. Analyzing pure sublimated materials *via* LC/UV and LC/MS no signals at $t_R = 22$ min were observed (see Figs. 1a, 2a and 3a).

To form one of these four theoretical possible isomers, the heteroleptic molecule Flrpic has to undergo a rearrangement reaction for the formation of the second isomer during the deposition process. Consequently, the formation of the second isomer occurs *via* the cleavage of one covalent bond, followed by 180° rotation of one ligand and formation a new isomer which results in a mixture of two Ir products. The result is a mixture of two species containing iridium.

Because of the nearly identical orientation of ligands of the Flrpic isomer, both analytes were eluted at nearly the same time. The applied HPLC method was just suited to detect the other isomers of Flrpic.

Nonetheless, it should be noted that not only Flrpic will be evaporated on the devices but also additionally one of theoretical four possible isomers, due to the manufacture conditions. These findings were similar to the report from Baranoff *et al.* using (Ir(2-phenylpyridine)2(2-carboxy-4-dimethyl amino pyridine)) [22]. Pure sublimated Flrpic material did show only one signal whereas in device manufacture a mixture of isomers from the light blue emitting material Flrpic could be detected. The other very important aspect is that the obtained data indicate that isomerization could also occur during the process of electrical stressing. The spectra showed an increased intensity of the second isomer after the electrical stressing of the device. Only in the stressed device the concentration of the new isomer was high enough to be detected within the detection limits of the UV-detector. These findings suggest that the rearrangement of the blue Flrpic emitter during the stressing might be one aspect which is responsible for an insufficient lifetime of this emitter. Possibilities that the main isomer is being consumed during 24 h device operation can be excluded by comparing the signal intensities from Flrpic (see Figs. 2b,c and 3b,c).

If the rearrangement can even occur in an active device, this might have considerable influence on the device performance. As the emitter is surrounded by matrix molecules it can not be ruled out that during the rearrangement a complex formation of the matrix molecule with the free site of the rearranged emitter is

taking place. This could lead to the transformation of the emitter, which could show radiationless recombination and therefore might limit the lifetime of the blue emission of Flrpic emitters. The extraction of the materials of the device would most likely only deliver the different isomers of Flrpic as the solution process might interrupt the instable complex.

Small amounts of further unidentified compounds were detected in the extracts of the aged devices, which could not be fully characterized structurally up to now and are under further investigation.

It has to be noticed that the focus of this work was the investigation of the chemical transformation of the emitter during the manufacture and aging process. Reasons that chemical reaction and degradation products can not be observed might be due the aging of the device for a relatively short time. Further causes may be due the different device setups, which were used by other research groups [21,23]. It is important to note that analyzing and observing chemical reactions products *via* LC/MS is quite a challenging task compared to LDI/TOF/MS, where different methods parameters such as choosing the right analytical column and mobile phases have to be considered.

To the best of our knowledge, this is the first report highlighting the isomerization of Flrpic during the device manufacture and operation process. However, up to now, chemical degradation of organic light emitting materials in devices was not as deeply investigated as it should have been. Additionally, experiments using HPLC/MS but also DFT- based quantum chemical calculation are being carried out to prove which isomer of the phosphorescent emitter Flrpic is formed during the evaporation process. Experiments including peak isolation and separation *via* HPLC/MS are currently in progress.

4. Conclusions

This paper describes one analytical approach towards the HPLC separation of OLED materials and identification of new products that are formed during manufacture and electrical stressing of PhOLEDs. It is shown that chemical isomerization phenomena occurring during the operation of OLEDs could be an important aspect that influences the lifetime of devices using Flrpic as an emitter. The findings contribute to an understanding of the behavior of Flrpic during the deposition- and stressing process. At present many methods are available to characterize OLED degradation regarding the physical degradation mechanisms, but HPLC coupled with a mass spectrometer using ESI as ion source appear to be

one important analytical technique. These results show the systematic analytical application of this technique in the study of multilayer devices prepared by vacuum deposition.

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References

- [1] U. Mitschke, P. Bauerle, *J. Mater. Chem.* 10(7), 1471 (2000)
- [2] M. Miyata, H.S. Nalwa, *Organic Electroluminescent Materials and Devices* (Gordon and Breach, Reading, UK, 1997) 487
- [3] C.H. Chen, J. Shi, C.W. Tang, *Macromol. Symp.* 125, 1 (1997)
- [4] L.S. Hung, C.H. Chen, *Mater. Sci. Eng. R Rep.* R39(5-6), 143 (2002)
- [5] C.W. Tang, S.A. VanSlyke, *Appl. Phys. Lett.* 51(12), 913 (1987)
- [6] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, *Nature* (London) 395(6698), 151 (1998)
- [7] K.A. King, P.J. Spellane, R.J. Watts, *J. Am. Chem. Soc.* 107(5), 1431 (1985)
- [8] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 79(13), 2082 (2001)
- [9] R.J. Holmes, S.R. Forrest, Y.J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, *Appl. Phys. Lett.* 82(15), 2422 (2003)
- [10] J. Li, P.I. Djurovich, B.D. Alleyne, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, *Polyhedron* 23(2-3), 419 (2004)
- [11] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 75(1), 4 (1999)
- [12] J.-R. Gong, L.-J. Wan, S.-B. Lei, C.-L. Bai, X.-H. Zhang, S.-T. Lee, *J. Phys. Chem. B* 109(5), 1675 (2005)
- [13] M. Kawaharada, M. Ooishi, T. Saito, E. Hasegawa, *Synth. Met.* 91(1-3), 113 (1997)
- [14] A. Uddin, C.B. Lee, X. Hu, *Proc. SPIE-Int. Soc. Opt. Eng.* 5648 (Smart Materials (III)), 114 (2005)
- [15] E. Ettetdgui, G.T. Davis, B. Hu, F.E. Karasz, *Synth. Met.* 90(1), 73 (1997)
- [16] C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* 56(9), 799 (1990)
- [17] L.M. Do, E.M. Han, Y. Niidome, M. Fujihira, T. Kanno, S. Yoshida, A. Maeda, A.J. Ikushima, *J. Appl. Phys.* 76(9), 5118 (1994)
- [18] H.M. Grandin et al., *Org. Electron.* 4(1), 9 (2003)
- [19] J. McElvian, H. Antoniadis, M.R. Hueschen, J.N. Miller, D.M. Roitman, J.R. Sheats, R.L. Moon, *J. Appl. Phys.* 80(10), 6002 (1996)
- [20] P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D.M. McCarty, M.E. Thompson, *Appl. Phys. Lett.* 65(23), 2922 (1994)
- [21] D.Y. Kondakov, W.C. Lenhart, W.F. Nichols, *J. Appl. Phys.* 101(2), 024512 (2007)
- [22] E. Baranoff et al., *Inorg. Chem.* 47(15), 6575 (2008)
- [23] S. Scholz, R. Meerheim, K. Walzer, K. Leo, *Proc. SPIE*, 6999 (Organic Optoelectronics and Photonics III), 69991B/1 (2008)