

Isomeric Separations of Cyclometalated Iridium (III) Complexes Using the ACQUITY UPC² System

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Abstract

This application note demonstrates the isomeric separations of a homoleptic iridium complex and a heteroleptic complex using UltraPerformance Convergence Chromatography (UPC²). Geometric isomers of the homoleptic complex were separated in less than five minutes. Simultaneous separation of four isomers in the heteroleptic complex was achieved in a single run.

Benefits

- Fast separation of geometric isomers in a homoleptic iridium complex enables real time monitoring of material purification.
- Simultaneous separations of geometric and optical isomers in a heteroleptic iridium complex in a single chromatographic run enables accurate purity assessment, otherwise requiring multiple chromatographic runs.
- Easy method transfer from UPC² to semi-preparative SFC to purify desired isomers with easy recovery of collected fractions under mild conditions to mitigate isomer formation, allowing for high purity material for OLED device preparation.

Introduction

Synthesis and characterization of cyclometalated iridium (III) complexes in organic light emitting display (OLED) applications is of great interest, as these complexes display high emission quantum yields and can be readily color-tuned through systematic modification of the ligands using facile syntheses. Depending on the types of ligands surrounding the central iridium atom, these organometallic complexes can be categorized as homo- and heteroleptic. Both homo- and heteroleptic complexes can exist as geometric isomers often referred to as meridional (*mer*) and facial (*fac*) isomers. Geometric isomers display vastly different photophysical and chemical properties,¹⁻³ which can affect the performance and lifetime stability of OLED devices. In addition, heteroleptic complexes possess optical isomerism. Enantio-enriched complexes emit circularly polarized light and can be used for three-dimensional electronic displays.⁴

The multiple forms of isomerism present a particular challenge for the separation of these isomers required for assessing material purity, as well as for understanding failure mechanisms of light emitting devices. This challenge is further compounded by the currently prevalent purification technique for these materials, namely sublimation.⁵⁻⁶ Thermal isomerization could take place in situ during sublimation. The purification process often results in an isomeric mixture in lieu of the desired single isomer for device manufacturing, leading to

compromised performance. Clearly, a purification technique under mild conditions to mitigate isomerization is of great value.

Due to the low solubility of most cyclometalated iridium complexes in polar solvents, current chromatographic analyses of cyclometalated iridium complexes typically employ normal phase liquid chromatography (NPLC). Supercritical fluid chromatography (SFC), and more recently, UltraPerformance Convergence Chromatography (UPC²) offer attractive alternatives to NPLC, providing improved resolution, shortened analysis time, and reduced organic solvent consumption.

In this application, we conduct isomeric separations of tris(2-(2,4-difluorophenyl) pyridine)iridium(III) (Ir(Fppy)₃) and iridium(III)bis(4,6-difluorophenyl)-pyridinato-N,C2')picolinate (Flrpic) structures, shown Figure 1, using a Waters ACQUITY UPC² System. The feasibility of applying SFC to purify Flrpic is also demonstrated using a Waters Investigator SFC System.

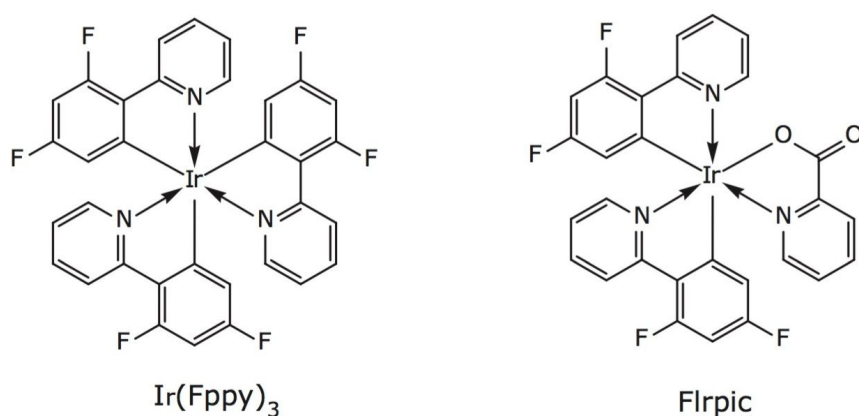


Figure 1. Chemical structures of Ir (Fppy)₃ and Flrpic.

Experimental

Instruments:

All analytical experiments were performed on the ACQUITY UPC² System controlled by Empower 3 Software. The preparative experiments were performed on the Investigator SFC System controlled by ChromScope Software.

Columns:

ACQUITY UPC² BEH and 2-Ethyl Pyridine 3.0 x 100 mm, 1.7 μm from Waters Corporation. CHIRALPAK AS-H 4.6 x

150 mm, 5 μ m columns were purchased from Chiral Technologies (West Chester, PA).

Sample description

Samples were purchased from Sigma Aldrich and 1-Material. In order to form isomers, samples were heat-stressed in a temperature controlled oven to induce the isomerization reactions. After being cooled to room temperature, these samples were dissolved in chloroform for subsequent analysis.

Results and Discussion

Figure 2 shows the UPC²/UV chromatograms of the untreated and the heat-stressed Ir (Fppy)₃ samples. Peaks 1 and 2 have the same mass spectra (not shown) but distinctly different UV spectra (inserts), suggesting that they are most likely the fac and mer isomers. The peak labeled "desfluoro" resulted from the loss of one F atom from the Ir (Fppy)₃. The main difference between the two chromatograms, however, lies in the relative ratio of peaks 1 and 2. Upon heating, the peak ratio of 1/2 increased. It is likely due to the thermal isomerization process, where the less stable mer isomer (peak 2) was converted into the more stable fac isomer (peak 1). Figure 2 clearly demonstrates that the geometric isomers of Ir (Fppy)₃ can be readily separated using the ACQUITY UPC² System.

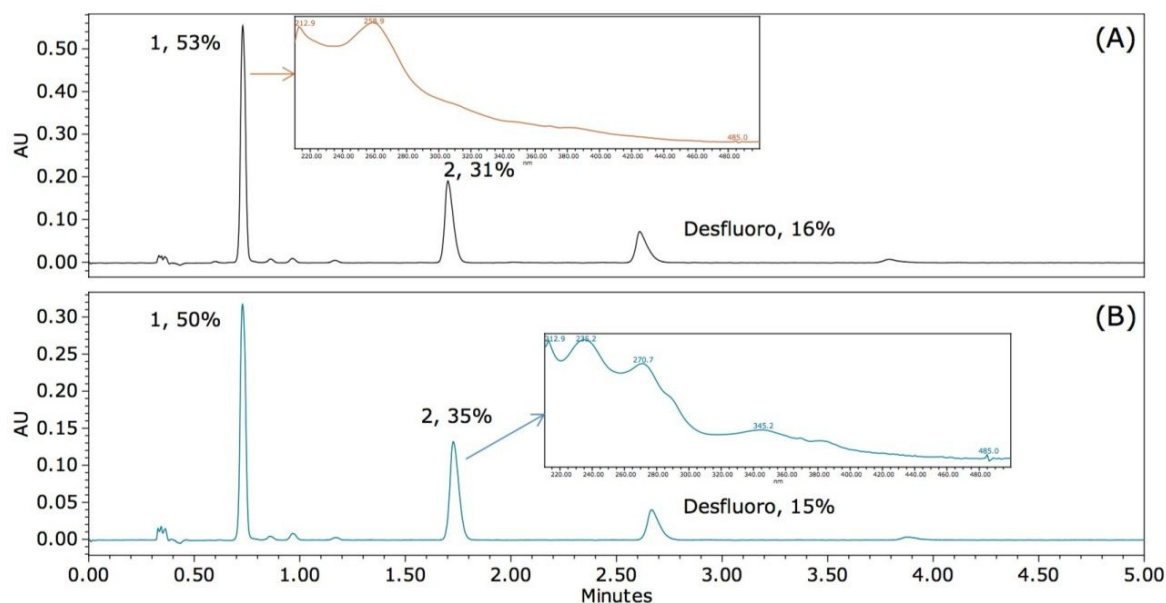


Figure 2. UPC²/UV chromatograms of Ir(Fppy)₃ using the ACQUITY UPC² 2-EP 3 x 100 mm, 1.7 μ m Column. (A) Sample treated at 280 °C for 24 h, and (B) untreated sample at 25 °C. Flow rate was 1.5 mL/min; back pressure was 2175 psi; isocratic with 30% isopropanol co-solvent; and the temperature was 40 °C. The numbers after peak notations denote the relative percentage of each peak based on peak area.

Figure 3 shows the UPC²/UV chromatograms of Flrpic using both achiral and chiral stationary phases. On the chiral column, Flrpic was split into two peaks, as shown in Figure 3B. The two peaks in Figure 3B have identical m/z (not shown) and UV spectra (inserts), indicating that these two peaks most likely originate from a pair of enantiomers. Unlike homoleptic Ir (Fppy)₃, heteroleptic Flrpic is comprised of two different types of ligands. This molecular dissymmetry, in turn, results in optical isomerism. For practical applications such as three-dimensional displays, it is highly desirable to have a high emission dissymmetry. In this case, UPC² offers a facile means to measure the enantiomeric ratio for chiral luminescent compounds, which is of great importance in order to correlate chemical structure with emission dissymmetry.

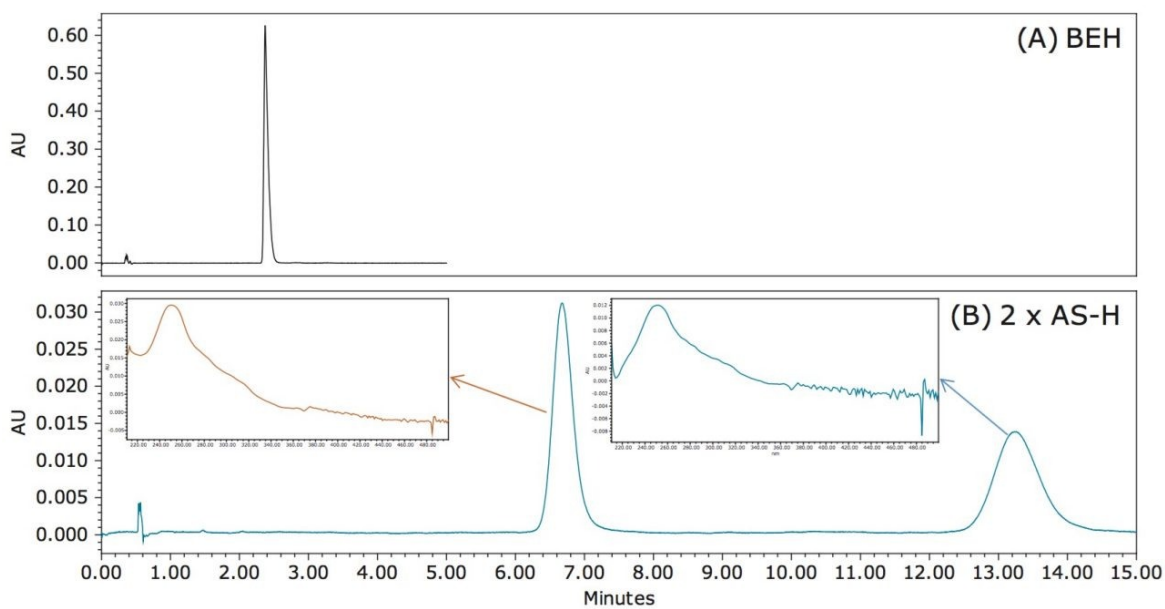


Figure 3. UPC²/UV chromatograms of standard grade Flrpic. (A) Using an ACQUITY UPC² BEH 3 x 100 mm, 1.7 μ m Column; flow rate was 1.5 mL/min, back pressure was 1740 psi, isocratic with 35% isopropanol, and temperature was 40 °C. (B) Using two CHIRALPAK AS-H 4.6 x 150 mm each, 5 μ m columns. Flow rate was 3 mL/min, back pressure was 2175 psi, isocratic with 23% isopropanol, and the temperature was 50 °C.

Figure 4 shows the UPC²/UV chromatograms of the untreated and heat-stressed Flrpic on an ACQUITY UPC² BEH Column. An additional peak was observed for the heat-stressed sample, as shown in Figure 4B. The resulting mass spectra of the two peaks were identical (results not shown). Closer examination of the UV spectra, shown in Figure 5, reveals that the UV spectra of the peaks in Figure 4B were different, unlike the enantiomers shown in Figure 3B where the UV spectra were identical. The minor peak in Figure 4B has a λ_{max} of 245 nm, while the major peak has a λ_{max} of 251 nm. These results suggest that the heat-stressed sample has undergone thermal isomerization to form an additional geometric isomer, similar to those observed during sublimation.⁵⁻⁶ Since the overall analysis time was less than 5 min, UPC² enables a quick assessment of material purity post-sublimation and can be adopted as a quality control (QC) technique prior to device manufacturing.

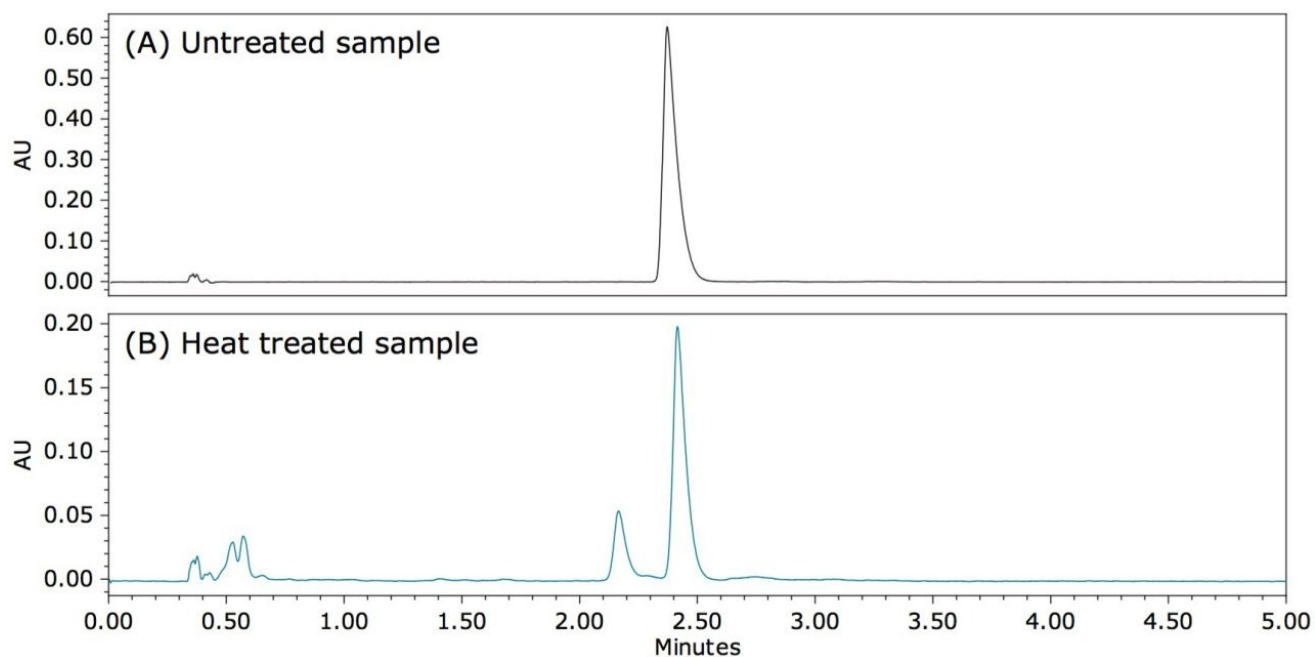


Figure 4. UPC²/UV chromatograms of (A) untreated Flrpic, and (B) heat-stressed Flrpic on an ACQUITY UPC² BEH 3 x 100 mm, 1.7 μ m Column under isocratic conditions (35% co-solvent). Flow rate was 1.5 mL/min; back pressure was 2175 psi; isocratic with 35% isopropanol co-solvent; and the temperature was 40 °C.

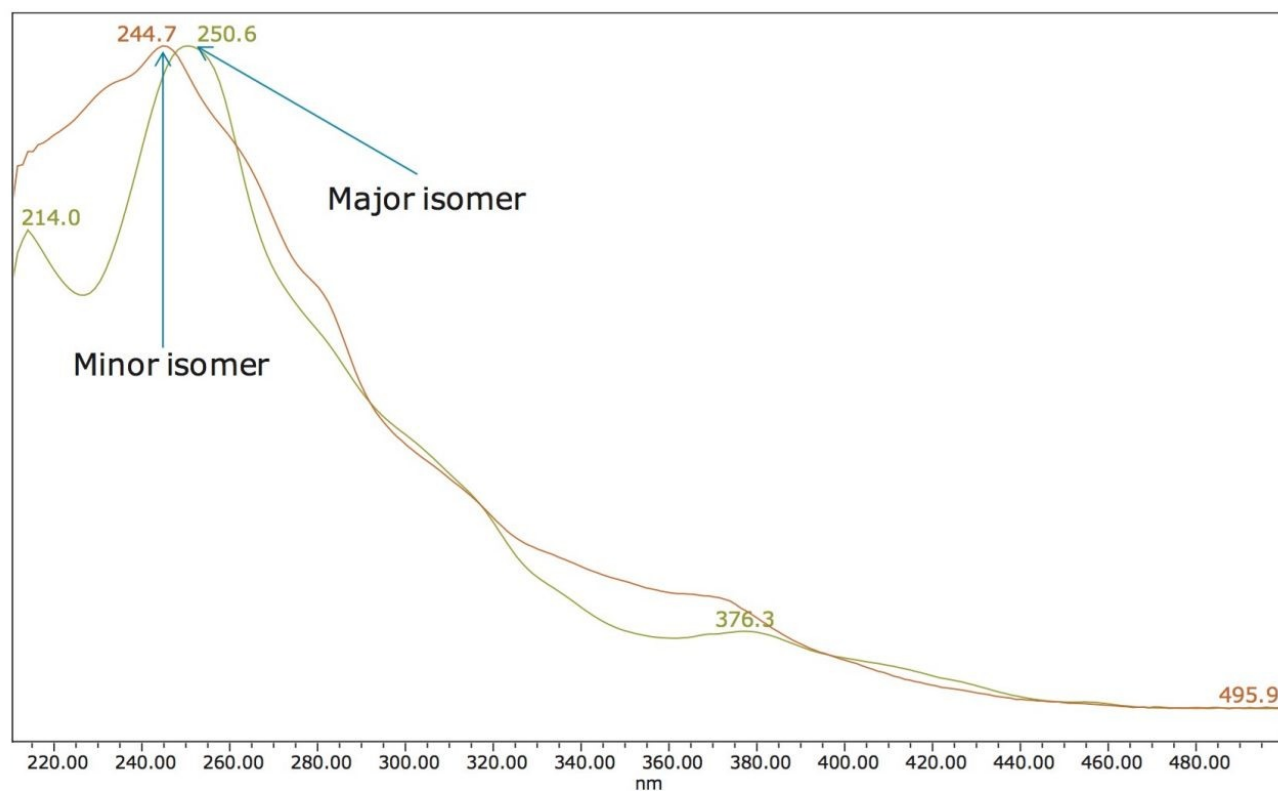


Figure 5. UV spectra of a pair of geometric isomers of Flrpic.

Each geometric isomer can, in theory, contain a pair of enantiomers. Thus, the simultaneous separation of the four isomers of the heat-stressed Flrpic, as shown in sample 4B, was attempted. The resulting UV chromatograms are shown in Figure 6. E₁/E₁' and E₂/E₂' are two pairs of enantiomers; whereas, E₁/E₂ and E₁'/E₂' are two pairs of geometric isomers.

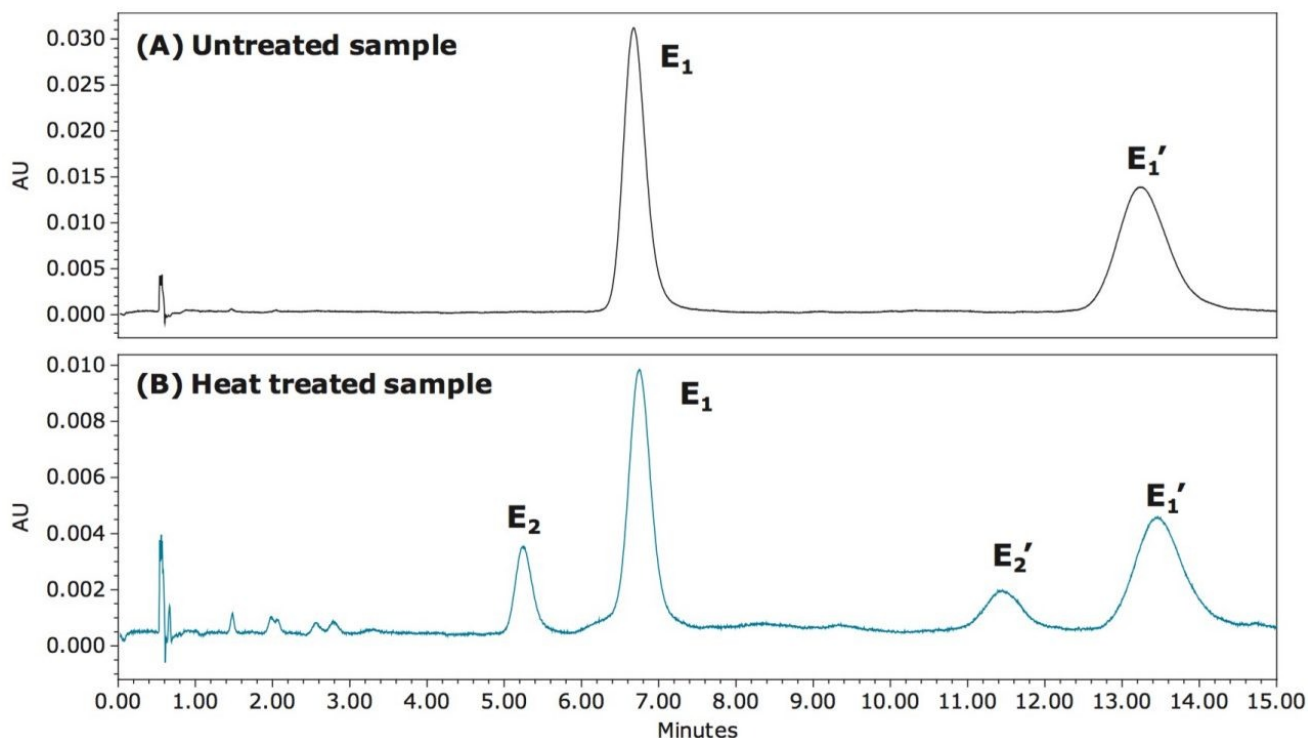


Figure 6. UPC²/UV chromatograms of (A) untreated Flrpic and (B) heat-stressed Flrpic using two CHIRALPAK AS-H 4.6 x 150 mm each, 5 μ m columns. Flow rate was 3 mL/min, back pressure was 2175 psi, isocratic with 23% isopropanol, and the temperature was 50 $^{\circ}$ C.

The implications of the isomeric separations shown in Figure 6 are beyond simple analysis. As the primary purification technique for cyclometalated iridium complexes used in light emitting devices, sublimation induces in situ, adverse thermal isomerization, as demonstrated in Figures 2, 4, 6, and others.⁵⁻⁶ As a result, a mixture of isomers rather than pure material is doped in the device, often leading to degraded performance and reduced lifetime. The separation shown in Figure 6 illustrates that SFC could potentially lend itself as an alternative to sublimation for the purification of these materials.

Figure 7 shows an SFC/UV chromatogram of the heat-stressed Flrpic using a semi-preparative SFC. Baseline resolutions of all four isomers were obtained. At 50 $^{\circ}$ C, using isopropanol as the co-solvent, pure isomers can be recovered under mild conditions, mitigating the possibility of isomer formation. It should be noted that although Figures 6B and 7 were obtained under identical chromatographic conditions, the resolutions shown in Figure 6B

were far superior to those in Figure 7. The improved resolutions are largely due to the minimized system volume of UPC² resulting in reduced peak dispersion.

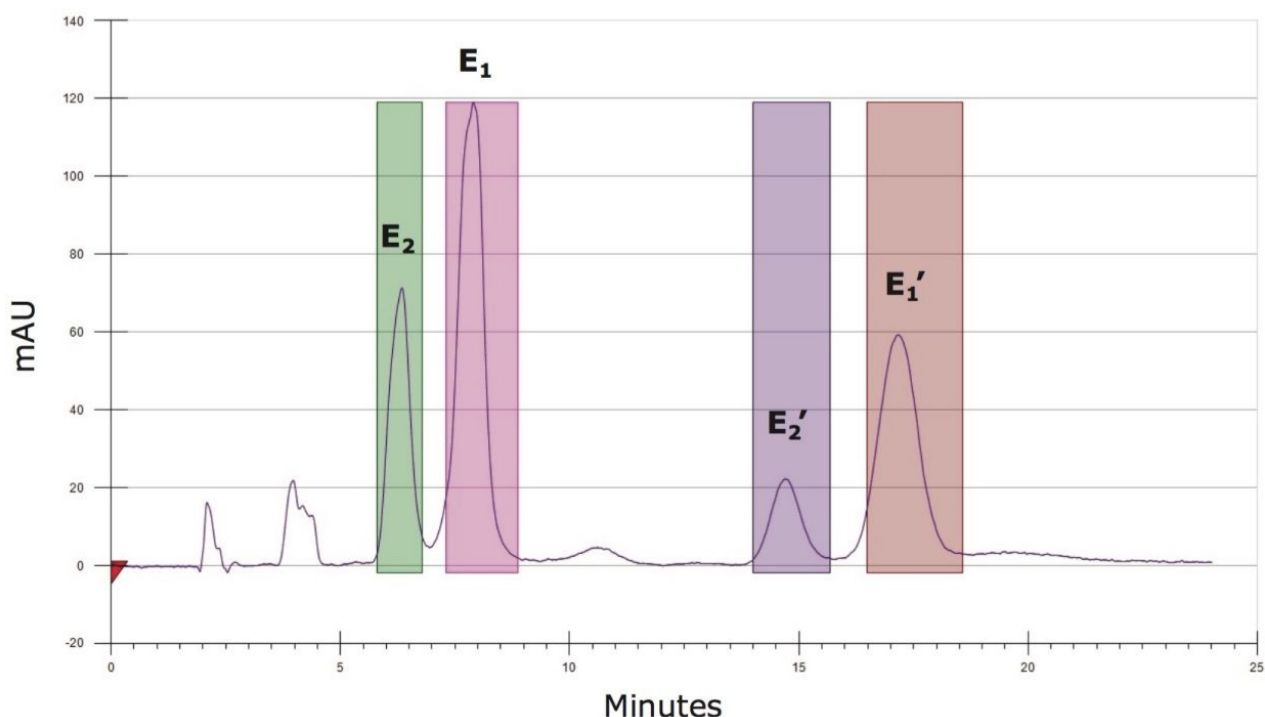


Figure 7. SFC/UV chromatogram of the heat-stressed Flrpic using two CHIRALPAK AS-H 4.6 x150 mm each, 5 μ m columns on a Waters Investigator SFC System. Flow rate was 3 mL/min, back pressure was 2175 psi, isocratic with 23% isopropanol, and the temperature was 50 $^{\circ}$ C. The shaded area indicates the collected fractions.

Conclusion

In this application, we demonstrated the isomeric separations of a homoleptic iridium complex, Ir (Fppy)₃, and a heteroleptic complex, Flrpic, using UPC². For Ir(Fppy)₃, the geometric *fac*- and *mer*- isomers were readily separated in less than 5 min. For Flrpic, simultaneous separations of four isomers, both geometric and optical, were achieved in a single run. The presented methodologies augment the conventional analytical techniques used for purity assessment, one of the key analytical challenges in synthesis, process, and manufacture of OLED devices and associated materials. Furthermore, the underlying supercritical fluid technology also allows for a method transfer from UPC² to a semi-preparative SFC instrument to purify desired material.

References

1. Kappaun S, Slugovc C, List EJW. Phosphorescent organic light-emitting devices: Working principle and iridium based emitter materials. *Int J Mol Sci.* 2008; 9: 1527-47.
2. Tamayo B, Alleyne BD, Djurovich PI, Lamansky S, Tsyba I, Ho NN, Bau R, Thompson ME. Synthesis and characterization of facial and meridional tris-cyclometalated iridium(III) complexes. *J Am Chem Soc.* 2003; 125(24): 7377-87.
3. McDonald AR, Lutz M, von Chrzanowski LS, van Klink GPM, Spek AL, van Koten G. Probing the mer- to fac-isomerization of tris-cyclometallated homo- and heteroleptic (C,N)₃ iridium(III) complexes. *Inorg Chem.* 2008; 47: 6681-91.
4. Coughlin FJ, Westrol MS, Oyler KD, Byrne N, Kraml C, Zysman-Colman E, Lowry MS, Bernhard S. Synthesis, separation, and circularly polarized luminescence studies of enantiomers of iridium (III) luminop. *Inorg Chem.* 2008; 47: 2039-48.
5. Baranoff E, Saurez S, Bugnon P, Barola C, Buscaino R, Scopeletti R, Zuperoll L, Graetzel M, Nazeeruddin MK. Sublimation not an innocent technique: A case of bis-cyclometalated iridium emitter for OLED. *Inorg Chem.* 2008; 47: 6575-77.
6. Baranoff E, Bolink HJ, De Angelis F, Fantacci S, Di Censo D, Djellab K, Gratzel M, Nazeeruddin MK. An inconvenient influence of iridium (III) isomer on OLED efficiency. *Dalton Trans.* 2010; 39: 8914-18.
7. Sivasubramaniam V, Brodkord F, Haning S, Loebl HP, van Elsbergen V, Boerner H, Scherf U, Kreyenschmidt M. Investigation of Irpic in PhOLEDs via LC/MS technique. *Cent Eur J Chem.* 2009; 7(4): 836-845.

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