FINE-TUNING SOLID STATE LUMINESCENCE PROPERTIES OF MOLECULAR CRYSTALS *VIA* SOLID SOLUTION FORMATION

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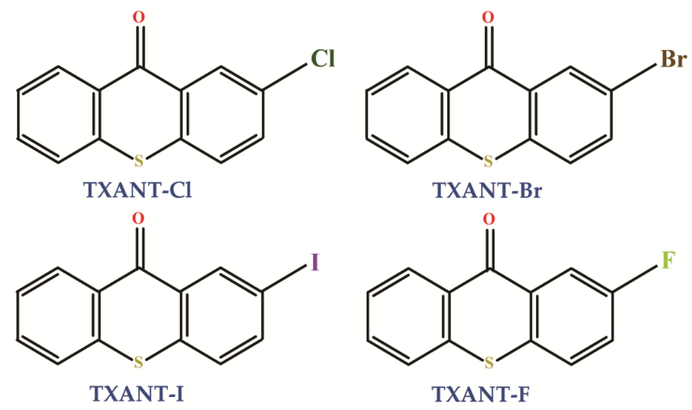
Introduction

Four different halogenated derivatives of thioxanthone (pure compounds exhibit technologically relevant luminescence properties) – TXANT-Cl, TXANT-Br, TXANT-I, and TXANT-F –, see below, were studied experimentally.



Molecular structure of thioxanthone halogenated derivatives

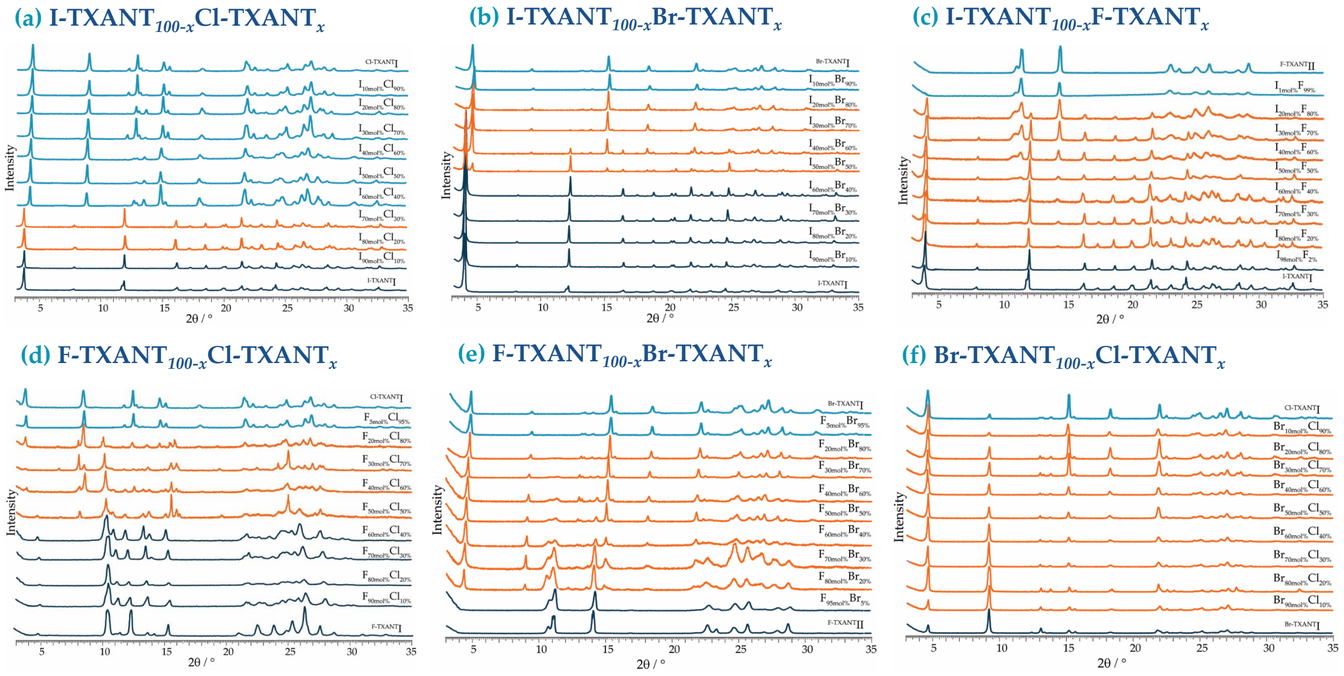
Aim

To explore the solid solution formation between thioxanthone halogenated derivatives by:

- Crystallizing two component system in different component ratio;
- Characterize crystalline phases using PXRD and thermal methods of analysis;
- Studying results from photoluminescence spectra of all crystalline phases in powder form to confirm that fine-tuning solid state luminescence properties of molecular crystals can be modulated *via* solid solution formation.

Identification of solid solutions

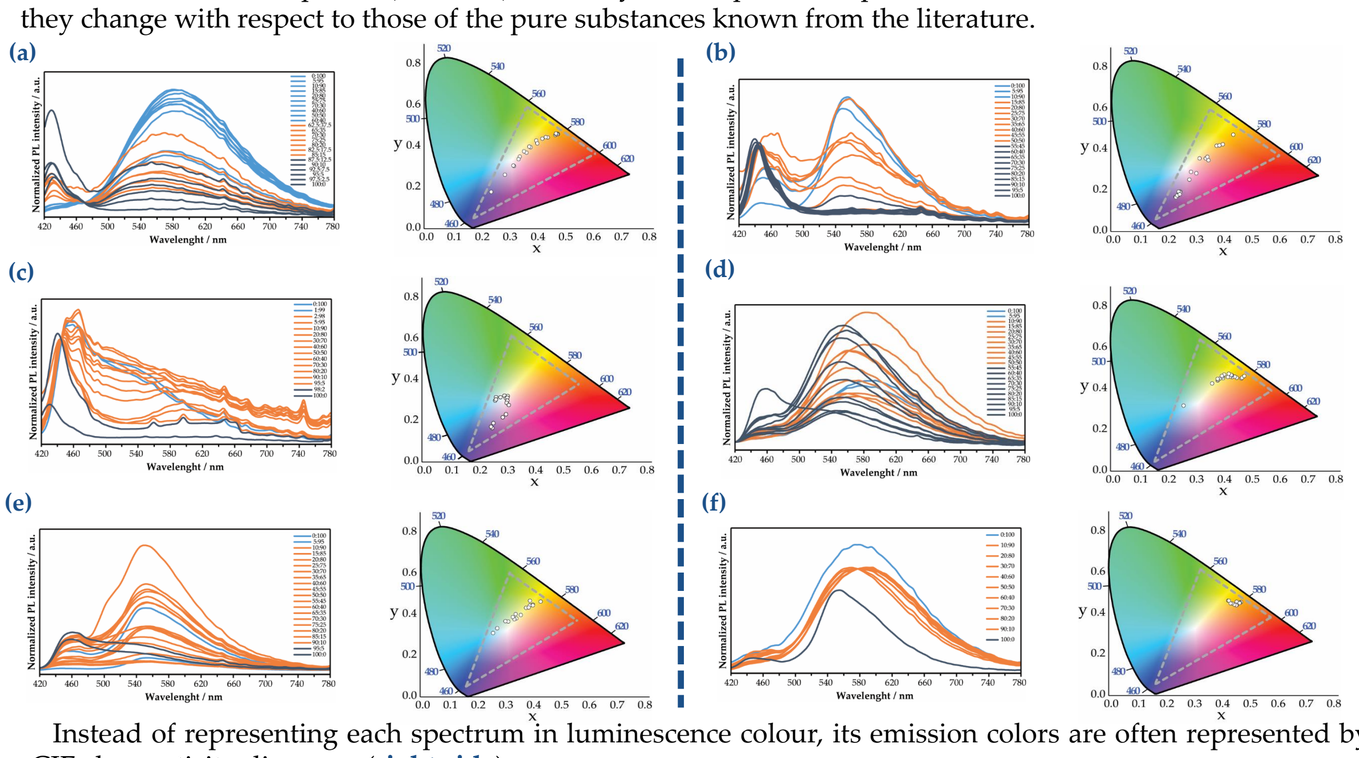
The obtained crystalline phases were characterized using powder X-ray diffraction (PXRD), those results are consistent with the melt phase diagrams.



Powder X-ray diffraction patterns of selected thioxanthone halogenated derivative mixture system composition samples (PXRD scenes are ranked from 0 to 100% (***x*** in **5** to **10%** increments)).

Engineering novel crystalline phases

Photoluminescence spectra (**left side**) of all crystalline phases in powder form were recorded to see how they change with respect to those of the pure substances known from the literature.



Instead of representing each spectrum in luminescence colour, its emission colors are often represented by CIE chromaticity diagrams (**right side**).

Construction of binary melt phase diagrams

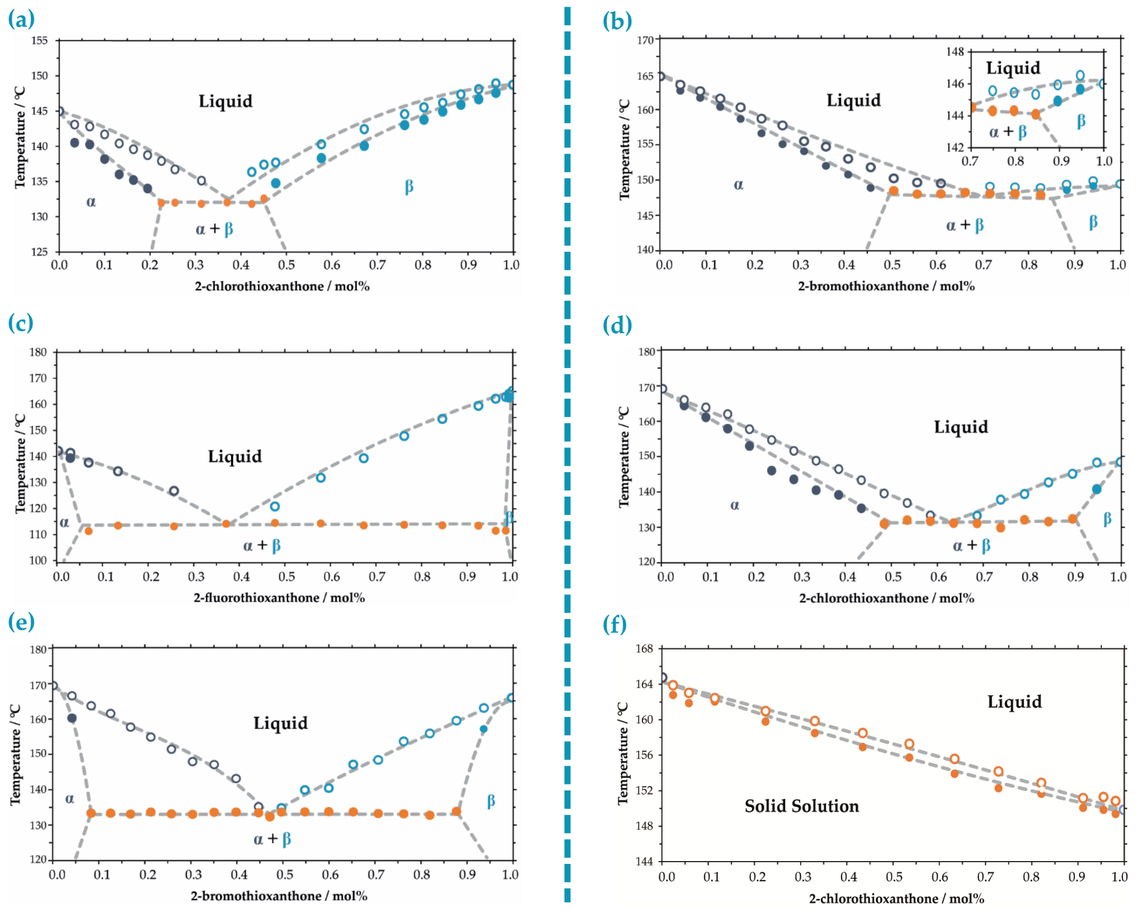
Crystallization experiments were performed for mixtures of thioxanthone halogenated derivatives, in different compositions (**$\alpha_{100-x}\beta_x$ / %**), from ***100-x*** to ***x***, where **$0 \le x \le 100$**, using an analytical balance and the resulting mechanical mixtures were then completely dissolved in acetonitrile at 70°C. The clear solutions were left to evaporate till dryness.

Experimentally obtained crystalline phases from thioxanthone halogenated derivative mixtures, and quantities of solvent volume and mass of substances used in crystallization experiments

Substance ratio / mol%	System											
	I-TXANT$_{100-x}$Cl-TXANT$_x$		I-TXANT$_{100-x}$Br-TXANT$_x$		F-TXANT$_{100-x}$Cl-TXANT$_x$		F-TXANT$_{100-x}$Br-TXANT$_x$		I-TXANT$_{100-x}$F-TXANT$_x$		Br-TXANT$_{100-x}$Cl-TXANT$_x$	
	Obtained crystalline phase and volume of acetonitrile / mL											
0:100		12		12		12		12		12		12
1:99	-	-	-	-	-	-	-	-	β	-	-	-
2:98	-	-	-	-	-	-	-	-	α+β	12	α+β	12
5:95	β	15	β	15	β	15	β	15	α+β	12	α+β	12
10:90	β	15	β	15	α+β	15	α+β	15	α+β	12	α+β	12
15:85	β	15	α+β	15	α+β	15	α+β	15	-	-	-	-
20:80	β	15	α+β	15	α+β	15	α+β	15	α+β	12	α+β	12
25:75	β	15	α+β	15	α+β	15	α+β	15	-	-	-	-
30:70	β	15	α+β	15	α+β	15	α+β	15	α+β	12	α+β	12
35:65	-	-	α+β	15	α+β	15	α+β	15	-	-	-	-
40:60	β	15	α+β	15	α+β	15	α+β	15	α+β	12	α+β	12
45:55	-	-	α+β	15	α+β	15	α+β	15	-	-	-	-
47.5:52.5	-	-	-	-	-	-	α+β	15	-	-	-	-
50:50	β	15	α+β	15	α+β	15	α+β	15	α+β	12	α+β	15
55:45	-	-	α	15	α	15	α+β	15	-	-	-	-
60:40	β	15	α	15	α	15	α+β	15	α+β	12	α+β	15
62.5:37.2	α+β	15	-	-	-	-	-	-	-	-	-	-
65:35	α+β	15	α	15	α	15	α+β	15	-	-	-	-
70:30	α+β	15	α	15	α	15	α+β	15	α+β	12	α+β	18
75:25	α+β	15	α	15	α	15	α+β	15	-	-	-	-
80:20	α+β	15	α	15	α	15	α+β	15	α+β	12	α+β	18
82.5:17.5	α+β	15	-	-	-	-	-	-	-	-	-	-
85:15	α+β	15	α	15	α	15	α+β	15	-	-	-	-
87.5:12.5	α	15	-	-	-	-	-	-	-	-	-	-
90:10	α	15	α	15	α	15	α+β	15	α+β	12	α+β	18
92.5:7.5	α	15	-	-	-	-	-	-	-	-	-	-
95:5	α	15	α	15	α	15	α	15	α+β	12	α+β	18
97.2:2.5	α	15	-	-	-	-	-	-	-	-	-	-
98:2	-	-	-	-	-	-	-	-	α	12	α+β	18
100:0		12		12		12		12		12		12

- Pure phase / Solid solution (α or β) *- Eutectic (α+β)* *- Not viewed (-)*

Solid solution formation can be confirmed by means of melting phase diagram. It precisely demonstrate that the thioxanthone halogenated derivatives form solid solutions between each other, both - in limited and unlimited solubility of components. For the construction of the solidus and liquidus lines the peak onset and offset temperatures were used, obtained using differential scanning calorimetry (DSC) analysis.



Graphically depicting the **melting** of the crystallization products depending on the weight fraction of the thioxanthone halogenated derivative, as well as including the **maximum** temperature, a two-component phase diagram is formed (**eutectic**, **soliduss** – $T_{melt.}$, **liquiduss** – $T_{max.}$).

Conclusions

- The binary systems of thioxanthone halogenated derivatives have been explored showing that four different solid solutions (formed based on parent structures respectively) can be formed;
- The demonstrated approach shows that as far as single-phase materials are considered, the properties can be tuned in a continuous fashion, which is not possible with chemically modifying the luminescent organic molecules or using other crystal engineering approaches.

References

1. Lusi M. *Crystal Growth & Design*, **2018**, *18(6)*, 3704-3712.
2. Saršūns K, Bērziņš A, Reķis T. *Crystal Growth & Design*, **2020**, *20(12)*, 7997-8004.
3. Wen Y, Liu H, Zhang S, Gao Y, Yan Y, Yang B. *J. Mater. Chem. C*, **2019**, *7*, 12502-12508.
4. Saršūns K, Kemere M, Karziņins A, Kļimenkovs I, Bērziņš A, Šarakovskis A, Rekis T. Submitted to *Journal of Materials Chemistry C*, **2022**.
5. Kenry Chen C, Liu B. *Nature Communications*, **2019**, *10(1)*, 2111.

Acknowledgments

This work has been supported by the European Social Fund, project "Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model", identification No. 8.2.2.0/20/I/006 and University of Latvia foundation through "Mikrotīkls" doctoral scholarship in the field of natural and medical sciences.

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Presented at: 30th Annual Meeting of the German Crystallographic Society, Online, March 14-17, 2022