FORMATION OF SOLID SOLUTIONS IN THIOXANTHONE DERIVATIVE SYSTEMS

EXHIBITING LUMINESCENCE PROPERTIES

LATVIJAS UNIVERSITĀTE

UNIVERSITY OF LATVIA Laboratory of Molecular Crystals

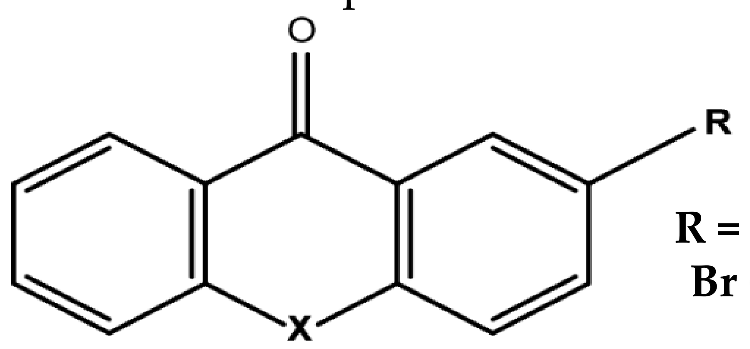
Kristaps Saršūns[a,*], Kaspars Leduskrasts[b], Agris Bērziņš[a], Toms Rekis[a]

[a] Faculty of Chemistry, University of Latvia, Riga, Latvia, kristaps.sarsuns@lu.lv

[b] Latvian Institute of Organic Synthesis, Riga, Latvia

Introduction

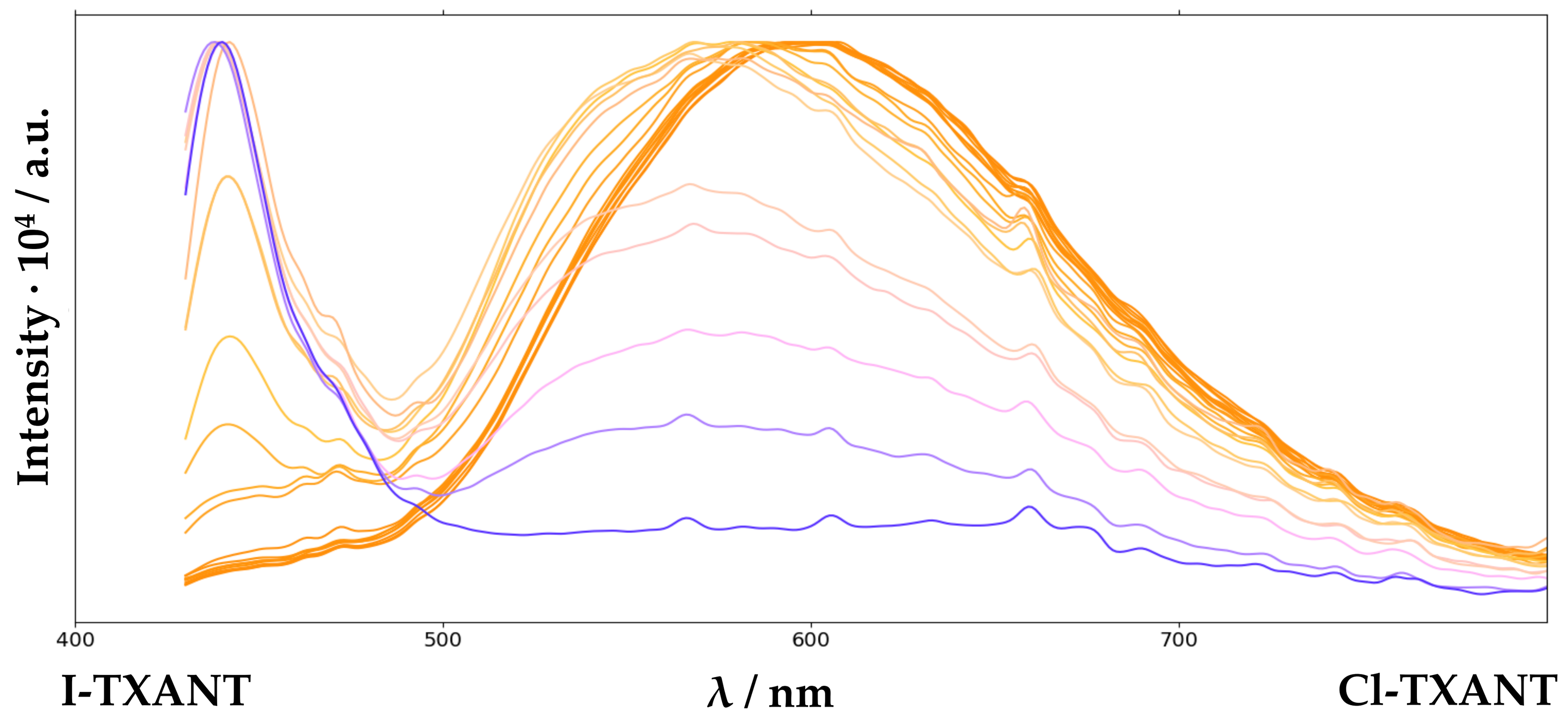
Several thioxanthone **(TXANT)** derivatives have been selected based on reported room-temperature solid-state luminescence phenomena. In this study we explore solid solution formation in thioxanthone derivative systems. Their composition limits are summarized in respective two component phase diagrams. Photoluminescence spectra 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.



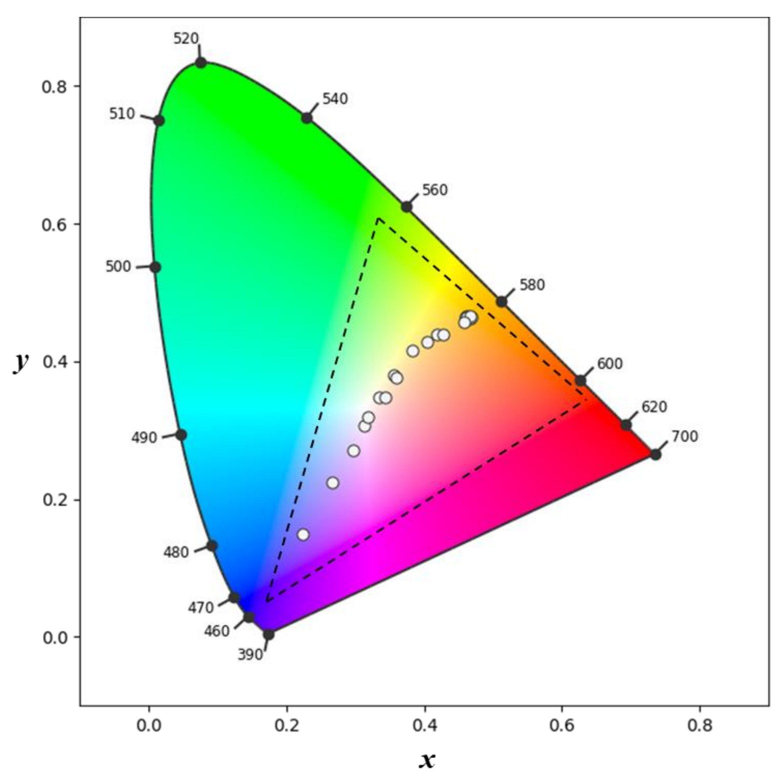
R = Cl (TXANT-Cl), I (TXANT-I), Br (TXANT-Br) or F (TXANT-F)

Molecular structure of thioxanthone derivatives

Crystallization products with modulated properties



Photoluminescence spectra 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. The maximum emission of pure substances is ~ 440nm (**Blue**) I-TXANT and ~ 600nm (**Orange**) Cl-TXANT, respectively[a].



Instead of representing each spectrum in luminescence color, its emission colors are often represented in CIE chromaticity diagrams.

[b] – The color transition across the entire CIE chromaticity diagram occurs from a ratio of 100:0 to about 85:15, which is a relatively small concentration range, so it can be concluded that even the replacement of small amounts of I-thioxanthone molecules in the crystal structure with Cl-thioxanthone molecules causes significant changes in the spectral properties of the material.

CIE chromaticity diagram for the characterization of the luminescence color of I-thioxanthone[b].

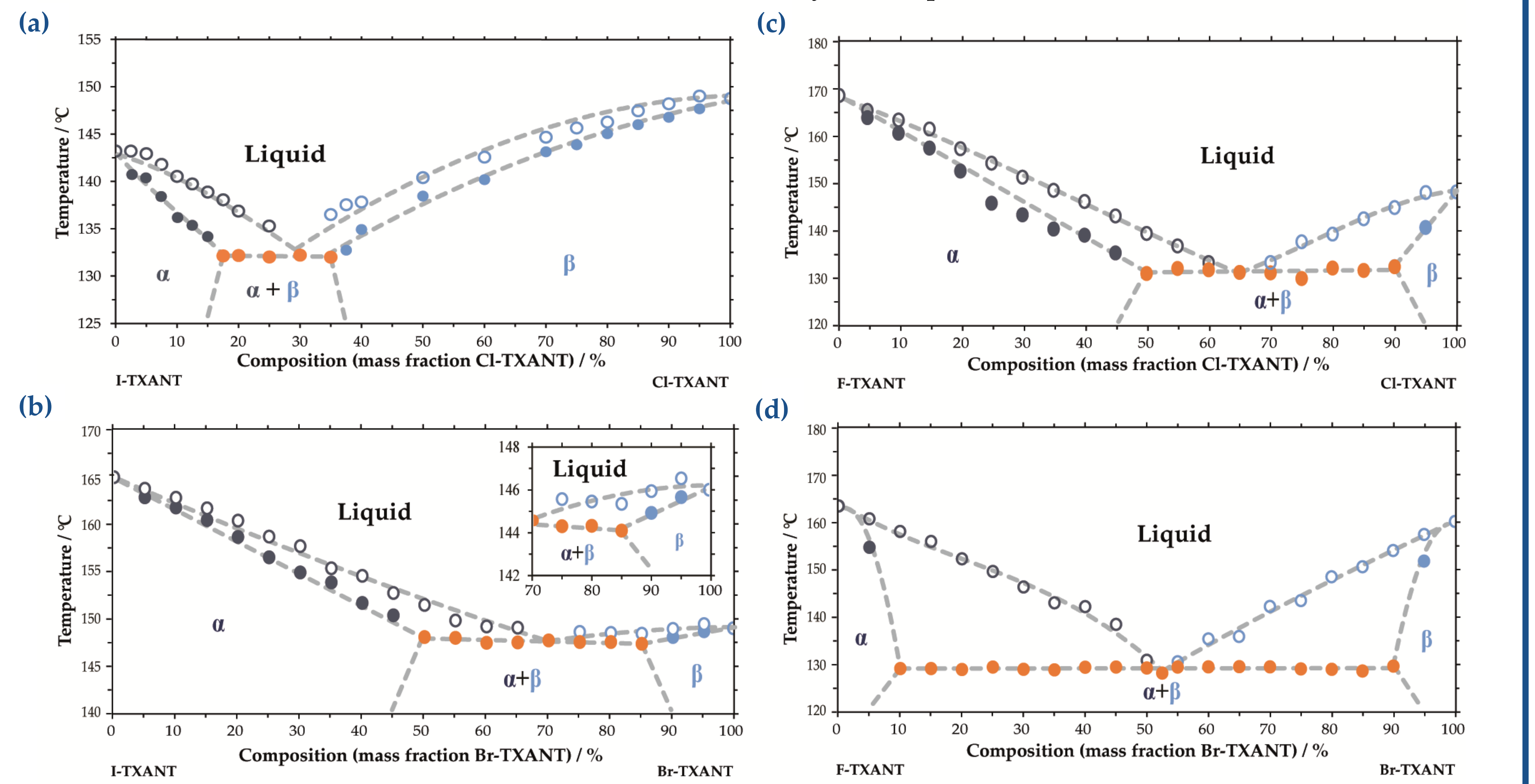
Abstract

Solid solutions **(SS)** are single multicomponent phases for which the constituent component ratio can vary in continuum. Along with the composition, also properties of solid solutions are modulated. The changes in composition are often accompanied by a continuous change in some physical and/or chemical properties (e.g., solubility, melting point), and more complex properties such as solid-state luminescence and phosphorescence properties, that are composition-dependent.

[a] – By changing the composition of organic components in a two-component system (I-$TXANT_{100-x}$Cl-$TXANT_x$), new crystalline materials with modulated luminescence properties can be obtained, the luminescence color changes even with a 2,5 - 5% change in the composition of the components from **Blue** to **Yellow**/**Orange** at 85%).

Identification of solid solutions

Solid solution formation can be confirmed by means of melting phase diagram, in case **(a) I-$XANT_{100-x}$Cl-$TXANT_x$, (b) I-$TXANT_{100-x}$Br-$TXANT_x$, (c) F-$TXANT_{100-x}$Cl-$TXANT_x$** and **(d) F-$TXANT_{100-x}$Br-$TXANT_x$**. It precisely demonstrate that the thioxanthone derivatives form solid solutions between each other, in this case solid solutions forms in limited solubility of components.



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

Crystallization results

The preparation of the solid solutions of thioxanthone derivative systems was based on crystallization from solvent (in this case from acetonitrile), in different proportions **($\alpha_{100-x}\beta_x$ / %)**, from ***100-x*** to ***x***, where **$0 \le x \le 100$**.

Experimentally obtained crystalline phases from thioxanthone derivative mixture systems

System	Substance ratio / %																				
	100:0	95:5	90:10	85:15	80:20	75:25	70:30	65:35	60:40	55:45	50:50	45:55	40:60	35:65	30:70	25:75	20:80	15:85	10:90	5:95	0:100
I-$XANT_{100-x}$ Cl-$TXANT_x$		α	α	α + β	α + β	α + β	α + β	α + β	β	-	β	-	β	-	β	β	β	β	β	β	
I-$XANT_{100-x}$ Br-$TXANT_x$		α	α	α	α	α	α	α	α	α	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	β	β	
F-$XANT_{100-x}$ Cl-$TXANT_x$		α	α	α	α	α	α	α	α	α	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	β	
F-$XANT_{100-x}$ Br-$TXANT_x$		α	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	β	

- **Solid solution (α or β)** - Phase mixture - Pure single component phase - Not viewed

Conclusions

- The binary systems of thioxanthone derivatives have been explored showing that eight different solid solutions (formed based on parent structures of thioxanthone derivatives, respectively) can be formed.
- 2-iodothioxanthone : 2-chlorothioxanthone system the modulation of the luminescence spectra is large and the luminescence colour changes significantly even for little variation in composition. This indicates that technologically relevant properties can be modulated via solid solution formation, and it can thus be done in a continuous fashion.

Acknowledgments

FLPP FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

LATVIJAS UNIVERSITĀTES FONDS

This work has been supported by the Latvian Council of Science, project "Crystal engineering of pharmaceutical multicomponent phases for more efficient crystalline phase design", project No. lzp-2018/1-0312 and University of Latvia foundation through "Mikrotīkls" doctoral scholarship in the field of natural and medical sciences.

Presented at: 11[th] convention on Crystal Forms, Online, September 10-11, 2021