MODULATION OF LUMINESCENCE SPECTRA

VIA SOLID SOLUTION FORMATION OF XANTHONE DERIVATIVES

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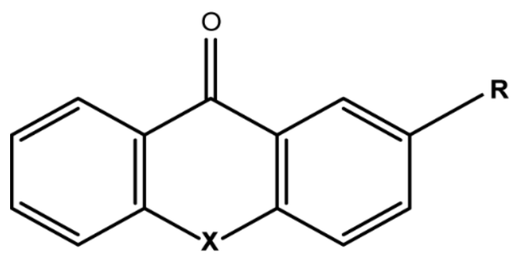
Abstract

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. Among simple properties, like density, solubility, and melting temperature, the phases could also exhibit diverse optoelectronic effects that are composition-dependent

Introduction

Various xanthone **(XANT)** derivatives have been selected based on reported room-temperature solid-state luminescence phenomena. In this study we explore solid solution formation in xanthone derivative systems, namely xanthone : thioxanthone and 2-iodothioxanthone : 2-chlorothioxanthone.



X = O (XANT) or S (TXANT); R = H (XANT and TXANT), Cl (TXANT-Cl) or I (TXANT-I)

Molecular structure of xanthone derivatives

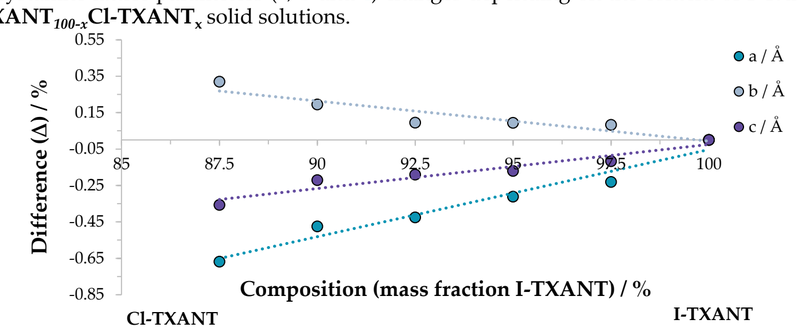
The most thermodynamically stable forms crystallizes in the monoclinic ($P2_1/c$, $P2_1$), triclinic ($P\text{-}1$) and orthorhombic ($P2_12_12_1$) space group.

Aim

- Using both experimental studies and quantum chemistry calculations, to identify the main factors that contribute to the formation of solid solutions between structurally similar organic molecules, as well as to obtain crystallization products with modulated physico-chemical properties.

Structural aspects of solid solutions

Crystalline lattice parameters (a, b and c) changes depending on the content of **I-TXANT in I-TXANT$_{100-x}$Cl-TXANT$_x$** solid solutions.



In the case of non-solvated solid solutions, it can be observed that the crystal lattice parameters, depending on the content of xanthone derivative, form a monotonous function, this means that the ***Vegard's Law*** is fulfilled.

The volume of cells were estimated as known the fact that when replacing a "native" molecule in a crystalline structure, attributable to a substituted structure (as it is in the case of a solid solution), the cell must expand, resulting in a volume change.

Volumes of xanthone derivative crystalline structures[a]

Molecule	Replaced with	V / Å³	ΔV / Å³	
		Original	Substituted	Isotructural
I-TXANT	-Cl	1080,0	-8,2 ▼	-55,1 ▼
Cl-TXANT	-I	495,5	**19,9** ▲	**42,8** ▲

[a] – **Crystal structures were used after full geometry optimization in *Quantum ESPRESSO v6.3***

▲ - Volume increases ▼ - Volume decreases

Quantum chemical calculations

Intermolecular interaction energies of xanthone derivatives[b]

System	Molecule	Replaced with	$E_{Inter.}$ / kJ·mol⁻¹	ΔE / kJ·mol⁻¹		Corellation with experimental data
			Original	Substituted	Isotructural	
I-TXANT$_{100-x}$ Cl-TXANT$_x$	I-TXANT	-Cl	-183,1	**-11,2**	6,0	More preferably -I replaced by -Cl
	Cl-TXANT	-I	-194,6	28,3	22,4	

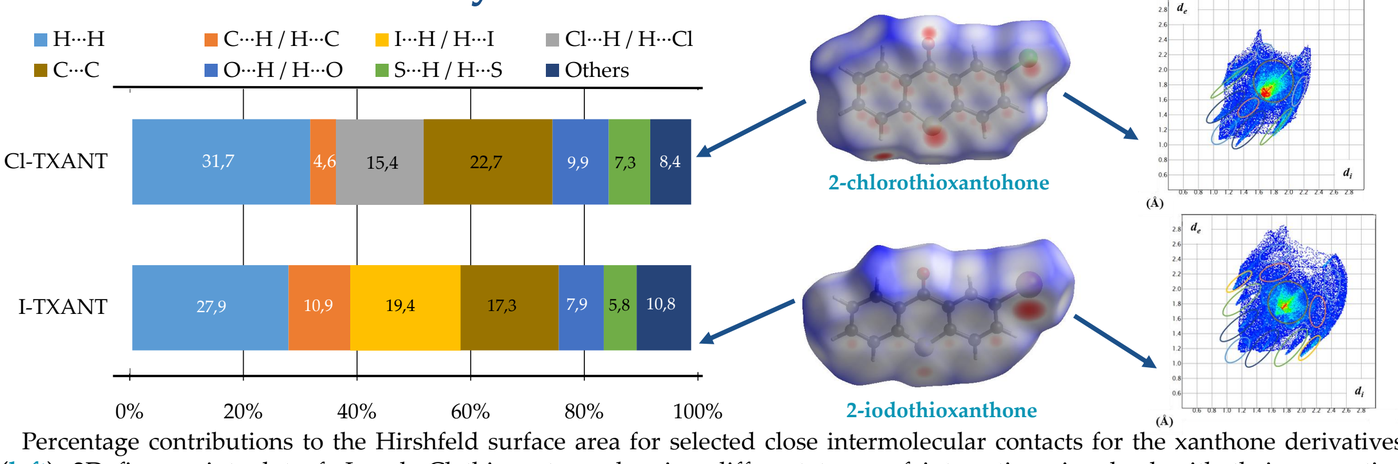
[b] – **The *CrystalExplorer v17.5* was used for calculation of intermolecular interaction energy between molecule pairs at the B3LYP-D2/3-21G level**

Lattice energies of various structures of xanthone derivatives[c]

System	Molecule	Replaced with	$E_{Lattice}$ / kJ·mol⁻¹	ΔE / kJ·mol⁻¹		Corellation with experimental data
			Original	Substituted	Isotructural	
I-TXANT$_{100-x}$ Cl-TXANT$_x$	I-TXANT	-Cl	-145,7	3,2	7,6	More preferably -Cl replaced by -I
	Cl-TXANT	-I	-145,6	**-1,7**	**-5,5**	

[c] – **Calculation of lattice energy was performed in *Quantum ESPRESSO v6.3* using *SCF* and *VC-relax* solution**

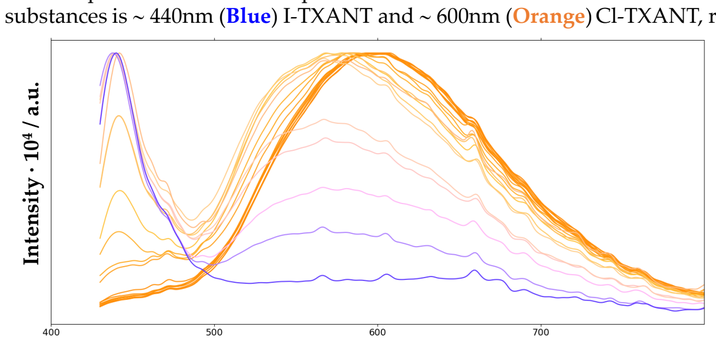
Hirshfeld surface analyses



Percentage contributions to the Hirshfeld surface area for selected close intermolecular contacts for the xanthone derivatives (**left**). 2D fingerprint plot of -I and -Cl thioxantone showing different types of interactions involved with their respective contributions (**right**).

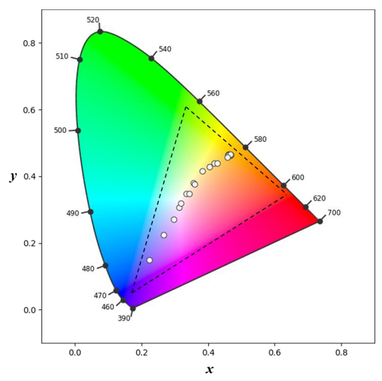
Crystallization products with modulated physico-chemical properties

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.



Emission spectra of crystallization products, schematically showing how the emission peaks change (color of luminescent radiation, **upper**)[d].

[d] – 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%)



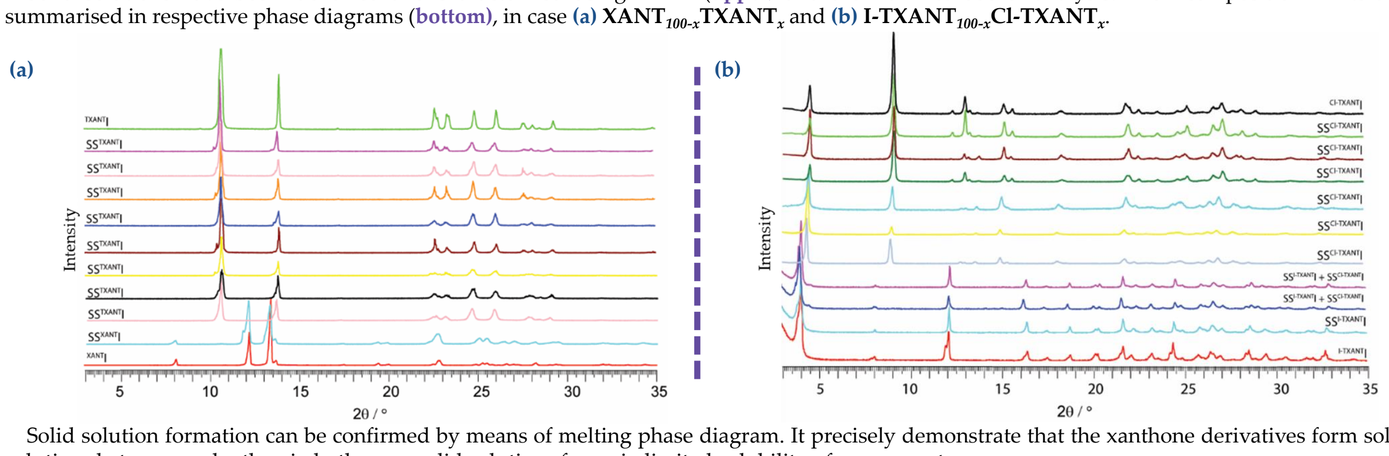
Instead of representing each spectrum in luminescence color, its emission colors are often represented in CIE chromaticity diagrams.

[e] – 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.

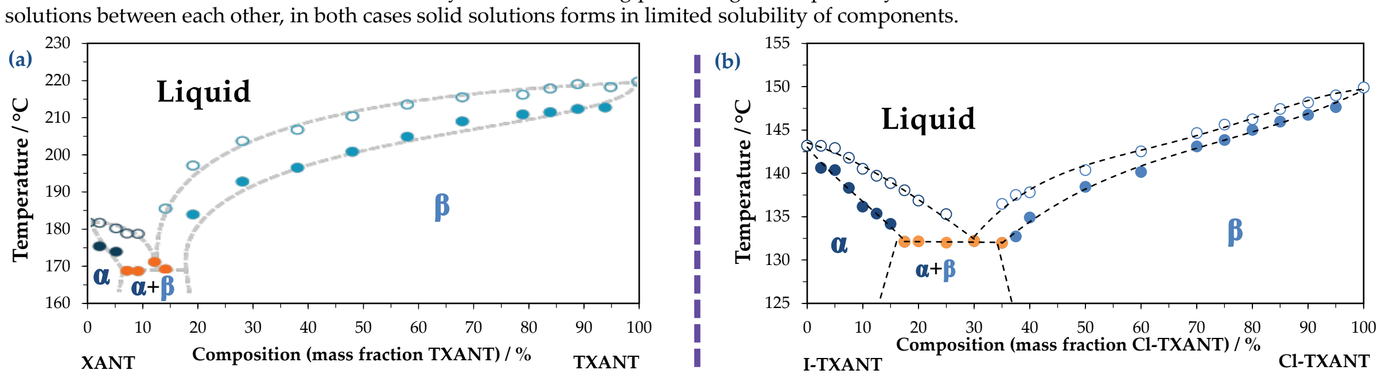
CIE chromaticity diagram for the characterization of the luminescence color of I-thioxanthone (**left**)[e].

Identification of solid solutions

Solid solutions have been identified and characterized using PXRD (**upper**) and thermal methods of analysis. Their composition limits are summarised in respective phase diagrams (**bottom**), in case **(a) XANT$_{100-x}$TXANT$_x$** and **(b) I-TXANT$_{100-x}$Cl-TXANT$_x$**.



Solid solution formation can be confirmed by means of melting phase diagram. It precisely demonstrate that the xanthone derivatives form solid solutions between each other, in both cases 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 xanthone 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 xanthone 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 xanthone derivative mixture systems

System	Substance ratio / %																
	100:0	95:5	90:10	85:15	80:20	75:25	70:30	65:35	60:40	50:50	40:60	30:70	25:75	20:80	15:85	10:90	5:95	0:100
XANT$_{100-x}$ TXANT$_x$		α	α	α + β	β	-	β	-	β	β	β	β	-	β	β	β	β	
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	

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

Conclusions

- The binary systems of xanthone derivatives (XANT : TXANT and TXANT-I : TXANT-Cl) have been explored showing that four different solid solutions (formed based on parent structures of xanthone derivatives, respectively) can be formed.
- Quantum chemical calculations show that xanthone derivative molecules can exist in both substituted and isostructural structures, thus the calculations confirm that the existence of model structures is energetically possible, and the results of the calculations correlate with the experimentally obtained results.
- 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.

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