

# Quinolinium-based organic electro-optic crystals: Crystal characteristics in solvent mixtures and optical properties in the terahertz range

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## HIGHLIGHTS

- Crystal characteristics of highly efficient electro-optic organic crystals based on 4-hydroxy-3-methoxystyryl quinolinium.
- Strong influence of solvent characteristics on solubility based on contribution of  $\pi$ - $\pi$  interactions with solvent molecules.
- Crystal growth and crystal characteristics including optical properties in THz region of efficient electro-optic crystals.

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## ABSTRACT

We investigate crystal characteristics of ionic organic  $\pi$ -conjugated crystals based on 4-hydroxy-3-methoxystyryl quinolinium (HMQ), which are recently developed acentric crystals showing a large nonlinear optical response and a high THz generation efficiency. Among a few of HMQ derivatives, HMQ-T crystal consisting of the HMQ cation and the 4-methylbenzenesulfonate anion, is chosen for the investigation of solubility, morphology and crystal growth characteristics including optical properties in various single solvents and solvent mixtures. Compared to the solvent mixture of non-aromatic methanol and acetonitrile, HMQ-T crystals in a solvent mixture containing an aromatic solvent (methanol/toluene mixture) exhibits a similar solubility variation with the solvent composition ratio, but based on distinguishable intermolecular interactions with solvent molecules. In addition, solvent mixtures containing an aromatic solvent show a significantly different equilibrium between benzenoid and quinoid forms of the HMQ cation. In contrast to the strong influence of solvent characteristics on solubility behavior, the investigated solvent systems only slightly influence the crystal morphology. Large HMQ-T single crystals with size up to  $37 \times 6 \times 2 \text{ mm}^3$  are grown by slow cooling method. We also determine the refractive index and absorption of as-grown single HMQ-T crystals in the broad THz frequency range of 0.3–10 THz.

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## 1. Introduction

Acentric crystals having a noncentrosymmetric arrangement of molecules are potential materials for nonlinear photonic applications such as THz generation and detection [1–9], large-scale

integrated optics [10–14] and second harmonic generation (SHG) imaging [15–17]. For obtaining an acentric ordering of molecules in the crystalline state, many acentric core structures have been developed. For example, the widely-investigated ionic core structure DAS (4-(4-(dimethylamino)styryl)-1-methylpyridinium) is used in the highly nonlinear optical DAST crystal (4-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methylbenzenesulfonate) [18], DSTMS (4-(4-(dimethylamino)styryl)-1-methylpyridinium 2,4,6-trimethylbenzenesulfonate) [19], and their analogous derivatives [20–26]. Another successful core structure is the non-

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ionic core structure SCM (2-(3-styrylcyclohex-2-enylidene)malononitrile), which is used in OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile) [27], OH2 (2-(3-(4-hydroxystyryl)-5-methylcyclohex-2-enylidene)malononitrile) [28] and their analogous derivatives [29–33]. Such analogous crystals based on an identical acentric core structure usually possess similar crystal characteristics, including the solubility, morphology and crystal growth characteristics, which is due to very similar main supramolecular interactions [27–38]. For example, the main supramolecular interactions of ionic DAS analogous crystals are strong Coulombic interactions between the stilbazolium cation and benzenesulfonate anions,  $\pi$ - $\pi$  stacking interactions between cations and  $-S-O^-\cdots H-C=$  interactions between the sulfonate group on anions and hydrogen atoms on cations [34,35]. In non-ionic phenolic SCM analogous crystals, the main supramolecular interactions are strong hydrogen bonds between phenolic  $-OH$  groups and  $-CN$  groups [27–30]. Therefore, understanding crystal characteristics of a core structure is very important and can give useful information for developing new nonlinear optical crystals.

Recently, a new acentric core structure, 4-hydroxy-3-methoxystyryl quinolinium (HMQ) has been reported for nonlinear photonic applications [39–44]. The HMQ analogous crystals consisting of the HMQ cation and various benzenesulfonate counter anions exhibit a highly efficient nonlinear optical and an electro-optic response comparable (or higher) to benchmark DAST and OH1 crystals [39–42]. In addition, HMQ crystals show excellent THz generation characteristics by optical rectification [39,40,45,46]. In contrast to widely investigated crystal characteristics of acentric-core-structure DAS [25,35,47–54] and SCM derivatives [55–61], the crystal characteristics of HMQ-core-structure materials have not been investigated thoroughly yet [62].

In this work, a very promising example of HMQ derivatives, HMQ-T (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate, see Fig. 1) crystal [39] is chosen for the investigation of the solubility behavior and crystal-growth characteristics in various single solvents and solvent mixtures. Compared to a solvent mixture of polar non-aromatic solvents (methanol/acetonitrile (MeOH/AcCN)), a solvent mixture of a polar non-aromatic and a non-polar aromatic solvents (methanol/toluene) shows distinguishable intermolecular interactions with HMQ-T and a different equilibrium between benzenoid and quinoid forms varying with the solvent composition ratio. Crystal growth characteristics of HMQ-T are examined in various solvent systems. While solvent characteristics strongly influence the solubility behavior, they only slightly influence the crystal morphology, which is different as observed e.g. in non-ionic phenolic SCM analogous crystals [63]. This is attributed to stronger Coulombic interactions and  $\pi$ - $\pi$  stacking interactions of HMQ cations compared to the interactions between solvent and solute molecules. Large HMQ-T crystals with a size of up to  $37 \times 6 \times 2 \text{ mm}^3$  are successfully grown by slow cooling method. We also characterize the optical properties of as-grown HMQ-T crystals in both optical

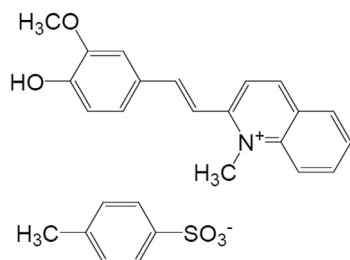


Fig. 1. Chemical structure of HMQ-T crystal.

and THz frequency regions.

## 2. Experimental

### 2.1. Solubility

The solubility in mixed solvent systems, excepting methanol/DMSO (dimethylsulfoxide), is determined by measuring the remaining HMQ-T powder after completely evaporating the solvent of a saturated solution at given temperature. In the solvent mixture of methanol/DMSO, due to difficult evaporation of DMSO having a high boiling point, the solubility is determined by a calibration with a standard solution (methanol/DMSO,  $1.14 \times 10^{-5} \text{ M}$ ) using the UV–vis absorption spectroscopy.

#### 2.1.1. Solubility as a function of the solvent composition ratio

The saturated solutions of HMQ-T are prepared by keeping the solvent mixtures with excess solute at an oven for 7 days at a temperature of  $40^\circ\text{C}$  and subsequently filtering out the solution. The solubility is determined by evaporation method as described above. The results are shown in Fig. 2 and listed in Table 1.

#### 2.1.2. Solubility temperature dependence

The solubility in the mixed solvent systems, methanol/acetonitrile 1:0.78 mol/mol (mole fraction  $x_{\text{AcCN}} = 0.44$ ) and methanol/toluene 1:1 mol/mol ( $x_{\text{toluene}} = 0.5$ ) is measured in the temperature range of  $25$ – $50^\circ\text{C}$ . The excess amount of HMQ-T crystalline powder is stirred in the solvent mixture for 2 days. The solubility is determined by evaporation method as described above.

### 2.2. Crystal growth by slow cooling method

Bulk HMQ-T crystals are grown by slow cooling method in methanol, methanol/acetonitrile and methanol/toluene mixtures. In order to prevent uncontrolled nucleation by filtration of saturated HMQ-T solution, the solutions filtered were kept in an oven at a higher (or similar) temperature than saturated temperature during few hours or 1 day before starting the growth experiment.

#### 2.2.1. Methanol

A solution of HMQ-T saturated in methanol (1000 mL) at  $40^\circ\text{C}$  is filtered and kept in an oven at  $47^\circ\text{C}$ . After 1 day, the solution is cooled down to  $30^\circ\text{C}$  within 30 min and nucleation does not

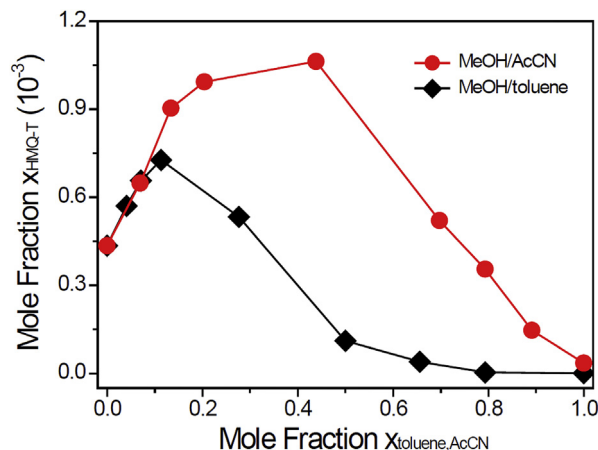


Fig. 2. Solubility of HMQ-T crystals in mixed solvent systems of methanol/acetonitrile and methanol/toluene as a function of solvent composition ratio at a temperature of  $40^\circ\text{C}$ .

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