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Organic styryl quinolinium crystal with aromatic anion bearing electron-rich vinyl group

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ABSTRACT

A new organic π-conjugated quinolinium derivative was designed and synthesized in order to investigate the influence of the anion structure on characteristics of the crystal. The quinolinium derivative consists of a 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium (HMQ) cation and a 4-vinylbenzenesulfonate (VBS) counter anion, which contains an electron-rich vinyl group. Single HMQ-VBS crystals, grown by a solution growth method in methanol, exhibited a monoclinic $P2_1/c$ space group symmetry. Compared to the previously reported HMQ analogous crystal (HMQ-T), which bears a 4-methylbenzenesulfonate counter anion, the HMQ-VBS crystals generally have similar features of molecular alignment, but show different characteristics of hydrogen bonds related to the anion–anion and anion–cation interactions, as well as π–π stacking associated with the cation–cation interactions. Consequently, HMQ-VBS exhibits significantly different physical properties, including linear absorption and fluorescence in the crystalline state, even though these properties are identical to HMQ-T's in the solution state.

1. Introduction

Organic crystals based on a push–pull π-conjugated bridge with different electron donor and acceptor groups are very attractive for various nonlinear optical, fluorescent, and optoelectronic applications [1–11]. Organic ionic crystals with heteroaromatic electron acceptors such as pyridinium, imidazolium, and quinolinium cations, which possess a strong electron-withdrawing characteristic [12–14], exhibit large second- and third-order nonlinear optical responses [15–18] and various fluorescent activities [19]. The molecular ordering in the crystalline state strongly influences their physical properties, including linear and nonlinear optical properties [1,20–22]. For example, noncentrosymmetric molecular ordering in the crystalline state is required for second-order nonlinear optical properties, while both noncentrosymmetric and centrosymmetric molecular ordering lead to third-order nonlinear optical properties [1]. In the case of fluorescent properties, the aggregation types (e.g., *J*- and *H*- aggregations) of molecules are very important [21,22].

In organic π-conjugated crystals based on heteroaromatic cationic electron acceptors, various counter anions can be introduced [15,17,23–36]. The chemical structure of the counter anion significantly influences the final crystal characteristics as well as their physical properties, although the main functionality stems from the same cation molecule [15,17,23–36]. Therefore, understanding the relation between the molecular structure of counter anion and the resulting crystal characteristics is very important in order to obtain the desired physical properties for specific applications. For organic salt crystals that are based on heteroaromatic cations, the influence of the counter anions on crystal characteristics is still not fully understood.

In this study, we designed and synthesized a new organic π-conjugated ionic derivative based on a heteroaromatic quinolinium cationic electron acceptor in order to investigate the influence of the counter anions on crystal characteristics. The quinolinium derivative consists of the 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium (HMQ) cation and the 4-vinylbenzenesulfonate (VBS) counter anion, which contains the electron-rich vinyl group (see Fig. 1). The crystal characteristics and physical properties of the HMQ-VBS crystals were investigated. For comparison, the previously reported analogous HMQ crystal with 4-methylbenzenesulfonate (HMQ-T) [17] were also characterized. HMQ-VBS and HMQ-T crystals have roughly similar features in terms of their molecular alignment, resulting in identical physical properties in the solution state but are significantly different in the crystalline state.

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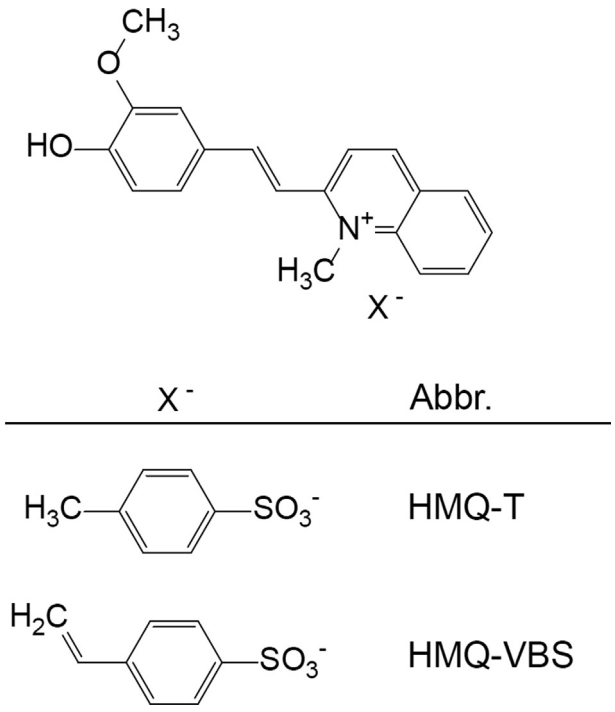

Fig. 1. Chemical structure of the investigated HMQ derivatives with different counter anions.

2. Experimental section

2.1. Synthesis

HMQ-VBS was synthesized by a methathesization reaction between 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium iodide and sodium 4-vinylbenzenesulfonate in methanol at room temperature. 2-(4-Hydroxy-3-methoxystyryl)-1-methylquinolinium iodide (0.50 g, 1.2 mmol) dissolved in methanol (400 mL) was mixed with sodium 4-vinylbenzenesulfonate (0.74 g, 3.6 mmol) dissolved in methanol (50 mL) at room temperature. After evaporating the solvent (100 mL), the mixed solution was kept at −24 °C to give a red crystalline powder. Yield: 75%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.96 (d, 1H, J = 8.8 Hz, C_5H_2N), 8.54 (d, 1H, J = 9.6 Hz, C_6H_4), 8.51 (d, 1H, J = 9.6 Hz, C_6H_4), 8.31 (d, 1H, J = 8.0 Hz, C_5H_2N), 8.21 (d, 1H, J = 15.6 Hz, CH), 8.14 (t, 1H, J = 8.2 Hz, C_6H_4), 7.91 (t, 1H, J = 8.8 Hz, C_6H_4), 7.87 (d, 2H, J = 7.6 Hz, C_6H_4), 7.71 (d, 1H, J = 16.0 Hz, CH), 7.55 (d, 2H, J = 7.2 Hz, $C_6H_4SO_3^-$), 7.41 (d, 2H, J = 7.6 Hz, $C_6H_4SO_3^-$), 6.92 (d, 2H, J = 7.2 Hz, $C_6H_4SO_3^-$), 6.72 (m, 1H, C_2H_3), 5.84 (d, 1H, J = 17.6 Hz, C_2H_3), 5.26 (d, 2H, J = 10.8 Hz, C_2H_3), 4.51 (s, 3H, J = NCH_3). Elemental analysis for $C_{27}H_{25}NO_5S$: Calcd. C 68.19, H 5.30, N 2.95, S 6.74; Found: C 68.30, H 5.29, N 2.96, S 6.79.

2.2. Crystal structure analysis

For the X-ray single crystal structure analysis, single HMQ-VBS crystals were grown by a slow evaporation method in methanol. $C_{27}H_{25}NO_5S$, M_r = 475.54 monoclinic, space group $P2_1/c$, a = 11.0225(14) Å, b = 14.2990(16) Å, c = 15.7887(18) Å, β = 111.743(3)°, V = 2311.4 (5) Å^3, Z = 4, T = 290(1) K, μ(MoKα) = 0.18 mm^{-1}. The details of the crystallographic data are listed in Table 1. Parameters for all hydrogen atoms were refined isotropically. The crystal structure was solved and refined against F^2 using SHELX97 [37], 407 variables, wR_2 = 0.161, R_1 = 0.052 ($Fo^2 > 2\sigma(Fo^2)$), GOF = 1.1. CCDC 1048478.

3. Results and discussion

3.1. Design and synthesis

Fig. 1 shows the chemical structure of the investigated quinolinium derivatives with different counter anions. HMQ (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium) cation forms strong Coulombic interactions with benzenesulfonate anions. In the previously reported HMQ-T (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate) crystal [17], the counter anion is 4-methylbenzenesulfonate. In HMQ-T crystals, the methyl group on 4-methylbenzenesulfonate plays a significant role in the formation of the anion layer in the crystalline state, as the hydrogen atom of the methyl group and the oxygen atom of the sulfonate group forms the second strongest hydrogen bond (−C−H···$^-$OS−) in the anion layer [17,32]. Here, instead of having an aliphatic methyl group on the benzenesulfonate counter anion, a relatively large, electron-rich π-conjugated vinyl group was introduced to obtain HMQ-VBS, synthesized by a methathesization reaction between 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium iodide and sodium 4-vinylbenzenesulfonate. Compared to the hydrogen atoms of the methyl group, the hydrogen atoms belonging to the π-conjugated vinyl group exhibit a more positive partial charge [38,39], which leads to stronger hydrogen bonds.

3.2. Supramolecular interactions

In order to perform a single crystal X-ray structural analysis, HMQ-VBS single crystals were grown by a solution growth method in methanol. HMQ-VBS crystals grown by the rapid cooling and slow evaporating methods exhibited practically identical powder X-ray diffraction patterns. Fig. 2 shows an image of HMQ-VBS single crystals with an elongated hexagonal plate-like shape, grown by the slow evaporation method. For single crystal X-ray structural analysis, HMQ-VBS single crystal grown from same growth batch in Fig. 2 was used. Single HMQ-VBS crystals exhibit the monoclinic $P2_1/c$ space group symmetry (details in the Experimental section

Table 1
Summary of crystallographic data for HMQ-VBS.

	HMQ-VBS
Empirical formula	$C_{27}H_{25}NO_5S$
Formula weight	475.54
Temperature/K	290
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	11.0225(14)
b (Å)	14.2990(16)
c (Å)	15.7887(18)
α (deg.)	90
β (deg.)	111.743(3)
γ (deg.)	90
Volume (Å^3)	2311.4(5)
Z	4
ρ_{calc} (mg/mm^3)	1.367
Absorption coefficient (mm^{-1})	0.18
F(0 0 0)	1000
Crystal size (mm^3)	0.90 × 0.50 × 0.20
θ range for data collection(°)	3.1–27.5
Limiting indices	$-14 \le h \le 14$, $-18 \le k \le 16$, $-20 \le l \le 20$
Reflections collected	22065
Completeness to θ = 27.5	99.8%
Data/restraints/parameters	5299/0/407
Goodness-of-fit on F^2	1.14
Final R index [$I \ge 2\sigma(I)$]	$R[F^2 > 2\sigma(F^2)]$ = 0.052
Final R index [all data]	$wR(F^2)$ = 0.161
Largest diff. peak/hole (e Å^{-3})	0.34/−0.31