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Growth and Characterization of A Novel Organic Stilbazolium Family Single Crystal: 4-(4-Methoxystyryl)-1-Methylpyridinium 4-Chlorobenzenesulfonate

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Abstract

A new organic stilbazolium family single crystal of 4-(4-methoxystyryl)-1-methylpyridinium 4-chlorobenzene sulfonate (MBSC) has been successfully grown from methanol solution by adopting slow solvent evaporation technique. Single crystal X-ray diffraction analysis revealed that the crystal belongs to triclinic system with space group P1. The chemical composition of the title compound was identified by CHN elemental analysis. The characteristic functional groups of the grown crystal were identified by FT-IR spectroscopy. The crystal was found to be transparent in the region between 490 and 700 nm as indicated by the UV-Vis spectral studies. Photoluminescence spectrum of MBSC crystal shows a strong blue emission peak at 485 nm and a green emission at 521 nm.

Keywords: Organic compound; X-ray diffraction; Optical properties; Stilbazolium

1. Introduction

In recent scientific trend, organic nonlinear optical (NLO) materials attracted increasing attention due to remarkable growth of optoelectronic and photonic technologies because of their potential applications in optical communications, high-speed information processing, optical data storage devices, optical bi-stability etc [1]. Organic crystals with extended π-conjugated systems with hydrogen bonding greatly enhance the mobility of the electron density, which leads to high optical nonlinearity and molecular hyperpolarizability. In this context, many research efforts have been made to design and synthesize of new π-conjugated crystal structure for second and third harmonic generation applications [2].

In this article, we have synthesized a novel stilbazolium derivative crystal 4-(4-methoxy styryl)-1-methylpyridinium 4-chlorobenzenesulfonate (MBSC). Single crystals of MBSC were grown by slow evaporation method at room temperature and subjected to structural, spectral, optical and photoluminescence studies.

2. Experimental

2.1. Synthesis and crystal growth

4-(4-Methoxystyryl)-1-methylpyridinium iodide (MBSI) cation was synthesized by the condensation of 1,4-dimethyl pyridinium iodide (2.35 g, 10 mmol), methanol (50 ml) and 4-methoxy benzaldehyde (1.63 g, 10 mmol) in the presence of piperidine (0.2 ml).The mixture was taken in a round-bottom flask of a Dean-Stark apparatus and refluxed at 60 °C for 8 h and then cooled to room temperature. The product was filtered and recrystallized from methanol at least three times.

During the next stage, the metathesization reaction was carried out by the following procedure. MBSI

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(0.706 g, 2 mmol) was dissolved in 60 ml of distilled water and simultaneously sodium p-chlorobenzene sulfonate (0.429 g, 2 mmol) was dissolved in 30 ml of distilled water by heating at 70 °C.These two hot solutions were mixed and further heated for 30 min. Yellow colour precipitate was obtained as a result of exchange reaction between anion and cation. Crystal growth was performed by employing slow solvent evaporation technique. Saturated solution of MBSC in methanol was prepared and sealed with a perforated cap, which was kept for crystallization at room temperature. After a period of 10-15 days of evaporation, MBSC crystals were obtained. Photograph of MBSC crystal is shown in Figure1.

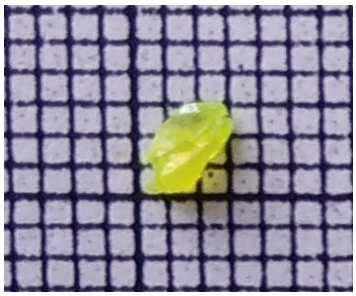

Figure 1. Photograph of MBSC crystal

3. Result and discussions

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was performed by using Bruker Kappa APEX II diffractometer with MoKα radiation of wavelength 0.7170 Å. The calculated lattice parameters show that the MBSC crystal belongs to triclinic system with space group P1. The unit cell parameters are found to be a = 6.72 Å, b = 7.90 Å, c = 9.56 Å, α = 78.68°, β = 81.72°, γ = 84.66° and volume = 492 Å^3.

3.2. CHN analysis

The elemental composition of the MBSC crystal was analyzed using PerkinElmer series-II 2400 CHNS/O elemental analyzer. The percentage of calculated values (Figure2) of $C_{21}H_{20}ClNO_4S$ are C = 60.35%, H = 4.82%, N = 3.35% and the values experimentally found are C =60.14%, H = 4.98% and N = 3.49%. Thus, there is a close agreement between the calculated and experimental values of CHN.

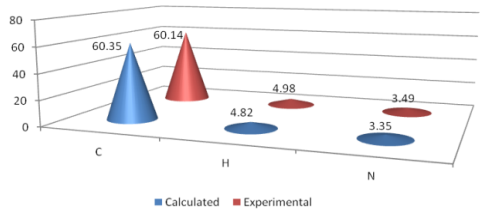

Figure 2. CHN data of MBSC crystal

3.3. FT-IR analysis

In order to identify the functional groups and detect the vibrational modes of molecules, the sample was characterized by Fourier transform infrared (FT-IR) spectroscopy. The measurement was done with KBr pellet technique in the wavelength range of 400–4000 cm^{-1}. The FT-IR spectrum of the MBSC crystal is shown in Figure 3. The peak observed at 3435 cm^{-1} is due to the stretching of hydroxyl group. The aromatic C–H group is confirmed by the presence of peak at 3066 cm^{-1} [3]. The peak corresponds to C=C stretch of the olefinic double bond is seen at 1589 cm^{-1}. The aromatic ring skeletal in-plane stretching vibration can be confirmed by the presence of the peaks at 1518 and 1467 cm^{-1}. Asymmetric and symmetric stretching mode vibrations of sulfonate group give peak around 1344 and 1117 cm^{-1}, respectively [4]. The peaks at 1032 and 838 cm^{-1} are assigned to the phenolic C–O stretch and olefinic C–H bond vibrations. Cis orientation of the substitute at the olefinic double bond produces peak at 637 cm^{-1}. The characteristic frequencies observed between 500 and 700 cm^{-1} are due to the out-of-plane ring bending modes and frequencies between 1100 and 1200 cm^{-1} are assigned to the in-plane ring deformation modes

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are observed [5]. Thus, the presence of various functional groups in the structure has been confirmed. The wavenumbers correspond to different modes of vibration are given in Table 1.

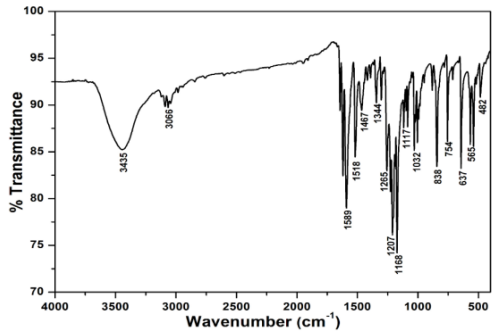

Figure 3. FT-IR spectrum of MBSC crystal

Table 1. FT-IR wavenumber assignments for MBSC

Wavenumber (cm^{-1})	Assignment
3435	O–H stretch
3066	Aromatic C–H stretch
1589	C=C stretch of the olefinic double bond
1518, 1467	Aromatic ring vibrations
1344, 1117	Asymmetric and symmetric stretching vibrations of $–SO_2$
1265	Phenolic C–O stretch
1032	Olefinic C–H bond
838	C–H bending vibration of 1,4 disubstituted aromatic rings
637	Cis orientation of the substitute at the olefinic double bond

3.4. UV-Vis absorption study

UV-Vis absorption spectrum was recorded in the wavelength range of 200-700 nm in solution form using methanol as solvent. The UV-Vis spectrum (Figure4) shows two distinct absorption peaks; the minor peak observed at 220 nm corresponds to the n-π^* transition and the major peak with maximum absorption at around 380 nm represents the π-π^* transition [6].The material shows a wide transparency in the region between 450 and 700 nm. The lower absorption of light in the visible and good transparency window over a near IR wavelength range are highly desired parameters for NLO applications [7].

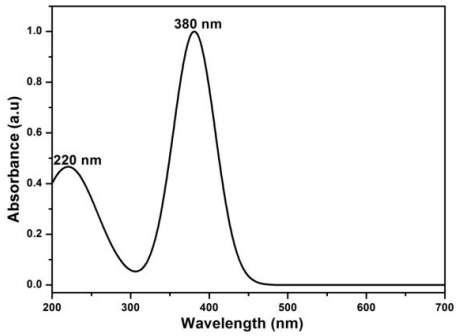

Figure 4. UV-Vis absorption spectrum of MBSC crystal

3.5. Photoluminescence study

Photoluminescence (PL) study for MBSC crystal was performed at room temperature. The sample was excited at the wavelength of 380 nm chosen from UV-Vis spectral studies, and the emission spectrum was recorded in the wavelength range of 450-650 nm (Figure5). The spectrum consists of two peaks in the visible region. The highly intense emission peak at 485 nm corresponds to blue emission and the other one at 521 nm refers to green emission, which may due to the anionic and cationic group present in MBSC crystal matrix [8]. The PL spectrum reveals that organic molecules with strong donor-π-acceptor system exhibit high photoluminescence properties. Especially, organic stilbazolium salts are potentially

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used as fluorescence probe monitor in the active area of biomedical research [9,10].

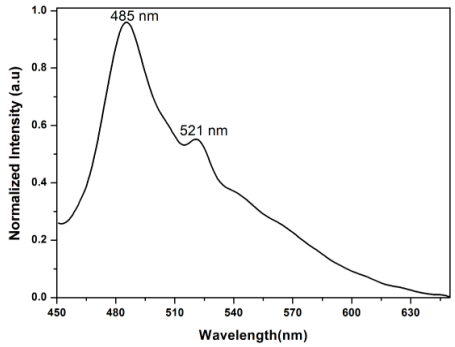

Figure 4. PL spectrum of MBSC crystal

4. Conclusion

A novel stilbazolium derivative crystal, 4-(4-methoxystyryl)-1-methylpyridinium 4-chlorobenzenesulfonate (MBSC) was successfully synthesized by condensation followed by metathesization reaction mechanism. Single crystal of MBSC was grown by slow solvent evaporation technique and the crystal structure was confirmed by single crystal XRD analysis. The functional groups identification and the structure of compound were confirmed by FT-IR spectral analysis. The percentage of carbon, hydrogen, and nitrogen in the synthesized sample was identified by CHN elemental analysis. From the absorption spectrum, the nature of transition was identified. Photoluminescence result suggests that the MBSC crystal could be used as a blue or green emission material by employing appropriate filters depending on the applications.

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