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A new multicomponent salt of imidazole and tetrabromoterepthalic acid: Structural, optical, thermal, electrical transport properties and antibacterial activity along with Hirshfeld surface analysis

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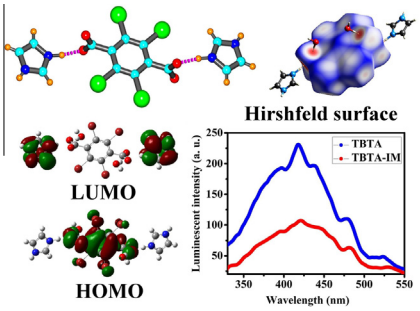
HIGHLIGHTS

- The crystal structure of multicomponent salt has been determined both from SCXRD and PXRD technique.
- Supramolecular interactions and short contacts through Hirshfeld surface analysis.
- The optical band gap has been found by Density Functional Theory.
- The salt is more active than imidazole against Gram-negative bacteria.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report the structural, optical, thermal and electrical transport properties of a new multicomponent salt ($TBTA^{2-}$)·2(IM^{+})·(water) [TBTA–IM] of tetrabromoterepthalic acid (TBTA) with imidazole (IM). The crystal structure of TBTA–IM is determined by both the single crystal and powder X-ray diffraction techniques. The structural analysis has revealed that the supramolecular charge assisted $O^{-}\cdots H{-}N^{+}$ hydrogen bonding and Br···π interactions play the most vital role in formation of this multicomponent supramolecular assembly. The Hirshfeld surface analysis has been carried out to investigate supramolecular interactions and associated 2D fingerprint plots reveal the relative contribution of these interactions in the crystal structure quantitatively. According to theoretical analysis the HOMO–LUMO energy gap of the salt is 2.92 eV. The salt has been characterized by IR, UV–vis and photoluminescence spectroscopic studies. It shows direct optical transition with band gaps of 4.1 eV, which indicates that the salt is insulating in nature. The photoluminescence spectrum of the salt is significantly different from that of TBTA. Further, a comparative study on the antibacterial activity of the salt with respect to imidazole, Gatifloxacin and Ciprofloxacin has been performed. Moreover, the current–voltage (*I–V*) characteristic of ITO/TBTA–IM/Al sandwich structure exhibits good rectifying property and the electron tunneling process governs the electrical transport mechanism of the device.

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Introduction

The fundamental objective of crystal engineering is to understand the weak non-covalent interactions and utilize those in a properly tuned manner to encompass novel functionalities in crystalline materials [1–5]. Additionally, the multicomponent organic compounds have attracted significant attention in the perspective of supramolecular chemistry and development of novel functional materials [6–13]. The supramolecular interactions lead to the formation of organic co-crystals and salts under specific conditions [14]. A co-crystal is supramolecular assembly of two or more different molecules in a single asymmetric unit in presence or absence of solvent molecules. The co-crystallization offers a unique opportunity to understand the behavior of an organic molecule in a particular environment, i.e., how an organic molecule with a specific functional group involves in supramolecular aggregation with other organic molecules. In some cases, the proton transfer takes place from one molecule to other which leads to the formation of multicomponent organic salts. The physicochemical properties, such as, solubility, dissolution rate, stability, melting point etc. of multicomponent organic crystals change drastically with respect to their co-formers as the physical and chemical properties of such systems crucially depend on the molecular packing within the crystal structure and supramolecular interactions between the constituent molecules [15–21]. Among multicomponent organic crystals, the pharmaceutical co-crystals offer enhanced stability with improved physicochemical properties compared to their parent bioactive molecules [22,23]. Besides, the studies on design, synthesis, bioactivity and physicochemical properties of the multicomponent organic salts have provided many interesting results.

In recent years, a great deal of emphasis has been devoted to modify the functional properties (such as, optical, electronic properties etc.) of organic molecules through co-crystallizations or salts formation [24,25]. Recently, we have shown that TBTA is an excellent co-crystallizing as well as multicomponent salt forming agent with different organic base molecules [26]. We have also established that the multicomponent organic salt of TBTA and 4,4′-bipyridine having 1D supramolecular chain formed by charge assisted hydrogen bonding interaction exhibits Schottky barrier effect. In our previous study, we have not used any bioactive molecules for having multicomponent crystals with TBTA. So, as a logical extension of our previous work, in this endeavor, we have fixed our target to realize a pharmaceutically active multicomponent compound of TBTA with biologically active molecule. To achieve the goal we have chosen imidazole as a bioactive organic molecule because it has a deprotonated N for which it can behave like base and may form multicomponent salt with TBTA. It may be noted that imidazole derivatives show antibacterial, antifungal and antiviral activities [27]. Imidazole is also used as basic skeleton of mercaptopurine, an anticancer drug, which combats leukemia by interfering with the DNA activities [28].

In this background, we have successfully synthesized an organic multicomponent salt: $(TBTA^{2-})\cdot 2(IM^{+})\cdot(water)$ [TBTA–IM] and presented the structural, thermal, optical, electrical and antibacterial properties of the salt. The structural analysis reveals that this multicomponent supramolecular assembly has built up by the hydrogen bonding and Br···π interactions between the TBTA and imidazole moieties. During crystallization, protons are transferred from TBTA to free 'N' atoms of imidazole. The HOMO–LUMO energy gap of TBTA–IM has been calculated by DFT method. The Hirshfeld surface analysis and associated 2D finger print plots are utilized to investigate the supramolecular close contacts and type of intermolecular interactions. The photoluminescence spectrum of TBTA–IM is significantly different from that of TBTA. The electrical property of TBTA–IM has been studied by fabricating ITO/TBTA–IM/Al sandwich structure. The current–voltage (I–V) characteristic curve of the device is nonlinear in nature and the device displays rectifying behavior.

Experimental

All the reagents and the solvents used were purchased from commercial source and used without further purification. The elemental analysis (CHN analysis) was carried out using the Perkin-Elmer 240C elemental analyzer. The IR spectrum of the salt was recorded by Perkin Elmer L120-000A FT-IR spectrophotometers. The thermal study was performed by TGA-Q500 (TA Instruments) thermogravimetric analyzer. The sample was heated over the temperature range of 25–500 °C at a constant heating rate of 10 °C/min with a stream of flowing N_2 gas throughout the experiment at 40 ml/min. The solid state UV–vis spectrum of the salt was recorded by Varian Cary 5000 UV–vis–NIR absorption spectrophotometer. The photoluminescence spectra were collected on a Shimadzu RF-5301PC spectrophotometer.

Synthesis of the salt $\{(C_8Br_4O_4)^{2-}\cdot 2(C_3H_5N_2)^{+}\cdot 2(H_2O)\}$

0.0005 mol of TBTA (0.241 g) was dissolved in 50 ml (1:1, v/v) ethanol–water mixture. The solution was stirred for 30 min. 0.001 mol of imidazole (0.068 g) was dissolved in 10 ml ethanol and it was mixed slowly with the TBTA ethanol–water solution. The solution was stirred for 30 min and it was allowed to evaporate under ambient temperature. After one week colorless block shaped single crystals suitable for X-ray structural characterization was collected. Yield: 75%. IR (cm^{-1}): 3340(b), 3019(w), 1716(s), 1588(s), 1540(s), 1519(w), 1443(s), 1414(w), 1235(s), 1061(w), 947(w). *Anal.Calc*., for the salt C: 34.31% (34.29% theo.); H: 2.25% (2.28% theo.) and N: 3.98% (4.00% theo.).

Single crystal X-ray diffraction data collection and refinement

Suitable single crystal of the salt was mounted on a Bruker SMART diffractometer equipped with molybdenum target and graphite monochromator. The data was recorded at 20 °C using Mo-K_α (λ = 0.71073 Å) radiation. The structure was solved by using the SHELXS97. The hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atoms. The positions of the non hydrogen atoms were determined by the subsequent difference Fourier synthesis and least-square refinement method. The non-hydrogen atoms were refined with independent anisotropic displacement parameters. The successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least square refinement. All calculations were carried out using SHELXL 97 [29], SHELXS 97 [30], PLATON 99 [31], ORTEP-3 [32] and WinGX [33] system Ver-1.64.

Powder X-ray diffraction data collection, structure solution and refinement

The powder X-ray diffraction (PXRD) data was collected at room temperature (20 °C) using Bruker D8 Advance diffractometer operating in the reflection mode using Cu-K_α radiation having wavelength 1.5418 Å. The generator was set at 40 kV and 40 mA. The PXRD data was collected within 2θ range of 5.0−80.0° (step size 0.02°) with scan speed of 6 s/step. The PXRD pattern was indexed using the program *TREOR 90* [34] of *Fullprof.2k* package [35]. The space group was obtained from statistical analysis of the PXRD pattern with the help of the *findspace* module of *EXPO 2009* software