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Electronic, infrared and morphological investigations on the charge-transfer complexations between 2-mercaptobenzothiazole donor and both iodine and picric acid electron acceptors

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ABSTRACT. Understanding the intermolecular charge transfer complexes between 2-mercaptobenthiazole (MBT) with picric acid (PA) and iodine (I_2) as π and σ acceptors was the main goal of this investigation. In $CHCl_3$, the charge-transfer interaction between the PA acceptor and the MBT electron donor has been investigated. The new CT-complex was formed using the general formula [MBT)(PA)] according to the resultant data. Following elemental analysis and photometric titration, the reaction's 1:1 stoichiometry was examined. However, the 1:1 iodine-MBT triiodide (I_3^-) charge-transfer complex, which has the general formula $[(MBT)_2I]^+I_3^-$, has been investigated spectrophotometrically in chloroform at ambient temperature. Around 332 and 290 nm are the locations of triiodide ion I_3^- electronic absorption bands. Due to symmetric stretching v_s(I-I) of the outer and inner bonds, respectively, the brown solid triiodide complex's Raman laser spectra exhibit two distinct vibration bands at 161 and 114 cm^{-1}. The morphological shape of MBT charge-transfer complexes as well as the intermolecular charge transfer interactions were discussed as seen by scanning electron microscopy (SEM) and their infrared spectra.

Keywords: Mercaptobenthiazole; triiodide; spectrophotometrically; picric acid; iodine; Raman laser.

INTRODUCTION

Benzothiazole derivatives are heterocyclic compounds with two rings: one is a benzene ring, and the other is a five-member ring with S and N atoms. Benzothiazole is used in antitumor, vasodilator, antitubercular, antifungal, antimicrobial, anticancer, antidiabetic, and antibacterial properties [1–4]. 2-Mercaptobenzothiazole (MBT) is also utilized in nonbiological fields, such as vulcanization, photographic materials, dyes, polymers, and growth regulators. This well-known analytical reagent for mercury, iron (II), and cadmium metal ions [5] and its derivatives have insecticidal capabilities [6]. It has also been discovered to be useful in the leather industry. For copper [7] and zinc [8], 2-

mercaptobenzothiazole is a commonly used organic corrosion inhibitor [9]. It is also used as a component of smart coatings that are anticorrosion and self-healing [10]. It was proposed by Larsson et al. [11] that MBT may be used as an additive in dye solar devices. MBT is one of several heterocyclomatic thiols that have been used as co-initiators for type II photo-initiators made of isopropylthioxanthone and camphoroquinone. Their effectiveness as co-initiators is like that of aromatic amines, according to kinetic data. Some of these "thiols" have been used as co-initiators of hexaarylbisimidazoles because of their propensity to give hydrogen atoms [12].

Because of the unique kind of interactions that accompany the transfer of an electron from the donor to the acceptor, charge-transfer complexes (CTCs) involving various organic species have been the subject of much research [13–21]. Iodine, as a sigma acceptor, reacted with various organic (aliphatic/aromatic) donors, including amines and crown ethers, to create polyiodide ions such as I_3^-, I_5^-, I_7^-, and I_9^-, which have intriguing uses in electronics and solar cells [22–29]. Charge-transfer complexes CTCs have been used successfully in a variety of intriguing research initiatives.

The main goal of developing and assembling different structures of organic CTCs is research focusing on the characteristics of metalloid, emission, high-power electronics, and ferroelectricity. They can also be used to study how drugs bind to their acceptors. For the investigation of pharmaceutical preparations and pharmaceuticals in their pure condition, CTC creation has been used to create quick, accurate, and simple spectrophotometric methods [30]. Because of their structural significance in many areas of chemistry, numerous attempts have been made to synthesize CTCs. As a result of their widespread application, CTCs have been thoroughly investigated in several domains, such as molecular electronics, medicine, biology [31], photoconductors [32], light detectors [33], ferroelectrics [34], liquid crystals [35], solar cells [36], photocatalysts [37], nonlinear optical materials [38], corrosion inhibitors [39], and chemosensors [40]. When an electron donor and an electron acceptor interact, charge transfer complexes (CTCs) are created. Charge transfer interactions or the creation of hydrogen bonds result in the creation of a new compound (CTC). This research explores the synthesis, properties, and recorded examples of CTCs. It examines the possibilities for future applications of CTCs and emphasizes current developments in their use across a range of industries. The intermolecular charge-transfer complexes of picric acid or iodine with 2-Mercaptobenzothiazole (MBT) have not been documented in any literature study.

EXPERIMENTAL

Chemicals

Aldrich, and Merck companies provided the 2-mercaptobenzothiazole (MBT; Formula I), iodine, picric acid, and other chemicals and solvents, which were used without additional purification.

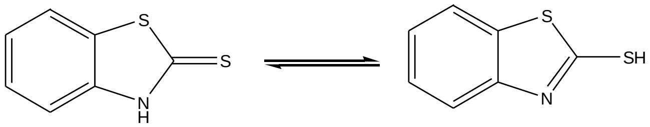
Instrumentals

A Perkin-Elmer CHN 2400 elemental analyzer was used for the elemental analyses. Jenway 4010 conductivity was used to assess the molar conductance of the MBT and their charge-transfer complexes using 10^{-3} mol/L in DMSO. KBr pellets were used to record IR spectra (4000–400 cm^{-1}) on a Bruker FT-IR Spectrophotometer, and samples' Raman laser spectra were examined using a 50-mW laser on a Bruker FT-Raman. Using a Jenway 6405 Spectrophotometer and a 1 cm quartz cell, the UV/vis spectra of the reactants and products were acquired in the 200–800 nm range in chloroform solvent (10^{-4} M). Analytical scanning electron microscopy was used to scan the samples for the Jeol JSM-63OLA. The elemental analysis was performed using the Energy-Dispersive X-ray Analysis (EDX) instrument, an optional add-on to the JEOL JSM-6390(LA).

Synthesis

Hofmann [41] first reported 2-mercaptobenzothiazole in 1887 (Formula I). The molecule exists in the solid form as the thione (A) and not as the thiol tautomer (B), as evidenced by the infrared spectra, which shows ν(NH) absorption bands at about 3100 cm^{-1} but no ν(SH) absorption at about 2500 cm^{-1}. Both of solid charge-transfer complexes of MBT with σ-acceptor (I_2) and π-acceptor (PA) were prepared by mixing (0.1 mmol; 0.168 g) of the MBT donor in 20 mL chloroform with saturated solution of each acceptor in the same solvent with continuously stirring for about 3 hr at room temperature. The mixtures were allowed to precipitate at room temperature, the resulted colored complexes in the solid state were filtered and washed with little amount of solvent, finally dried under vacuum over anhydrous calcium chloride. Analysis: The dark brown $[MBT)_2I]^+I_3^-$ complex with empirical formula $C_{14}H_{10}S_4N_2I_4$; %C, 19.85(19.97); %H, 1.17(1.20); and %N, 3.29(3.33). Analysis: The yellow solid [MBT)(PA)] charge transfer complex with empirical formula

$C_{13}H_8O_7S_2N_4$; %C, 39.36(39.39); %H, 2.01(2.03); and %N, 14.12(14.14) (theoretical values are shown in brackets and experimental data without brackets.



(A) (B)

Formula I. Tautomer's and deprotonated chemical structures of 2-mercaptobenzothiazole (MBT)

RESULTS AND DISCUSSIONS

Preface

The follow up of both brown and yellow colors formed upon the charge-transfer complexes between iodine and picric acid acceptors with electron donor MBT was spectrophotometrically studied to detect the optimal conditions for complexation process. The MBT has three types of donation atoms (Formula 1A), so it acts as a powerful electron donor. The three types of donation atoms are as exocyclic sulfur (C=S) group, endocyclic sulfur (C-S) group, and the nitrogen atom. In 2-mercaptobenzothiazole, the nitrogen atom is a secondary amine that is neutral and a part of an aromatic thiazole ring that has been fused with a benzene ring. In a secondary amine, the nitrogen atom hybridizes as sp^3. This is because the nitrogen atom has one lone pair of electrons and forms three sigma bonds, two with carbon atoms and one with a hydrogen atom, resulting in four regions of electron density, which is typical of (sp^3) hybridization.

For MBT-PA and $(MBT)_2$-$2I_2$ molar ratios between donor MBT and several attractive acceptors like PA and iodine, the fraction of carbon, hydrogen, and nitrogen components agrees with the 1:1 value. The initial materials' and the final MBT charge transfer complexes' conductivity measurements were carried out in DMSO at a concentration of 10^{-3} mol/L. The range of molar conductivities for MBT charge-transfer complexes was 38–42 $\Omega^{-1}cm^{-1}mol^{-1}$. According to the molar conductance values, the substance was rather electrolytic. The creation of intermolecular positive and negative dative anions (D^+—A^-) according to the acid-base theory is the cause of these data [13-26].

Electronic spectra

For the MBT-I_2 system, the UV-Vis electronic spectra (Figure 1) in $CHCl_3$ refers to both measured absorption bands at approximately 332 and 290 nm, which are absent for all reactants. Based on the absorption band at 332 nm, Figure 2 displays the photometric titration curve of the MBT-I_2 process. The MBT: I_2 ratio is 1:1, as the molar ratio of the MBT-I_2 reaction makes evident, and the intermolecular charge-transfer complex can be expressed as $[(MBT)_2I]^+I_3^-$. The elemental analysis and Raman laser spectroscopy discussions were consistent with this outcome. The literature review [22] states that the synthesis of one type of polyiodide molecule I_n^- (where n = 1, 3, 5, 7, 9, …) was attributed to the presence of similar absorption bands at 360 and 290 nm. The production of polyiodide charge transfer complexes is consistent with the triiodide I_3^- charge-transfer complex that was obtained in this investigation [22].

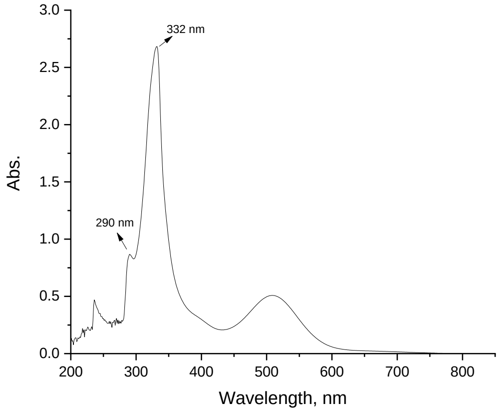


Figure 1. UV-Vis absorption spectrum of MBT-I_2 system in $CHCl_3$.

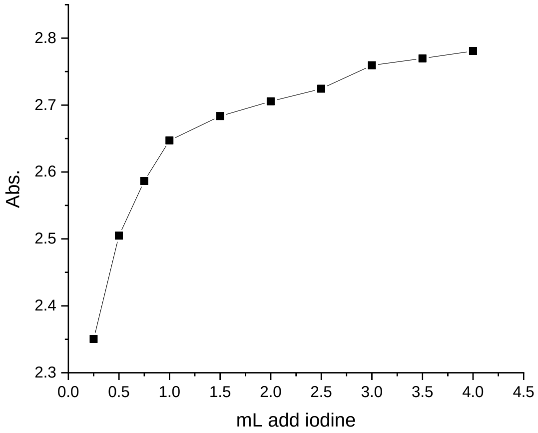


Figure 2. Photometric titration curve of MBT-I_2 system in $CHCl_3$ at 332 nm.

A pure grade of chloroform solvent was used to measure the electronic absorption spectra of MBT-PA charge-transfer complex. The CT complex is created by mixing 1.00 mL of 5.0×10^{-4} M MBT donor with ×mL of 5.0×10^{-4} M picric acid acceptor, where × = 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 3.50, and 4.00 mL. Using $CHCl_3$ solvent, each system's total volume was brought to 10 mL. While the concentration of PA changed from 0.25×10^{-4} M to 3.00×10^{-4} M for the MBT-PA system in $CHCl_3$ solvent, the concentration of MBT in the reaction mixture remained constant at 10^{-4} M. The MBT:PA ratios that result from these concentrations range from 1:0.50 to 1:4. Figure 3 displays the electronic absorption spectrum for the 1:1 ratio in chloroform. The characterization of the actual absorption bands, which are absent from the spectra of free reactants, is shown by the spectrum. This band is located at 410 nm because of the MBT-PA CT complex that was created when MBT and PA react in a $CHCl_3$ solvent. Based on these identified absorption bands, the photometric titration curve is displayed in Figure 4. Plotting the absorbance versus the mL of PA added as the π-acceptor yielded this photometric titration curve, which was achieved in accordance with established procedures [42]. It is evident from the curve's equivalency point that a 1:1 CT complex forms between MBT and picric acid. Observing that the solvent significantly affects the spectrum intensity of the generated [MBT)(PA)] complex was remarkable.

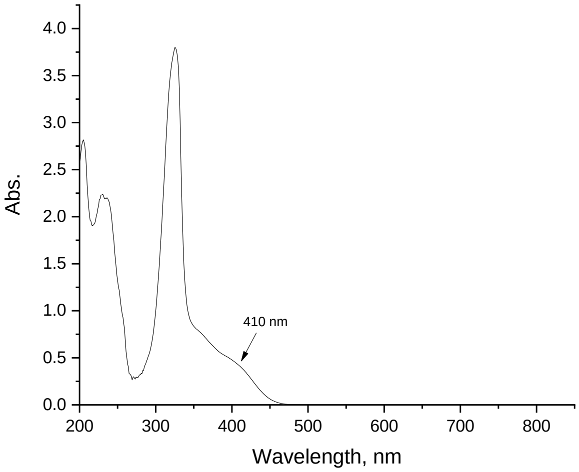


Figure 3. UV-Vis absorption spectrum of MBT-PA system in $CHCl_3$.

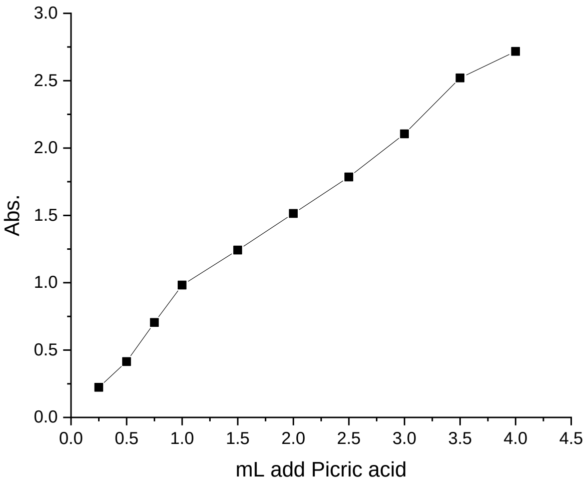


Figure 4. Photometric titration curve of MBT-PA system in $CHCl_3$ at 410 nm.

Infrared spectra

The infrared spectra of $[(MBT)_2I]^+.I_3^-$ and [(MBT)(PA)] charge-transfer complexes are shown in (Figures 5 & 6) and the bands of interest in the i.r. spectra of MBT and its charge transfer complexes are listed with assignments in Table 1. The FTIR spectrum peaks of pure MBT around 3081–2842 cm^{-1} was attributed to the aromatic hydrogen stretching vibration, and the peak at 3116 cm^{-1} corresponds to the N–H stretching vibration [43]. The peaks at 1597–1496 cm^{-1} and 1285 cm^{-1} were caused by the C=C and C=S stretching vibrations [43]. In addition, the presence of 1429 cm^{-1} and 671 cm^{-1} was due to C=N–S and C–S groups [43]. The–CH out-of-plane deformation characteristic vibrations bands of the aromatic naphthalene rings are at 970, 860 and 762 cm^{-1}. The spectra of the iodine and picric acid charge transfer complexes differ from that of the MBT ligand as follows:

i. The ν(N-H) band at 3116 cm^{-1} shifts to lower frequencies.
ii. The ν(N-C=S) band at 1429 cm^{-1} is less intense.
iii. The ν(C=S) band at 1322 cm^{-1} shows no frequency change but in all cases is less intense.
iv. The ν(C-S) band at 661 cm^{-1} is of medium strong intensity and presence in both charge transfer complexes.

The nitrogen atom is a more electron-rich donor atom than the sulfur atom in the thione structure of 2-mercaptobenzothiazole. Although both atoms have the potential to be donor sites, their complex behavior and relative electron richness are different. The nitrogen atom is more nucleophilic and a more advantageous reactive site for donation, according to theoretical and experimental research, especially when it comes to coordination complexes and adsorption onto surfaces. The N atom ability to donate electron density and create strong bonds is highlighted by the fact that it frequently takes part in additional stabilizing interactions during complex formation, such as hydrogen bonding (N-H...X). Consequently, in the thione structure, the N atom has a greater potential to donate electrons, particularly in the presence of strong dative or covalent interactions. These data are well agreement with the infrared data which supported the place of charge-transfer complexation through the migration of protons (–OH of phenolic group of picric acid acceptor) from acidic centers to sp^3 nitrogen atom (NH) which is more basicity than sulfur atoms (see Figure 7).

Table 1. Infrared frequencies (cm^{-1}) and band assignments of free MBT, $[(MBT)_2I]^+.I_3^-$ and [(MBT)(PA)] charge transfer complexes

Frequencies (cm^{-1})			Assignments
MBT	$[(MBT)_2I]^+.I_3^-$	[(MBT)(PA)]	
3116	3070	3099	ν(N-H)
–	2700–2500	2700–2500	Hydrogen bonding
1597, 1496	1587, 1494	1597, 1494	ν(C=C)
1429	1421	1421	ν(N-C=S)
1322	1317	1317	ν(C=S)
671	669	655	ν(C-S)

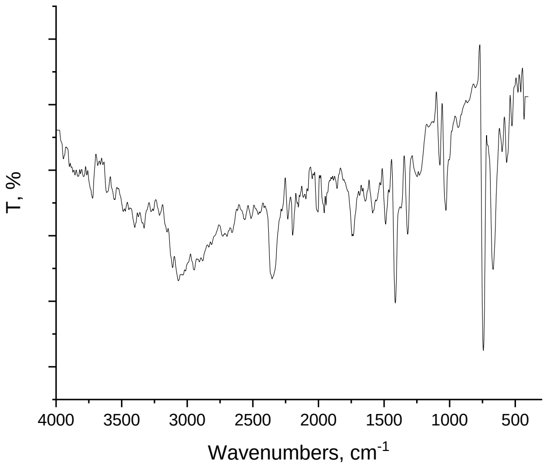


Figure 5. Infrared spectrum of $[MBT)_2I]^+I_3^-$ charge transfer complex

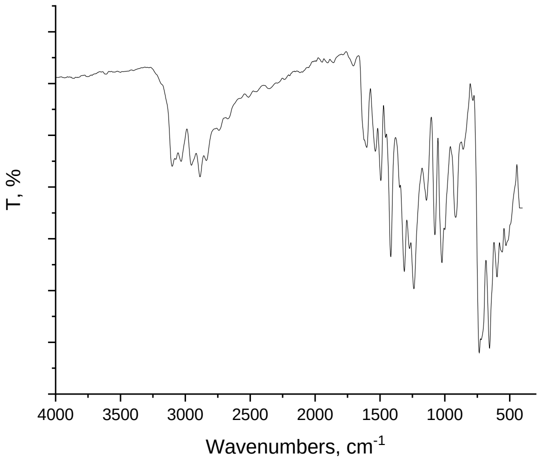


Figure 6. Infrared spectrum of [MBT)(PA)] charge transfer complex

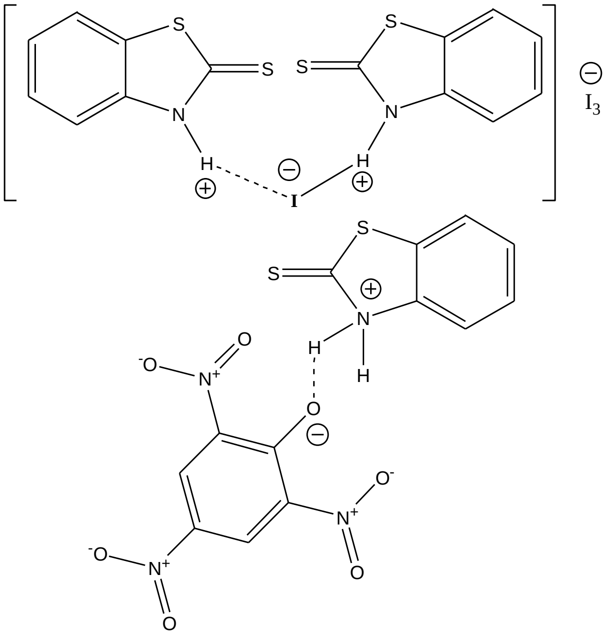


Figure 7. Suggested structures of $[(MBT)_2I]^+.I_3^-$ and [(MBT)(PA)] charge transfer complexes

Figure 8 displays the Raman spectrum of $[(MBT)_2I]^+.I_3^-$, and the measured absorption frequencies indicate the presence of the triiodide ion, I_3^- [22]. The asymmetric stretching vibrations ν_{as}(I–I); I_3^- are responsible for the medium-to-weak peaks at 161 cm^{-1}. The symmetrical stretching vibrations ν_s(I–I) are identified by the characteristic band that was observed; I_3^- is situated at 142 cm^{-1}.

Because of δ(I_3^-), the third band was present at 114 cm^{-1}. The I_3^- unit seems to be non-linear with C_{2v} symmetry since the Raman spectra contain both the triiodide ion's ν_s and ν_{as}.

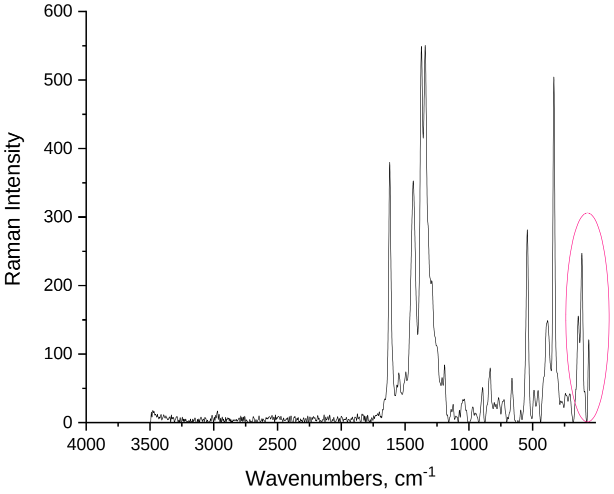


Figure 8. Raman laser spectrum of $[MBT)_2I]^+.I_3^-$ charge-transfer complex

SEM and EDX investigations

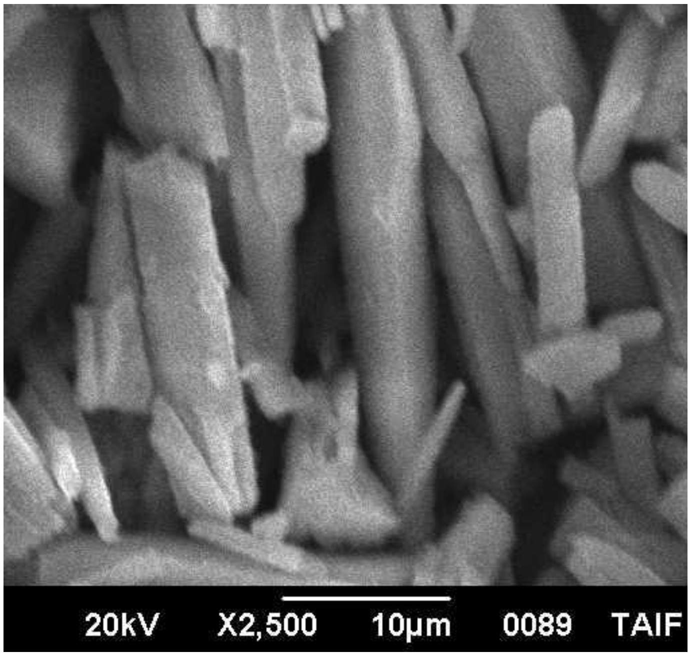


Figure 9A. SEM image of $[MBT)_2I]^+.I_3^-$ charge-transfer complex

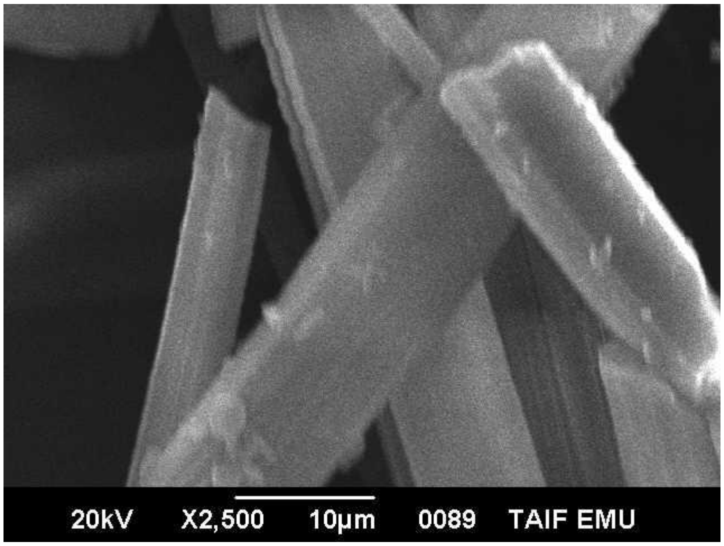


Figure 9B. SEM image of [MBT)(PA)] charge-transfer complex

Various microcrystal array morphologies can be seen in SEM pictures of a charge transfer complex, contingent on the materials and synthesis conditions. Energy-dispersive X-ray (EDX) spectroscopy and other characterization methods are frequently used in conjunction with these pictures to examine the complex elemental distribution and composition. While some complexes may self-assemble into crystalline structures, others, for instance, manifest as a film with needle-like characteristics. The synthetic $[(MBT)_2I]^+.I_3^-$ and [(MBT)(PA)] CT-complexes were subjected to microstructural investigation using a scanning electron microscope (SEM); the resulting images are displayed in Figure 9A&B. $[(MBT)_2I]^+.I_3^-$ and [(MBT)(PA)] both exhibit crystal-like structural morphology, which further demonstrates that donor/acceptor assembly is an energetically advantageous superstructure. According to microstructural morphology, the CTC structure's size was within the precise nanometer range.

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REFERENCES

1. El-Sayed, R. Synthesis, antibacterial and surface activity of 1,2,4-triazole derivatives. *Grasas Y Aceites*. **2006**, 57(2), 180–188. https://doi.org/10.3989/gya.2006.v57.i2.35

2. Gurupadayya, B.M.; Gopal, M.; Padmashali, B.; Vaidya, V.P. Synthesis and biological activities of fluoro benzothiazole. *Int J Heterocyclic Chem.* **2005**, 15, 169–172.

3. Geoffrey, W.; Tracey, D.B.; Patrizia, D.; Angela, S.; Dong-Fang, S.; Andrew, D.; Westwell, M.F.; Stevens, G. Antitumour Benzothiazoles. Part 10: The Synthesis and Antitumour Activity of Benzothiazole Substituted Quinol Derivatives. *Bioorg. & Med. Chem. Lett.* **2000**, 10, 513–515. https://doi.org/10.1016/S0960-894X(00)00027-5

4. Skotnicka, A.; Kabatc-Borcz, J. Design, Synthesis, and Spectral Properties of Novel 2-Mercaptobenzothiazole Derivatives. *Materials*. **2024**, 17, 246. https://doi.org/10.3390/ma17010246

5. Kochichiro, Y.; Katsumi, G.; Kazuya, Y.; Tominori, M.; Goro, T. Synthesis and evaluation of novel benzothiazole derivatives against human cervical cancer cell lines. *Int. J.Pharm. Sci.* **2007**, 69(1), 46–50.

6. Bhusari, K.P.; Khadekar, P.B.; Umathe, S.N.; Bahekar, R.H.; Rao, A.R. synthesis and anti-tubercular activity of some substituted 2-(4-aminophenyl sulphonamide) Benzothiazoles. *Indian J. Hetrocyclic Chem.* **2000**, 9, 213–216.

7. Garg, V.; Sharma, S.B.; Zanna, S.; Seyeux, A.; Wiame, F.; Maurice, V.; Marcus, P. Enhanced corrosion inhibition of copper in acidic environment by cathodic control of interface formation with 2-mercaptobenzothiazole. *Electrochim. Acta* **2023**, 447, 142162.

8. Finsgar, M.; Cakara, D. Spectroscopic analysis and in situ adsorption of 2-mercaptobenzothiazole corrosion inhibitor on Zn from a chloride solution. *Appl. Surf. Sci*. **2022**, 606, 154843.

9. Sun, X.; Liu, S.; Hu, P.; Sun, S.; Xie, Z.; Hu, G.; Hu, D.; Zhang, M. Microscale Corrosion Inhibition Behavior of Four Corrosion Inhibitors (BTA, MBI, MBT, and MBO) on Archeological Silver Artifacts Based on Scanning Electrochemical Cell Microscopy. *Anal. Chem*. **2023**, 95, 14686–14694.

10. Majidi, R.; Danaee, I.; Vrsalovi´c, L.; Zarei, D. Development of a smart anticorrosion epoxy coating containing a pH-sensitive GO/MOFnanocarrier loaded with 2-mercaptobenzothiazole corrosion inhibitor. *Mater. Chem. Phys*. **2023**, 308, 128291.

11. Larsson, L.F.G.; Tractz, G.T.; Camargo Matheus, A.P.; Pinto Rodrigues, P.R. The use of 2-Mercaptobenzothiazole as a new co-adsorbent in dye-sensitized solar cells. *Opt. Mater*. **2022**, 131, 112658.

12. Andrzejewska, E.; Zych-Tomkowiak, D.; Andrzejewski, M.; Hug, G.L.; Marciniak, B. Heteroaromatic thiols as co-initiators for type II photoinitiating systems based on camphorquinone and isopropylthioxanthone. *Macromolecules*. **2006**, 39, 3777–3785.

13. Khan, I.M.; Ahmad, A.; Aatif, M. Synthesis, single-crystal characterization, antimicrobial activity and remarkable *in vitro* DNA interaction of hydrogen-bonded proton-transfer complex of 1,10-phenanthroline with 2,4,6-trinitrophenol. *J. Photochem. Phtobiol. B: Biol*. **2011**, 105, 6-13.

14. Refat, M.S.; Killa, H.M.H.; El-Sayed, M.Y. IR, 1H-NMR, UV-Vis and thermal studies on the Rhodamine 6G charge-transfer complexes. *Bull. Chem. Soc. Ethiop.* **2011**, 25(1), 137-146.

15. Mohamed, H.M. Charge-transfer complexes formed between 1-hydroxybenzotriazole versus iodine and picric acid electron acceptors: electronic, infrared and morphological characterizations. *Bull. Chem. Soc. Ethiop.* **2025**, 39(7), 1437-1450.

16. Refat, M.S.; Ibrahim, O.B.; Saad, H.A.; Adam, A.M.A. Usefulness of charge–transfer complexation for the assessment of sympathomimetic drugs: Spectroscopic properties of drug ephedrine hydrochloride complexed with some π-acceptors. *J. Mol. Strut*. **2014**, 1064, 58-69.

17. Eldaroti, H.H.; Gadir, S.A.; Refat, M.S.; Adam, A.M.A. Spectroscopic investigations of the charge-transfer interaction between the drug reserpine and different acceptors: Towards understanding of drug–receptor mechanism. *Spectrochim. Acta A.* **2013**, 115, 309-323.

18. Adam, A.M.A.; Refat, M.S.; Saad, H.A. Spectral, thermal, XRD and SEM studies of charge-transfer complexation of hexamethylenediamine and three types of acceptors: π-, σ- and vacant *orbital* acceptors that include quinol, picric acid, bromine, iodine, $SnCl_4$ and $ZnCl_2$ acceptors. *J. Mol. Strut*. **2013**, 1051, 144-163.

19. Adam, A.M.A.; Refat, M.S.; Saad, H.A. Utilization of charge-transfer complexation for the detection of carcinogenic substances in foods: Spectroscopic characterization of ethyl carbamate with some traditional π-acceptors. *J. Mol. Strut.* **2013**, 1037, 376-392.

20. Khan, I.M.; Ahmad, A.; Kumar, S. Synthesis, spectroscopic characterization and structural investigations of a new charge transfer complex of 2,6-diaminopyridine with 3,5-dinitrobenzoic acid: DNA binding and antimicrobial studies. *J. Mol. Struct*. **2013**, 1035, 38-45.

21. Khan, I.M.; Ahmad, A.; Ullah, M.F. Synthesis, spectroscopic investigations, antimicrobial and DNA binding studies of a new charge transfer complex of o-phenylenediamine with 3,5-dinitrosalicylic acid. *Spectrochim. Acta A.* **2013**, 102, 82-87.

22. Nour, E.M.; Chen, L.H.; Laane, J. Far-infrared and Raman spectroscopic studies of polyiodides. *J. Phys. Chem*. **1986**, 90, 2841-2846.

23. Khan, I.M.; Ahmad, A. Synthesis, spectral investigations, antimicrobial activity and DNA-binding studies of novel charge transfer complex of 1,10-phenanthroline as an electron donor with π-acceptor p-Nitrophenol. *J. Mol. Strut*. **2010**, 977, 189-196.

24. Trotter, P.J.; White, P.A. Resonance Raman Determination of the Triiodide Structure in Bis(Tetrathiotetracene)Triiodide Organic Conductor Compared with the Poly(Vinyl Alcohol)-Iodine Complex. *Appl. Spectrosc*. **1978**, 32, 323-324.

25. Kiefer, W.; Bernstin, H.J. The UV-laser excited resonance raman spectrum of the I^{-}_{3} ion. *Chem. Phys. Lett*. **1972**, 16, 5-9.

26. Andrews, L.; Prochaska, E.S.; Loewenschuss, A. Resonance Raman and ultraviolet absorption spectra of the triiodide ion produced by alkali iodide-iodine argon matrix reactions. *Inorg. Chem*. **1980**, 19, 463-465.

27. Ikemoto, I.; Sakairi, M.; Tsutsumi, T.; Kuroda, H.; Harada, I.; Tasumi, M.; Shirakawa, H.; Ikeda, S. X-Ray Photoelectron Spectroscopic Study of Highly Conductive Iodine-Doped Polyacetylene. *Chem. Lett*. **1979**, 8(10), 1189-1192.

28. Rajpure, K.Y.; Bhosale, C.H. Sb_2S_3 semiconductor-septum rechargeable storage cell. *Chem. Mater. Chem. Phys*. **2000**, 64, 70-74.

29. Licht, S. Electrolyte modified photoelectrochemical solar cells. *Sol. Energy Mater. Sol. Cells* **1995**, 38, 305-319.

30. Gouda, A.A. Utility of certain sigma- and pi-acceptors for the spectrophotometric determination of ganciclovir in pharmaceutical formulations. *Talanta*. **2009**, 80, 151-157. https://doi.org/10.1016/j.talanta.2009.06.042.

31. Khawas, S.; Laskar, S. Two new spray reagents for the detection of amino acids on thin-layer plates, *J. Planar Chromatogr*. **2003**, 16, 165-166.

32. Sagar, A.; Jain, V.R.; Oza, A.T. Spectroscopic analysis and study of charge transport properties for Pinacyanol chloride-organic acceptor complex as potential optoelectronics material. *Am. J. Anal. Chem*. **2015**, 6, 694–707. https://api.semanticscholar.org/CorpusID:93727775.

33. Chaudhary, S.; Ramanand, R. Solid-state green synthesis of blue light emitting fluorescent novel organic charge transfer complex; its optical, physicochemical and thermal studies, *Mat. Chem. Phys*. **2023**, 308, 128279. https://api.semanticscholar.org/CorpusID:260673236.

34. Horiuchi, S.; Kobayashi, K.; Kumai, R.; Minami, N.; Kagawa, F.; Tokura, Y. Quantum ferroelectricity in charge-transfer complex crystals, *Nat. Commun*. **2015**, 6, 7469. https://doi.org/10.1038/ncomms8469.

35. Haverkate, L.A.; Zbiri, M.; Johnson, M.R.; Carter, E.; Kotlewski, A.; Picken, S.; Mulder, F.A.; Kearley, G.J. Electronic and vibronic properties of a discotic liquid-crystal and its charge transfer complex. *J. Chem. Phys*. **2014**, 140, 014903–8, https://doi. org/10.1063/1.4856815.

36. AlQaradawi, S.Y.; Nour, E.M. Synthesis and spectroscopic structural studies of the adducts formed in the reaction of aminopyridines with TCNQ, *J. Mol. Struct*. **2006**, 794, 251–254. https://doi.org/10.1016/j.molstruc.2006.02.031.

37. Karmakar, S.; Barman, S.; Rahimi, F.A. Confining charge-transfer complex in a metal-organic framework for photocatalytic CO2 reduction in water. *Nat. Commun*. **2023**, 14, 4508. https://doi.org/10.1038/s41467-023-40117-z.

38. Rezvan, V.H. DFT study of molecular structure, and optical properties of charge transfer complexes derived from tetrathiafulvalene and tetracyanoquinodimethane derivatives. *J. Chem. React. Synth*. **2021**, 11, 6–11.

39. Wr, W.; Yan, C.; Yan, H.; Pan, G.; Wan, L. Donor/acceptor complex of triphenylene and trinitrotoluene on au (111): a scanning tunneling microscopy study, *Chem. Commun*. **2011**, 47, 6915–6917. https://doi.org/10.1039/c1cc11358e.

40. Rezvan, V.H. Charge transfer complexes: a review survey. *Results in Chemistry*. **2025**, 17, 102600. https://doi.org/10.1016/j.rechem.2025.102600.

41. Hofmann, W. Zur Kenntniss des o-Amidophenylmercaptans. *Ber. Dtsch. Chem. Ges*. **1887**, 20, 1788-1797.

42. Skoog, D.A. *Principle of Instrumental Analysis*, 3rd ed., Saunders College Publishing: New York; USA, **1985**, Ch. 7.

43. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A: Theory and Applications in Inorganic Chemistry*. 6th ed., John Wiley & Sons: New Jersey, USA; **2009**.