

SYNTHESIS, GROWTH, STRUCTURAL, SPECTRAL, OPTICAL AND THERMAL CHARACTERIZATION OF IMIDAZOLIUM 4-NITROBENZOATE SINGLE CRYSTAL

ABSTRACT

The organic salt of Imidazolium 4-nitrobenzoate (I4NB) has been synthesized and single crystals grown by slow solvent evaporation solution growth technique at room temperature. The ^1H and ^{13}C NMR spectra were recorded to confirm the molecular structure of I4NB crystal. The single crystal XRD analysis shows that both the cation and the anion are interlinked to each other by two types of symmetrical intermolecular hydrogen bonds, namely $\text{N}(2)\text{-H}(2\text{A})\cdots\text{O}(3)$ and $\text{N}(3)\text{-H}(3\text{A})\cdots\text{O}(4)$. The title compound (I4NB) crystallizes in triclinic crystal system with the centrosymmetric space group P-1. Fourier transform infrared (FT IR) spectral analysis was used to confirm the presence of various functional groups in the grown crystal. The optical properties were analyzed by the UV-Vis-NIR transmittance and fluorescence emission studies. The thermal stability of the title crystal was investigated by thermogravimetric (TG) and differential thermal analyses (DTA). The surface morphology of the title crystal was studied by scanning electron microscopy.

Key words: X-ray diffraction, nonlinear, single crystal, solution growth, thermal analyses.

1. INTRODUCTION

The crystal engineering has its roots in the field of the design and synthesis of crystalline materials of the solid-state organic chemistry offers many possibilities to tailor the substances with desired properties through optimization of the microscopic hyperpolarizabilities and the incorporation of the molecules in a crystalline lattice. The organic materials with aromatic ring, which are of great interest for second and third-order nonlinear optical applications due to their high nonlinearity, high optical damage threshold and their ultrafast, almost purely electronic response [1-4]. The five membered aromatic heterocyclic compound imidazole, which is classified as an alkaloid and its derivatives have many pharmacological properties such as antiviral, antiulcer, antihypertension, and anticancer properties. The imidazole ring system is present in important biological molecules such as histidine, vitamin B₁₂, DNA, purines, histamine and biotin. The imidazoles have also found applications as a chromophore with readily tunable absorption wavelength, fluorophoric properties and synthetic building blocks in supramolecular chemistry [5-7]. The protonated and deprotonated nitrogen present in the imidazole molecule is a good source to co-ordinate with organic and inorganic compounds which help to make the multi-dimensional supramolecular assembly [8]. The focus based on generating chiral crystals from achiral molecule, the crystal structures of salts between nitrobenzoic acid and imidazoles have been analyzed by Hashime et al [9]. Taking into account of the above aspects we have synthesized and grown single crystals of the salt, imidazolium 4-nitro benzoate. In this paper we report the growth and characterization of the title crystal I4NB.

2. EXPERIMENTAL PROCEDURE

2.1 Material synthesis

Analar grade imidazole (0.67 g, 0.01 mol) and 4-nitrobenzoic acid (1.67 g, 0.01 mol) were dissolved separately in dry acetonitrile and ethanol respectively. Both the solutions were mixed together and stirred well for few minutes. The white colored precipitate was obtained and the reaction involved is illustrated in figure. 1. The precipitate was then filtered off and dried.

2.2 Growth of single crystals

A saturated solution of the charge transfer salt, I4NB was prepared in ethanol and acetone in the ratio of 1:1 and the resulting solution was stirred well for 4 hours. Suspended impurities were removed by using whatman 41 grade filter paper. The clear filtrate so obtained was kept aside unperturbed in a dust free room for the growth of single crystals. The colorless single crystals were collected after 2

weeks. The photograph of as-grown crystal of I4NB is shown in figure 2. The grown I4NB crystal was subjected to various characterization studies like ^1H and ^{13}C NMR spectral analyses, single crystal X-ray diffraction, Fourier transform infrared (FT IR), UV-Vis-NIR transmission studies, fluorescence emission, TG/DTA analyses and scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1 Spectroscopic studies

The ^1H and ^{13}C NMR spectra were recorded employing the 'BRUKER AVANCE III 500 MHz (AV 500) spectrometer with TMS as the internal reference standard and DMSO as the solvent. The ^1H NMR spectrum depicted in figure 3 exhibits of five proton signals which indicate the presence of five different proton environments in the title crystal. The singlet signal centered at δ 8.29 ppm is attributed to C2 and C3 protons of the same kind in imidazolium moiety in the salt and these protons are chemically and magnetically equivalent due to the resonance. The C2 and C6 aromatic protons of the same kind in 4-nitrobenzoate moiety appear as a doublet at δ 8.16 ppm. The splitting of the signal into doublet is due to coupling of C2 and C6 protons with the neighbouring C3 and C5 aromatic protons respectively. The singlet signal appearing at δ 7.99 ppm has been assigned to C5 aromatic proton of imidazolium moiety. The broad small hump appearing at δ 7.7 ppm is assigned to the deshielded $^+\text{N-H}$ protons. The singlet peak at δ 7.18 ppm is assigned to the C3 and C5 aromatic protons of the same kind in 4-nitrobenzoate moiety.

The ^{13}C NMR spectrum of the title crystal is shown in figure 4. The appearance of eight distinct carbon signals in the spectrum explicitly confirms the molecular structure of the title crystal. The signal at δ 166.94 ppm owes to the carboxylate carbon atom of 4-nitro benzoate moiety. The C1 and C4 carbon atom in the same moiety brings forth a signal at δ 150.0 and 139.13 ppm respectively. The intense signal at δ 135.47 ppm owes to the C2 and C3 carbon atoms of the same kind in the imidazolium moiety. The signal due to C2 and C6 carbon atoms of the same kind in 4-nitrobenzoate moiety appear as an intense signal at 135.38 ppm. The peaks appearing at δ 130.97 and 123.94 ppm have been assigned respectively to C3 and C5 carbon atoms in 4-nitrobenzoate moiety in the complex. The signal due to C5 carbon atom in the imidazolium moiety appears at δ 121.56 ppm.

The FT-IR spectrum of the I4NB crystal was recorded employing a SHIMADZU model IR Affinity-1 spectrometer in the range 4000-400 cm^{-1} following the KBr pellet technique (figure 5). It is evident from the spectrum that the band at 3157 cm^{-1} is assigned to the $\text{N}^+\text{-H}$ asymmetric stretching vibration. The band at 3093 and 3006 cm^{-1} are due to aromatic C-H asymmetric and symmetric stretching vibrations respectively. The bands at 2926 and 2848 cm^{-1} are assigned to the C-H asymmetric and symmetric stretching vibration of the imidazolium ring respectively. The bands at 1589 and 1668 cm^{-1} are due to the aromatic C=C stretching vibrations. The band observed at 1589 cm^{-1} is attributed to NO_2 asymmetric stretching vibration which almost overlaps with the aromatic C=C stretching vibration and the asymmetric COO^- stretching vibration. The symmetric COO^- stretching vibration of carboxylate anion is observed at 1387 cm^{-1} . A band at 1337 cm^{-1} corresponds to the NO_2 symmetric stretching vibration. The assignment of various vibrational frequencies is presented in table 1.

3.2 Single crystal X-ray diffraction analysis

The unit cell parameters and the crystal structure were established from the single crystal X-ray diffraction data obtained with an 'ENRAF (BRUKER) NONIUS CAD4' diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71073\text{\AA}$). A good optical quality colorless single crystal of dimension 0.35×0.30×0.30 mm was selected for diffraction analysis. A total of 8660 reflections (1770 Unique, $R(\text{int}) = 0.0242$) were collected by using a $\omega/2\theta$ scan mode at 293(2) K in the range of $2.79^\circ < \theta < 25.00^\circ$ with the index range $-7 \leq h \leq 7$, $-8 \leq k \leq 8$, $-14 \leq l \leq 14$. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXS-97 [10] crystallographic software package. All non-hydrogen atoms were refined using anisotropic displacement

parameters. All hydrogen atoms were placed in the riding mode and refined isotropically. The crystal data and details of the data collection and the structure refinement are given in table 2. The I4NB crystal belongs to triclinic crystal system with space group $p-1$ and its unit cell dimensions are determined as $a=5.95600(10)$ Å, $b=7.51400(10)$ Å, $c=11.8030(2)$ Å, $V=505.755(14)$ Å³. Selected bond lengths, bond angles and torsion angles of the complex are listed in table 3, table 4 and table 5 respectively. The molecular structure of the I4NB with atom numbering scheme is shown in figure 6. The asymmetric part of the unit cell contains an imidazolium cation and a nitrobenzoate anion. The imidazole molecule exists as an imidazolium ion due to the protonation at the N atom of the imidazole ring. The 4-nitrobenzoic acid exists as nitro benzoate since the proton gets transferred to the imidazole. The bond length and bond angles in the imidazolium moiety and 4-nitrobenzoate moiety normal as observed in the similar structure complexes [5, 11]. In the crystal, molecules are connected by the two symmetrical intermolecular N-H...O hydrogen bonds and were found between N(2)-H(2A)...O(3) [x,y,z-1], N(3)-H(3A)...O(4) [-x, -y+1, -z+1] with a donor-acceptor distances of 2.7376(15) Å, 2.6362(14) Å respectively. Figure 7(a) and 7(b) show the intermolecular hydrogen bonding interaction between the cation and anion species and the constituent molecules in one unit cell respectively. The packing diagram (figure 8) shows the N-H...O intermolecular hydrogen bonding interaction between the molecules in zigzag position and the rings are connected through C-H...O weak hydrogen bonds involving nitro group [12].

3.3 UV-Vis-NIR transmission studies

The optical transmission spectrum of I4NB crystal was recorded in the region 200-1100 nm employing a Shimadzu UV-1061 UV-Vis spectrophotometer in solution using DMSO as the solvent. The spectrum (figure 9) exhibits very good transparency around 98 % in the region between 436 and 1100 nm. The lower cut-off wavelength of the I4NB crystal was around 376 nm. Hence, the title crystal can be used for various optical applications owing to its wide transparency window in the entire visible and near infrared regions.

3.4 Fluorescence emission studies

Fluorescence may be normally expected in molecules that are aromatic or contain multiple conjugated system double bonds with a high degree of resonance stability [13]. The fluorescence emission spectrum of I4NB was recorded using HORIBA JASCO V-670 FLUOROLOG 3 spectrofluorometer. The fluorescence emission spectrum was recorded in the range from 500 to 900 nm and depicted in figure 10. A sharp peak at 553 nm observed in the emission spectrum indicates that I4NB crystal has a green fluorescence emission.

3.5 TG/DTA analyses

The TGA and DTA traces of the sample were recorded employing the instrument SII nano technology TG/DTA 6200 model with a heating rate of 20°C/min in nitrogen atmosphere. The I4NB sample weighing 6.577 mg was taken for the analysis and the thermogram is shown in figure 11. From the TG curve it is inferred that the decomposition of the title compound takes place in two stages. The first stage decomposition commences at 180°C and ends at 275°C with the elimination of 80.5 % material into gaseous products. The second stage decomposition noticed between the temperatures 275 and 500°C incurs a weight loss of 15.5 % of the material into gaseous products. The various gaseous products evolved in both the stages are CO₂, NO₂, NH₃ and hydrocarbon gases. The residual mass of 4% which is left out in the crucible may be carbon mass present after all the decomposition processes.

From the DTA thermogram (figure 11), it is observed that there is sharp endothermic peak at 197.6°C, which corresponds to the melting point of the compound. This is followed by a broad endotherm at 273.6°C, which may be attributed to the second decomposition temperature of I4NB.

3.6 Scanning electron microscopy

The surface morphology of the I4NB crystal was studied using an INCA Penta FETX3 scanning electron microscope and the SEM micrograph is shown in figure 12. It is seen from the figure that the I4NB complex exhibits the sheet-like structure with an average particle size of 5 μm to 25 μm and this may be due to solvent inclusions occurring during the growth of crystals from solution.

4. CONCLUSION

The organic molecular charge transfer complex salt I4NB was synthesized and single crystals of the title compound were grown by the slow solvent evaporation solution growth technique at ambient temperature. FT-IR and NMR spectroscopic studies confirm the formation of the title crystal. Single crystal X-ray diffraction analysis shows that the I4NB crystal belongs to triclinic crystal system with space group P-1. UV-Vis-NIR transmittance study shows that the crystal has wide transparency window in the entire visible and NIR regions. The fluorescence analysis confirms a green emission from the I4NB crystal. Thermal analyses indicate that the complex crystal is stable and the melting point is 197.6°C. The SEM micrograph of I4NB indicates that the crystal exhibits the sheet-like structure with an average particle size of 5 μm to 25 μm .

Observed frequency (in cm^{-1})	Assignment
3157	$^+\text{N-H}$ stretching
3093	Aromatic C-H asymmetric stretching
3006	Aromatic C-H symmetric stretching
2926	C-H asymmetric stretching vibration of imidazolium ring
2848	C-H symmetric stretching vibration of imidazolium ring
1589, 1668	Aromatic C=C stretching
1589	NO_2 asymmetric stretching/asymmetric COO^- stretching
1387	Symmetric COO^- stretching
1337	NO_2 symmetric stretching
1185, 1106 & 999	C-H in plane bending
869	C-N stretching
811	C-H out of plane bending

Table 1. FT-IR frequency assignment for I4NB crystal

Empirical Formula	C ₁₀ H ₉ N ₃ O ₄
Formula weight	235.20
Temperature	293(2) K
wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a= 5.95600(10) Å, α=103.019 (10)° b=7.51400(10) Å, β=100.1880(10)° c=11.8030(2) Å, γ=90.7580(10)°
Volume	505.755(14)Å ³
Z, Calculated density	2, 1.544 Mg/m ³
Absorption coefficient	0.122 mm ⁻¹
F(000)	244
Crystal size	0.35×0.30×0.30 mm
Theta range for data collection	2.79 to 25.00°
Limiting indices	-7<=h<=7, -8<=k<=8, -14<=l<=14
Reflections collected/unique	8660/1770 [R(int)=0.0242
Completeness to theta = 25.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9865 and 0.9243
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1770/0/154
Goodness-of-fit on F ²	1.054
Final R indices [I>2sigma(I)]	R1=0.0337, wR2=0.0922
R indices (all data)	R1=0.0384, wR2=0.1001
Largest diff.peak and hole	0.132 and -0.202 e.Å ⁻³

Table 2 Crystallographic data of I4NB crystal

C(1)—C(2)	1.3745(19)
C(1)—C(6)	1.3767(18)
C(1)—N(1)	1.4679(16)
C(2)—C(3)	1.3798(18)
C(3)—C(4)	1.3898(17)
C(4)—C(5)	1.3843(18)
C(4)—C(7)	1.5110(17)
C(5)—C(6)	1.3802(18)
C(7)—O(3)	1.2484(16)
C(7)—O(4)	1.2522(16)
C(8)—N(3)	1.3189(17)
C(8)—N(2)	1.3214(18)
C(9)—C(10)	1.342(2)

C(9)—N(2)	1.3604(19)
C(10)—N(3)	1.3637(19)
N(1)—O(1)	1.2199(17)
N(1)—O(2)	1.2205(17)

Table 3 Selected bond lengths in I4NB (Å)

C(2)	C(1)—C(6)	122.81(12)
C(2)	C(1)—N(1)	118.59(12)
C(6)	C(1)—N(1)	118.60(12)
C(1)	C(2)—C(3)	117.97(12)
C(2)	C(3)—C(4)	120.86(12)
C(5)	C(4)—C(3)	119.46(12)
C(5)	C(4)—C(7)	120.83(11)
C(3)	C(4)—C(7)	119.71(11)
C(6)	C(5)—C(4)	120.50(12)
C(1)	C(6)—C(5)	118.39(12)
O(3)	C(7)—O(4)	125.81(12)
O(3)	C(7)—C(4)	117.14(11)
O(4)	C(7)—C(4)	117.05(11)
N(3)	C(8)—N(2)	108.38(13)
C(10)	C(9)—N(2)	106.75(12)
C(9)	C(10)—N(3)	107.39(13)
O(1)	N(1)—O(2)	123.60(12)
O(1)	N(1)—C(1)	118.21(13)
O(2)	N(1)—C(1)	118.19(12)
C(8)	N(2)—C(9)	108.99(12)
C(8)	N(3)—C(10)	108.49(12)

Table 4 Selected bond angles in I4NB (°)

C(6)–C(1) C(2) C(3)	1.17(19)
N(1)–C(1) C(2) C(3)	-178.34(11)
C(1)–C(2) C(3) C(4)	-0.94(19)
C(2)–C(3) C(4) C(5)	-0.09(19)
C(2)–C(3) C(4) C(7)	179.87(11)
C(3)–C(4) C(5) C(6)	0.96(19)
C(7)–C(4) C(5) C(6)	-179.00(11)
C(2)–C(1) C(6) C(5)	-0.33(19)
N(1)–C(1) C(6) C(5)	179.18(11)
C(4)–C(5) C(6) C(1)	-0.75(19)
C(5)–C(4) C(7) O(3)	167.01(11)
C(3)–C(4) C(7) O(3)	-12.95(18)
C(5)–C(4) C(7) O(4)	-13.44(18)
C(3)–C(4) C(7) O(4)	166.60(12)
N(2)–C(9) C(10) N(3)	-0.20(15)
C(2)–C(1) N(1) O(1)	-0.73(19)
C(6)–C(1) N(1) O(1)	179.73(12)
C(2)–C(1) N(1) O(2)	178.61(12)
C(6)–C(1) N(1) O(2)	-0.93(19)
N(3)–C(8) N(2) C(9)	0.56(15)
C(10)–C(9) N(2) C(8)	-0.21(15)
N(2)–C(8) N(3) C(10)	-0.68(15)
C(9)–C(10) N(3) C(8)	0.54(15)

Table 5 Torsion angles in I4NB (°)

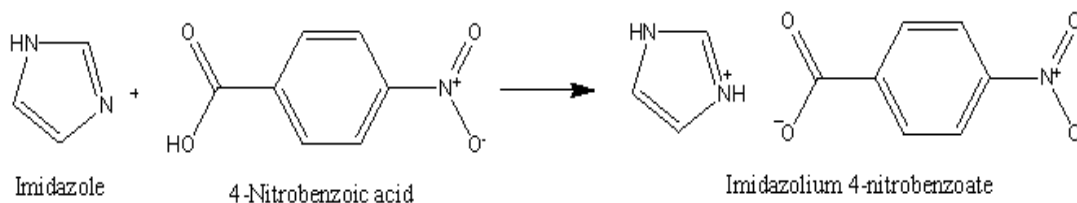


Figure 1. Reaction scheme of I4NB

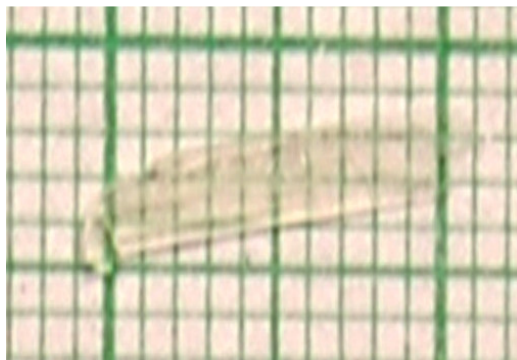


Figure 2. As grown single crystals of I4NB

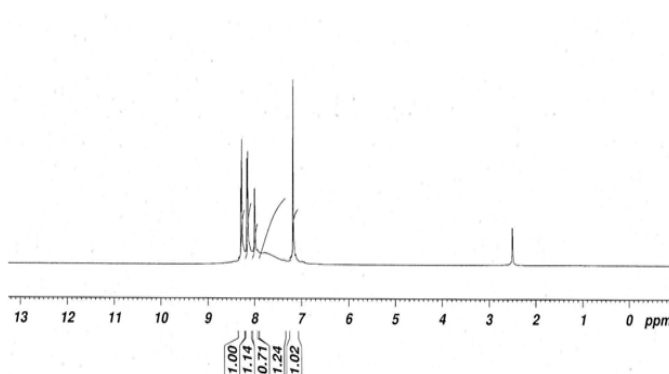


Figure 3. ^1H NMR spectrum of I4NB

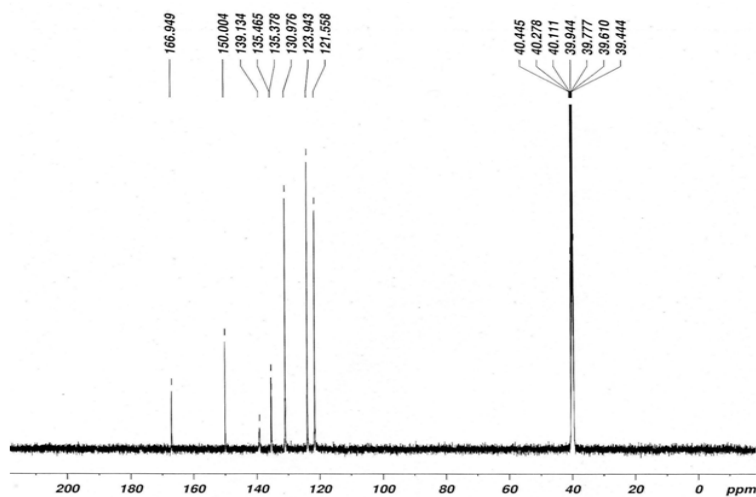


Figure 4. ^{13}C NMR spectrum of I4NB

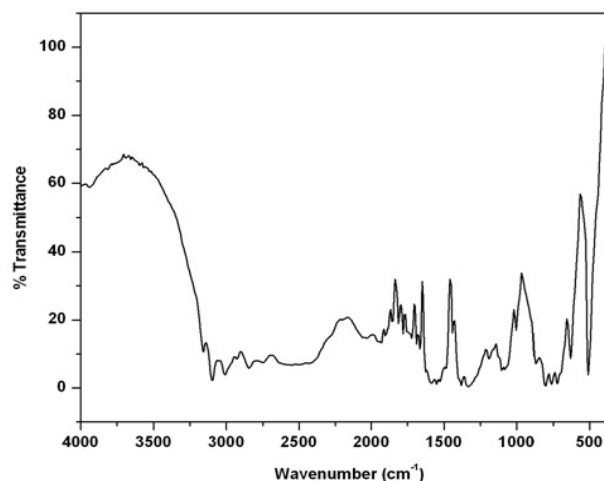


Figure 5. FT-IR Spectrum of I4NB

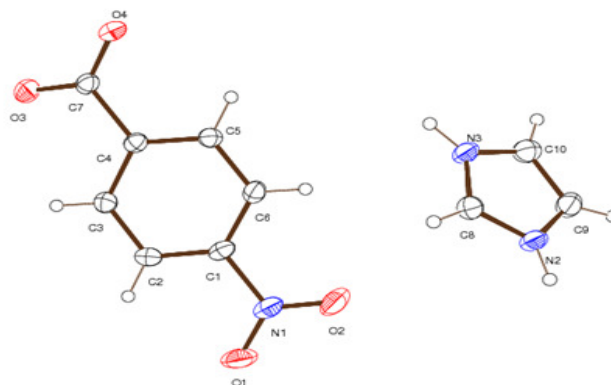


Figure 6. ORTEP diagram of I4NB

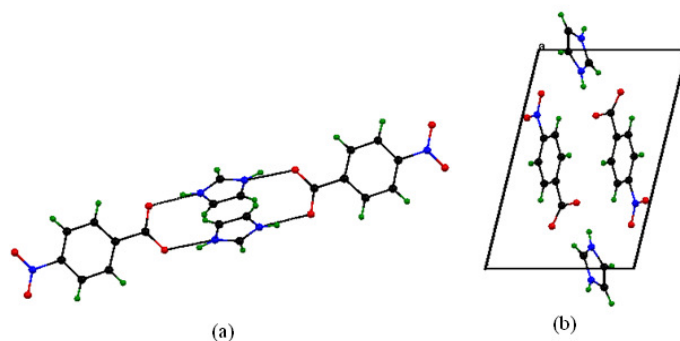


Figure 7. a) Hydrogen bonding interaction between the molecules. b) Molecules in one unit cell viewed down c axis.

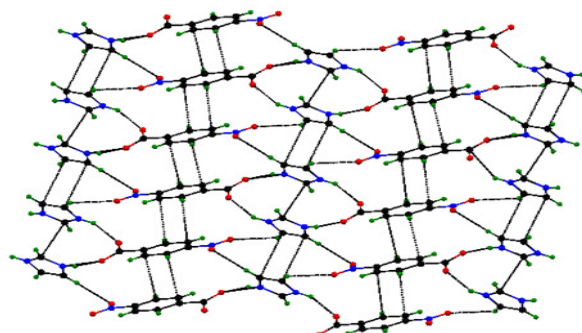


Figure 8. Packing arrangement of molecules showing the intermolecular N-H...O hydrogen bonding interactions in Zig-Zag position

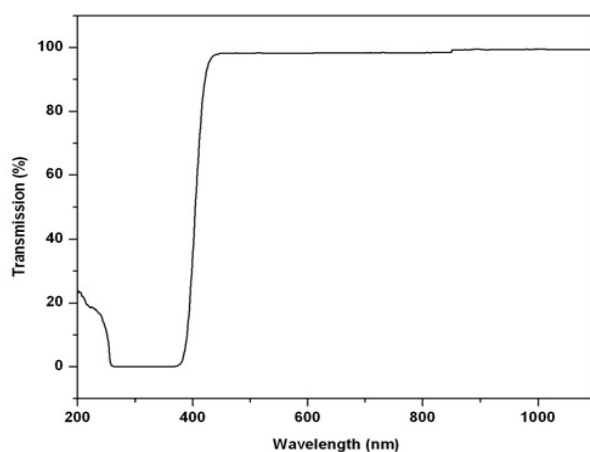


Figure 9. Optical transmission spectrum of I4NB

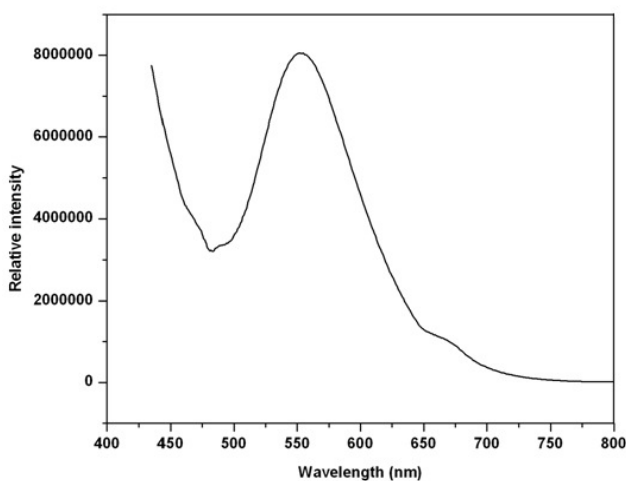


Figure 10. Fluorescence emission spectrum of I4NB

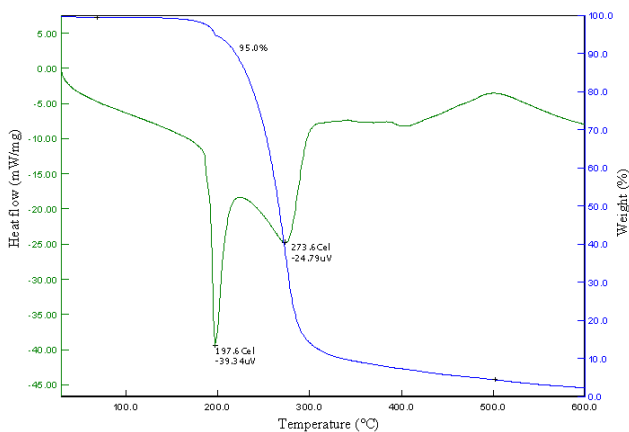


Figure 11. TG/DTA spectrum of I4NB

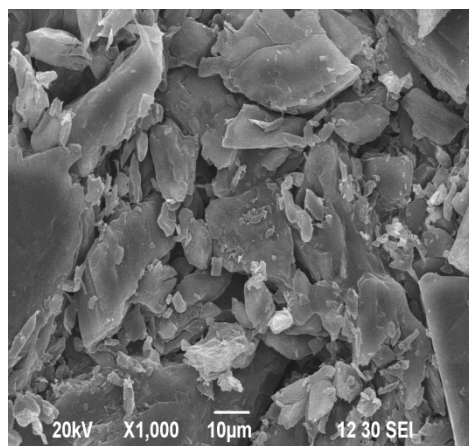


Figure 12. SEM image of as grown I4NB

SUPPLEMENTARY INFORMATION.A

The crystallographic information file has been deposited by us in the Cambridge structure database (CCDC 929001). These data can be obtained by free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data-request/cif.

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