SUPPLEMENTARY INFORMATION

Synthesis, crystal growth, physicochemical properties and quantum chemical investigations on D-π-A type organic single crystal: 2-amino-5-nitropyridinium p-phenolsulfonate (2A5NPP) for nonlinear optical (NLO) applications

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1. Determination of optical parameters

The band gap energy was estimated theoretically using cutoff wavelength by the following equation.

$$E_g = \frac{hc}{\lambda_{\max(nm)}} \text{ ---------- (1)}$$

where 'h' is the Planck's constant, 'c' is the velocity of light and 'λ_{max}' is the optical cutoff wavelength (408 nm). The band gap of grown crystal was estimated to be 3.0 eV. The absorption coefficient was evaluated from the measured transmittance data using the following equation.

$$\alpha = \frac{2.303 \times \log\left(\frac{1}{T}\right)}{t} \text{ ---------- (2)}$$

where 'T' is the percentage of transmittance and 't' is the thickness of the sample which was used in UV-Vis-NIR transmittance analysis. The optical band gap (E_g) was determined from the absorption coefficient near the absorption edge by Tauc's plot relation as given by the following equation [1].

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \text{ ----------} (3)$$

where 'E_g'denotes band gap of the sample, 'A' is a constant, 'h' is Planck's constant, 'υ' is the frequency of the incident photons and 'n' is the characteristics of electronic transition of the given material. According to the above equation n=1/2 for direct allowed transitions, n=3/2 for direct forbidden transitions, n=2 for indirect allowed transitions and n=3 for indirect forbidden transitions [2]. The optical band gap of 2A5NPP was found to be 2.98 eV. The obtained band gap value is well matched with the previously estimated value from the equation 1. The reflectance (R) in terms of absorption coefficient can be calculated from the following equation.

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha)\,T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) - \exp(-2\alpha)\,T} \text{ ------} (4)$$

The refractive index (n_0) was determined from the reflection data using the following equation [3].

$$n_0 = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \text{ ----------} (5)$$

The extinction coefficient of the title crystal was determined by the following equation.

$$K = \frac{\lambda\alpha}{4\pi} \text{ ----------} (6)$$

From the optical constants, the electric susceptibility (χ_c) can be calculated using the following relations [4].

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_c = n^2 - K^2 \text{ ----------} (7)$$

$$\chi_c = \frac{n^2 - K^2 - \varepsilon_0}{4\pi} \text{ ----------} (8)$$

where, ε_0 is the dielectric constant (305.08) for the 2A5NPP crystal at the frequency of 1 MHz. The real part of dielectric constant (ε_r) and imaginary part of dielectric constant (ε_i) can be calculated using the following relations [4].

$$\varepsilon_r = n^2 - K^2 \ and \ \ \varepsilon_i = 2nK \text{ ---------- (9)}$$

2. Determination of solid state parameters

The density of the grown crystal was calculated by the following equation.

$$\rho = \frac{M.W \times Z}{N_a \times V} \text{ ---------- (10)}$$

where M.W is the molecular weight of the grown crystal (313.29 g/mol), Z is the number of molecules in the unit cell, N_a is Avogadro's number (6.023×10^{23} mol^{-1}) and V is the volume of the unit cell (V = 1359.6 $Å^3$). The valence electron plasma energy ($\hbar\omega_P$) was calculated by the following equation [5].

$$\hbar\omega_p = 28.8\left(\frac{Z' \times \rho}{M.W}\right)^{\frac{1}{2}} \text{ ---------- (11)}$$

where, Z' is the total number of valence electrons for 2A5NPP molecule (chemical formula is $C_{11}H_{11}N_3O_6S$) and it can be calculated by the following equation.

$$Z' = (11 \times Z_C) + (11 \times Z_H) + (3 \times Z_N) + (6 \times Z_O) + (1\times Z_S) \text{ ---------- (12)}$$

From that, Z' was found to be 112 and it was obtained by the substituting for each atom of C, H, N, O and S the corresponding valence electrons 4, 1, 5, 6 and 6 respectively. The $\hbar\omega_p$ is valid for free electrons and it can be used for insulator and semiconducting materials [6]. The Penn energy (E_p) of the grown crystal was calculated by the following relation.

$$E_p = \frac{\hbar\omega_p}{\sqrt{(\varepsilon_r - 1)}} \text{ ---------- (13)}$$

The Fermi energy (E_f) of grown crystal was calculated from the following relation [6].

$$E_f = 0.2948\,(\hbar\omega_p)^{\frac{4}{3}} \text{ ---------- (14)}$$

Substituting the values of ($\hbar\omega_p$), (E_p) and (E_f) in the equation 15, we get electronic polarizability (α) of 2A5NPP single crystal.

$$\alpha = \left[\frac{(\hbar\omega_p)^2\ S_0}{(\hbar\omega_p)^2\ S_0 + 3E_p^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\, cm^3 \text{ ------- (15)}$$

where S_0 is a constant for the particular material and it can be calculated by the following relation.

$$S_0 = 1 - \left[\frac{E_p}{4E_f}\right] + \frac{1}{3}\left[\frac{E_p}{4E_f}\right]^2 \text{ ---------- (16)}$$

The value of electronic polarizability (α) can be also calculated using Clausius-Mossotti equation, which is given by the following relation [7].

$$\alpha = \frac{3M}{4\pi N_a \rho}\left[\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right] \text{ ---------- (17)}$$

Here, 'N_a' is Avogadro number (6.022×10^{23} mol^{-1}). The obtained (α) value (from equation.17) also confirmed by the Clausius-Mossoti equation, which closely matched with the values is obtained from equation 15.

According to Maxwell relation, the dielectric permittivity (ε) is equal to the square root of refractive index (for visible light (high-frequency electric field)), $\varepsilon = n_0^2$. The linear refractive index (n_0) of the grown crystal has been calculated from the UV-Vis-NIR analysis and it was found to be 1.43 at 532 nm. The relationship between the electronic polarizability (α) and the refractive index (n_0) in such fields can be described by the Lorentz- Lorenz equation [8] given by

$$\alpha = \frac{3M}{4\pi N_A \rho}\left(\frac{n_0^{\ 2} - 1}{n_0^{\ 2} + 2}\right) \text{ ---------- (18)}$$

The calculated electronic polarizability (α) is highly sensitive to the band gap (E_g) of the given material. The value of electronic polarizability (α) of the 2A5NPP crystal was also confirmed by using the optical band gap and it can be calculated by the following relation.

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \text{ ---------- (19)}$$

Here, substitution value of the band gap (E_g) is 2.98 eV, as determined through UV-Visible NIR analysis by Tauc's plot method. The electronic polarizability (α) value (from equation.19) is well matched with the value obtained from the equation 15.

The electronic polarizability of the grown crystal can be also calculated by the coupled dipole method (CDM). In this method, each atom in a cluster is considered as a Lorentz atom, in which the electron is bound to the nucleus by a harmonic force. The atoms have no permanent electric dipole moment, but their dipole moments are induced by the local electric field. Thus, if the electron is at a non-zero distance from the nucleus, each atom behaves as an induced electric dipole moment [8]. The electronic polarizability of the title crystal was calculated using the following relation.

$$\alpha = \frac{Z' e^2}{m_e \omega_o^2} \text{ ---------- (20)}$$

where Z' denotes the total number of valence electrons, e is the charge of the electron (1.602×10^{-19}), m_e is the mass of the electron (9.1×10^{-28}) and w_0 is the natural frequency ($2\pi f_0$), f_0 is 1 MHz.

References

1. J. Tauc, R. Grigorovic, A. Vancu, Phys. Status Solidi B, 1966, **15**, 627-637.
2. N. Sudharsana, V. Krishnakumar and R. Nagalakshmi, *J. Cryst. Growth*, 2014, **398**, 45-57.
3. G. Anandha babu, R. Ramasamy, P. Ramasamy, Mat. Chem. Phy., 117 (2009) 326-330.
4. M. A. Gaffar, A. A. El-Fadl, S. B. Anooz, Physica B, 2003, **327**, 43-54.
5. N. Ravindra, V. Srivastava, Infra. Phys., 1980, **20**, 67-69.
6. G. Morgan, N. Shahtahmasebi, Jour. of Phy. C: Sol. Sta. Phy., 1973, 63385-3402.
7. P. Rysselberghe, *J. Phys. Chem.*, 1932, **36**, 1152-1155.
8. P. Karuppasamy, V. Sivasubramani, M. Senthil Pandian, P. Ramasamy, *RSC Adv*., 2016, **6**, 109105-109123.

Figure captions

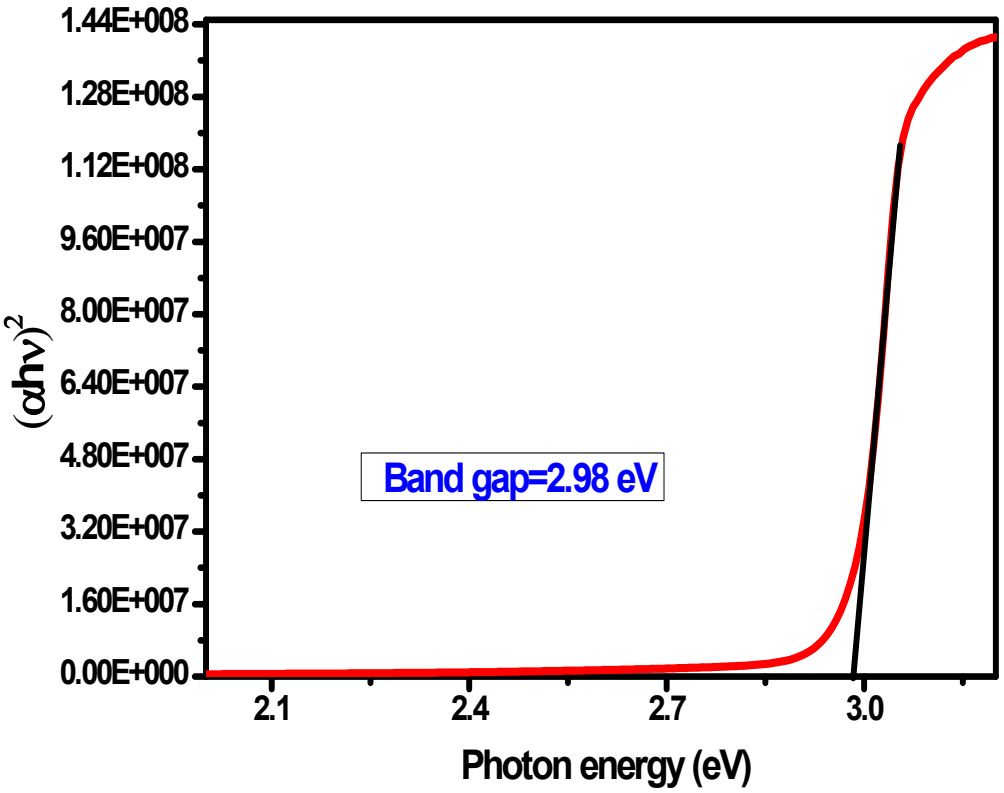
Figure S1. Band gap spectrum of 2A5NPP single crystal (E_g=2.98 eV)

Figure S2. Photoconductivity spectrum of 2A5NPP single crystal with respect to applied voltage

Table captions

Table S1 (a). The comparison of bond lengths for 2A5NPP molecule obtained from single crystal XRD and DFT method

Table S1 (b). The comparison of bond angles for 2A5NPP molecule obtained from single crystal XRD and DFT method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1.28E+008
1.12E+008
9.60E+007
8.00E+007
6.40E+007
4.80E+007
3.20E+007
1.60E+007
0.00E+000
(αhν)2
Band gap=2.98 eV
2.1
2.4
2.7
3.0
Photon energy (eV)

Figure S1.

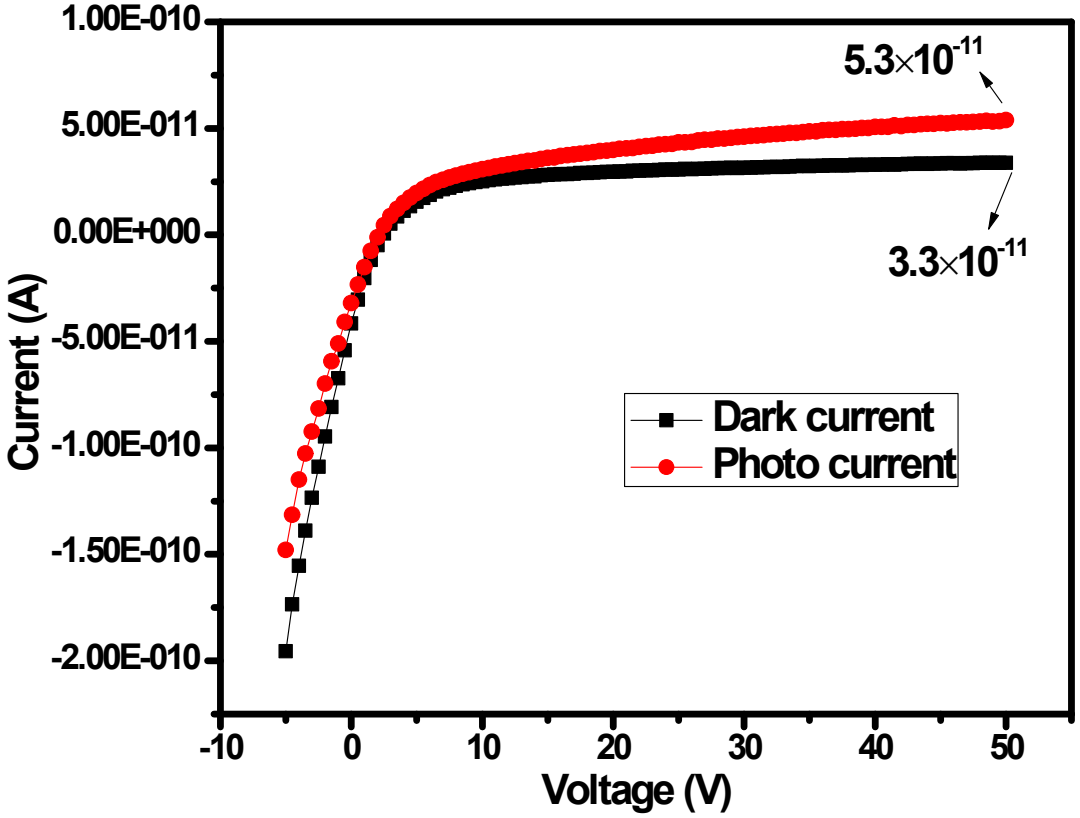
1.00E-010
5.00E-011
0.00E+000
-5.00E-011
-1.00E-010
-1.50E-010
-2.00E-010
Current (A)
-10
0
10
20
30
40
50
Voltage (V)
5.3×10-11
3.3×10-11
Dark current
Photo current

Figure S2.

Table S1 (a).

Bond length	Calculated values in (Å)	XRD (Å) taken from reference [48]
C1-C2	1.409	1.399
C1-C6	1.37	1.348
C1-H23	1.083	0.96
C2-C3	1.367	1.356
C2-N7	1.473	1.448
C3-N4	1.352	1.341
C3-H24	1.082	0.954
N4-C5	1.366	1.355
N4-H11	1.045	0.895
C5-C6	1.42	1.423
C5-N10	1.332	1.304
C6-H25	1.083	0.955
N7-O8	1.222	1.216
N7-O9	1.22	1.226
N10-H26	1.009	0.846
N10-H27	1.027	0.87
H11-O21	1.695	---
C12-C13	1.369	1.379
C12-C17	1.422	1.389
C12-H28	1.083	0.962
C13-C14	1.423	1.379
C13-H29	1.085	0.957
C14-C15	1.426	1.379
C14-O22	1.32	-
C15-C16	1.369	1.385
C15-H30	1.083	0.965
C16-C17	1.417	1.384
C16-H31	1.083	0.956
C17-S18	1.785	1.763

S18-O19	1.479	1.451
S18-O20	1.483	1.451
S18-O21	1.49	1.452
O19-H27	1.835	-
O22-H32	0.97	-

Table.S1 (b).

Bond angles	Calculated values in (°)	XRD (°) taken from reference [48]
C2-C1-C6	119.4	120.1
C2-C1-H24	119.1	120.2
C6-C1-H23	121.5	119.4
C1-C2-C3	120.1	120.1
C1-C2-N7	120.7	121.2
C3-C2-N7	119.2	118.7
C2-C3-N4	119.7	119.1
C2-C3-H24	123.1	120.2
N4-C3-H24	117.2	120.6
C3-N4-C5	123.1	123.6
C3-N4-H11	116.8	115.8
C5-N4-H11	120.1	120.4
N4-C5-C6	117.6	117.3
N4-C5-N10	119.0	119.7
C6-C5-N10	123.4	123.0
C1-C6-C5	120.2	119.6
C1-C6-H25	121.0	120.1
C5-C6-H25	118.8	120.2
C2-N7-O8	117.0	118.5
C2-N7-O9	116.7	116.9
O8-N7-O9	126.3	124.5
C5-N10-H26	119.1	116.5
C5-N10-H27	123.2	123.4
H26-N10-H27	117.6	116.8
C13-C12-C17	119.5	119.2
C13-C12-H28	121.2	120.1
C17-C12-H28	119.2	120.6
C12-C13-C14	119.1	120.1
C12-C13-H29	121.0	120.5
C14-C13-H29	119.9	119.3
C13-C14-C15	121.3	120.5
C14-C15-C16	119.3	120.1
C14-C15-H30	118.4	120.2
C16-C15-H30	122.3	119.7
C15-C16-C17	119.3	119.2
C15-C16-H31	121.4	120.4
C17-C16-H31	119.2	120.3
C12-C17-C16	121.4	120.8
C12-C17-S18	118.8	119.9