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**GRAPHICAL ABSTRACT** 



# Synthesis, molecular structure and vibrational analysis of D-D-A based carbazole decorated phenothiazine-3-carbaldehyde: Experimental (FT-IR, UV and NMR) and density functional theory (DFT) calculations

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#### ABSTRACT

A novel molecule, 10-(9-hexyl-9*H*-carbazol-3yl)-10*H*-phenothiazine-3-carbaldehyde (**CZPTZA**) has been synthesized and characterized through FT-IR, UV-Vis, NMR spectroscopic studies and molecular orbital calculations. Optimized geometrical structure, harmonic vibrational frequencies and NMR are computed with B3LYP method using 6-311++G(d,p) basis set. The geometrical parameters of the title compound obtained from Single Crystal XRD studies have been found in accord with the calculated (DFT) values. The experimentally observed vibrational frequencies are compared with the calculated ones, which were found to be in good agreement with each other. UV-Vis spectra of the title compound have also been recorded and the electronic properties, *viz.* excitation energies, calculated energies, oscillator strengths, frontier orbital energies and band gap energies are computed with TD-DFT/CAM-B3LYP method using 6-311++G(d,p) as the basis set. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the molecule have been calculated by the Gauge Independent Atomic Orbital (GIAO) method and compared with the experimental outcome. Also, the values of dipole moment, polarizabilities and first order hyperpolarizabilities have been computed.

#### Key words:

Carbazole, Phenothiazine, Vibrational analysis, HOMO-LUMO, Electrostatic potential.

#### Introduction

Organic molecules with donor-acceptor deeds are found as emerging materials towards solar energy cells [1] owing to their low cost, chemical versatility and trouble-free fabrication compared to other alternative solar cell technologies. In addition, the conjugated  $\pi$ -electron systems with specific functional scaffolds like cyanoacrylic acid [2] and carboxylic acid [3] have been stimulated to enhance the electrical and optical properties. In the past decades, a diverse range of molecules including organic dyes [4], metal-based dyes [5], dendrimers [6] and polymers [7] has been extensively used as efficient sensitizers in organic solar cells (OSCs). Recently, smaller molecules attracted the study in order to improve the efficiency of energy conversion and to realize the structure-property relationship. Thus, many researchers around the globe focused their attention to organic photoactive materials with simple synthetic processes and low costs.

Carbazole (CZ), also known as 9-azafluorene, is a nitrogen containing heteroaromatic compound. The presence of nitrogen at position 9 of the CZ ring increases the electron rich nature of CZ. Carbazole derivatives have been widely studied in OSC due to their ability to form stable radical cations [8], excellent thermal and photochemical stabilities [9] and easy availability. Further, the synthesis and applications of its derivatives have been an increasing area of research in the past couple of decades.

On the other hand, phenothiazine (PTZ) is an excellent electron donating chromophore as a result of its good thermal [10] and electrochemical stability [11]. Hence, it is widely used in chemical manufacturing as organic light emitting diodes (OLEDs) [12], semiconductors [13] and in solar cells applications [7]. Phenothiazine ring system has been chemically modified to exhibit various activities like anti-malarial [14], anti-cancer [15], anti-helminthic [16], anti-histamine [17] and anti-psychotic ones [18].

The wide variety of applications of organic molecules possessing carbazole and phenothiazine structural motifs reported in the literature inspired us to prosecute research on novel system carrying these two carbazole and phenothiazine moieties and, we herein report a D-D-A type molecule 10-(9-hexyl-9H-carbazol-3yl)-10H-phenothiazine-3-carbaldehyde (CZPTZA), in which the phenothiazine moiety is employed as primary unit. The compound CZPTZA was synthesized by adopting multi-steps synthetic strategy and analyzed using both experimental as well as computational methods. Optimized structural parameters were obtained by Density Functional Theory (DFT) by performing B3LYP/6-311++G(d,p) level of calculations. From the theoretical results, optimized structural parameters, vibrational assignments and chemical shift values are deduced and compared with the experimental results. The theoretical results are found to be in good agreement with the experimental ones.

## **Experimental section**

#### General

The melting point of the title compound was measured in open capillary and is uncorrected. FT-IR spectrum of the synthesized compound was recorded on Shimadzu IR Tracer-100 in the range of 400-4000 cm<sup>-1</sup> using KBr pellet form. The spectral features are reported in wavenumber (cm<sup>-1</sup>). <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker 400 MHz spectrometer. Chemical shift values are reported in parts per million (ppm) from tetramethylsilane (TMS). Single Crystal XRD data were collected on a Bruker, 2008 SMART APEX II diffractometer. All diffraction measurements were performed at 273 K using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å).

## Synthesis of 10-(9-hexyl-9H-carbazol-3yl)-10H-phenothiazine-3-carbaldehyde (CZPTZA)

The intermediates, 10*H*-phenothiazine-3-carbaldehyde and 9-hexyl-3-iodo-9*H*-carbazole are synthesized by adopting literature methods.

To a solution of 10*H*-phenothiazine-3-carbaldehyde (0.50 g, 2.4 mmol) and 9-hexyl-3iodo-9*H*-carbazole (0.94 g, 2.5 mmol) in 1,2-dichlorobenzene (20 mL) under nitrogen atmosphere, were added copper powder (0.30 g, 4.7 mmol), powdered potassium carbonate (0.90 g, 6.5 mmol) and 18-crown-6 (0.11 g, 0.4 mmol). The reaction mixture was heated to reflux for 48 h and filtered after cooling to room temperature. The solvent was removed under reduced pressure and the mixture was extracted with dichloromethane after the addition of water. The organic phase was then separated, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The solid thus obtained was subjected to column chromatography using 5~25% ethylacetate in hexane as eluent to afford pure 10-(9-hexyl-9*H*-carbazol-3-yl)-10*H*phenothiazine-3-carbaldehyde. Yield: 0.79 g (69%).

Pale Yellow solid; mp: 158-160 °C; FT-IR (KBr, cm<sup>-1</sup>): 3052-2805 (C-H<sub>aromatic & aliphatic</sub>), 1661 (C=O<sub>aldehyde</sub>), 1594 (C=C), 1245, 1204 (C-N), 1072 (C-S); <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 400 MHz): 9.66 (s, 1H), 6.16-8.08 (m, 14H), 4.35 (d, 2H, CH<sub>2</sub>); 1.33-1.94 (m, 8H); 0.87 (t, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>, 100 MHz): 14.07 (C1), 22.62 (C2), 27.07 (C4), 29.06 (C5), 31.61 (C3), 43.49 (C6), 189.82 (C=O<sub>aldehyde</sub>), 109.24, 110.93, 115.28, 116.78, 118.86, 119.55, 119.87, 120.69, 122.35, 122.45, 123.30, 124.75, 126.57, 126.65, 127.11, 127.37, 127.54, 130.01, 130.80, 130.82, 139.91, 141.07, 143.34, 150.07 (aromatic carbons).

#### Computational details

The entire set of calculations was performed in DFT-B3LYP method with 6-311++G(d,p) basis set using Gaussian 09 program package [19]. The gradient corrected density functional theory (DFT) with the three parameter hybrid functional Becke3 (B3) for the exchange part and the Lee-Yang-Parr (LYP) correlation function [20] have universally been used as a cost effective approach. The frequency values computed at these levels contain known systematic errors. To bring the theoretical frequencies in close proximity to the experimental values, the scaling factor value [21] of 0.96 was used. UV-Vis absorption spectra were calculated by time dependent-DFT with CAM-B3LYP/6-311++G(d,p) basis set in both gas and solution phase. NMR chemical shifts were computed at B3LYP/6-311++G(2d,p) level using the Gauge Independent Atomic Orbital (GIAO) method [22]. The <sup>1</sup>H and <sup>13</sup>C isotropic chemical shift values were referenced to the corresponding values of TMS, which was calculated at the same level of theory.

#### **Results and Discussion**

#### Synthesis

Copper mediated Ullman type coupling reaction between 10*H*-phenothiazine-3carbaldehyde,[23] synthesized by adopting Duff reaction on commercially available 10*H*- phenothiazine and 9-hexyl-3-iodo-9*H*-carbazole, [23] synthesized by using alkylation followed by iodination reaction on commercially available carbazole, provided the title compound 10-(9-hexyl-9*H*-carbazol-3-yl)-10*H*-phenothiazine-3-carbaldehyde in good yield (69 %). The schematic representation for the synthesis of **CZPTZA** is outlined in **Scheme 1**. The product was then characterized by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR and Single crystal X-ray diffraction analysis.

#### Scheme 1.

#### Molecular geometry

The analyzed crystal (CCDC No. 1479040) was grown by slow evaporation technique using chloroform as solvent at room temperature. Crystal system of the compound **CZPTZA** belongs to monoclinic with P21/n symmetry. Details of the crystal data and refinement parameters of **CZPTZA** are summarized in **Table 1**. An ORTEP view and numbering scheme of **CZPTZA** is shown in **Fig. 1a**. Selected bond lengths, bond angles and dihedral angles of **CZPTZA** are summarized in **Table 2**.

XRD single crystal structure reveals that the CZ and PTZ motifs are nearly perpendicular to each other as evidenced by the dihedral angle of C4/C8 and C22/C18 through N7-C17 are 93.1(4), -85.1(4), -89.3(4) and 92.5(4)°, respectively. The mean C-C single bond length is~1.46 Å, which is in good agreement with the expected range for a C-C single bond. Single bond lengths of carbon-nitrogen and carbon-sulfur are about~1.40, and~1.74 Å, respectively. Bond lengths among the CZ and PTZ ring carbons are around~1.39 Å, the expected range. Bond angles of sp<sup>2</sup> hybrid of CZ and PTZ rings are around 120°. The values of selected bond lengths, angles

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and torsion angles are given in **Table 2**. The geometric parameters of theoretically computed optimized structure of compound **CZPTZA** have been compared with the X-ray crystal structure which showed no significant difference; the largest deviation in bond distance is 0.1 Å.

The optimized molecular structure of CZPTZA is shown in Fig. 1b and geometrical parameters are presented in Table 2. In the optimized geometry, the bond angles and the dihedral angles between the planes C4-N7-C8 (121.7°)/C5-S10-C9 (98.9°) and N7-C4-C5-S10 (-6.9°) N7-C8-C9-S10 (8.6°) imply that the central six membered ring in the PTZ scaffold exists in nonplaner geometry [24] and this ring adopts a boat conformation while the CZ unit adopts planarlike geometry [25]. Further, the CZ structural motif is oriented in the equatorial position of the central heterocyclic ring of phenothiazine with boat conformation and, as a whole; this CZ motif is oriented in almost perpendicular to that of the phenothiazine structural unit. It is reported that all the carbon-carbon bond lengths in the CZ and PTZ structural motifs are between carboncarbon single bond and double bond, implying that there exists an extensive electron delocalization throughout the molecules [26]. The bond lengths in CZ and PTZ are~ 1.410Å; closer to the calculated values for carbon-carbon bond. The C-N bond lengths of the investigated compound are shorter than the average single C-N bond length of 1.472, being C4-N7 = 1.412(4), N7-C8 = 1.388(4), N7-C17 = 1.444(4), C20-N25 = 1.379(4), C24-N25 = 1.367(5) and N25-C30 = 1.462(5) Å, thus showing varying degrees of single bond character [27]. The other bond lengths and angles computed by DFT method show good agreement with their single crystal XRD values [28].

#### Fig. 1.

#### Table 2

#### Vibrational analysis

The molecular structure of **CZPTZA** consists of 63 atoms, showing a total number of 183 normal modes of vibrations which are assigned by using PED. Most of the observed vibrational patterns coincide with theoretically calculated vibrational modes. Both experimental and theoretical FT-IR spectra of compound **CZPTZA** are shown in **Fig. 2** and vibrational frequencies are furnished in **Table 3**.

The C-H stretching in alkyl groups occurs at lower frequencies than those in aromatic ring i.e., 2970-2840 cm<sup>-1</sup> [29]. In the present case, the weak and medium bands for C-H stretching vibrations of the hexyl side chain in CZ ring are observed at 2957-2805 cm<sup>-1</sup> in FT-IR, while the calculated stretching frequencies lies in the spectral range around 2963-2874 cm<sup>-1</sup>. The deformation vibrations of C-H at 1402-1369 and 920-842 cm<sup>-1</sup> in FT-IR are assigned to mixture of deformation modes with C-H and skeleton vibrations. All these assignments are in good agreement with literature values [28c, 30].

The C-H stretching vibrations in aromatic and hetero-aromatic rings appear in the range  $3100-3000 \text{ cm}^{-1}$  which is the characteristic region for the ready identification of such C-H

stretching vibrations [29]. The C-H stretching frequency is observed at 3052-3007 cm<sup>-1</sup> in the FT-IR spectrum and the computed C-H stretching vibrations of CZ and PTZ rings obtained at 3087-3033 cm<sup>-1</sup>. Hence, these experimental and computational C-H stretching vibrations are in good agreement with each other. The C-H in-plane bending vibrations of **CZPTZA** are observed at 1134-1015 cm<sup>-1</sup> in the FT-IR spectrum and the computed values of C-H in-plane and out of plane bending vibrations, listed in **Table 3**, are in good agreement with the experimental values.

#### Fig. 2.

In general, ring carbon-carbon vibrations (C-C and C=C) are observed in the region 1630-1480 cm<sup>-1</sup> [31]. In the present study, the wavenumbers observed in FT-IR at 1570-1463 cm<sup>-1</sup> are due to C-C stretching vibrations. The computed frequencies at 1594-1457 cm<sup>-1</sup> by DFT method show a good agreement with experimental results. The in-plane and out-of plane bending C-C-C modes of compound **CZPTZA** are presented in **Tables 3**.

#### Table 3

Compounds containing carbonyl group show a strong absorption in the region of 1750-1650 cm<sup>-1</sup> [32]. The characteristic FT-IR band appeared at 1661 cm<sup>-1</sup> in the title compound confirms the presence of carbonyl group in the same. The computed carbonyl stretching vibration of aldehyde carbonyl is observed at 1687 cm<sup>-1</sup> which correlates well with the experimental value. The assignment due to the C-N and C-S stretching vibrations is difficult to identify in the infrared spectrum as the band is of variable intensity and may be found over the wide range. The C-N and C-S stretching bands are found to be present at 1220 and 1080 cm<sup>-1</sup> [29,32]. The observed bands at 1204/1245 and 1072 cm<sup>-1</sup> correspond to C-N and C-S units, respectively. The corresponding calculated values for C-N and C-S are 1205/1248 and 1089 cm<sup>-1</sup>, respectively.

The linear regressions between the experimental and theoretical scaled wavenumbers obtained for CZPTZA with B3LYP/6-311++G(d,p) method are presented in supplementary Fig. S1. The minimal RMS deviation confirms the reliability of the assignments of the fundamental modes of the compound CZPTZA.

## Fig. S1.

## Mulliken population analysis

The partial atomic charge distribution of individual atom is established using Mulliken population method. Electrons population of compound **CZPTZA** were obtained from the optimized structural calculation at B3LYP/6-311++G(d,p) level and the values are listed in supplementary **Table S1**. The net atomic charge distribution of compound **CZPTZA** is furnished in **Fig. 3**. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule [33]. In the compound **CZPTZA**, nitrogen, N7 and carbon, C13 atoms have attained more positive charge and become more acidic, whereas the carbons, C17 and C35 have more negative charge than other atoms due to the connection

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through more electronegative nitrogen atom. In the carbazole and phenothiazine moieties, the positive charges are localized on the hydrogen atoms and all the carbon atoms have negative charges except C5, C6, C13, C15 and pyrrole skeleton in carbazole which suggests that the electron delocalization takes place in the entire molecule [34].

#### Fig. 3.

### Table S1

#### UV-Vis spectral analysis

The UV-Vis spectroscopic parameters such as wavelengths, excitation energies, band gap energies and oscillator strengths of the title compound have been computed by TD-DFT method with CAM-B3LYP/6-311++G(d,p) basis set in both vacuum as well as solvent phase and their pertinent parameters are tabulated in supplementary **Table S2**. The experimental UV-Vis spectrum of the **CZPTZA** has been obtained in acetonitrile, dichloromethane, dimethylsulfoxide, ethanol and hexane. The experimental and simulated UV-Vis spectra of the **CZPTZA**, are displayed in **Fig. 4**.

As can be seen in **Fig. 4** and supplementary **Table S2**, three distinctive bands are observed for the compound **CZPTZA** in all solvents. The bands observed in the wavelengths of ~ 400,~ 350 and~ 290 nm have been assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions, associated with the carbaldehyde functional group and CZ & PTZ groups, respectively (i.e., ~400 nm;  $n \rightarrow \pi^*$ ; CHO and ~350 & 290 nm;  $\pi \rightarrow \pi^*$ ; CZ & PTZ). The absorption intensities are slightly increased in non-polar solvents compared to polar solvents (**Fig. 4**). This hyperchromic shift probably points to

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the deprotonation of the compound in the solution. The observed  $\lambda_{max}$  values and the calculated  $\lambda$  excitation wavelengths agree reasonably well except the lowest energy excitation above 300 nm.

Fig. 4.

#### Table S2

#### HOMO-LUMO analysis

The electron distribution of frontier molecular orbitals HOMO and LUMO of compound **CZPTZA** is shown in supplementary **Fig. S2** and their corresponding energy values are provided in supplementary **Table S3**. The charge transport properties and electronic structure of the molecule are mainly depending on energy differences; hence, it is necessary to examine the HOMO-LUMO energy gap [35]. The difference in calculated HOMO-LUMO energy values of ground state, first and second excited states are found to be 1.5484, 3.0809 and 4.1172 eV, respectively. As can be seen from the molecular orbitals of **CZPTZA**, the HOMOs of molecular charges are nearly located over the CZ moiety, while the LUMO and LUMO+1 are almost localized over the entire **CZ** and PTZ moieties. Thus, the electronic transition from the HOMO (ground state) to the LUMO (excited state) is mainly electron flowing from the CZ ring to the PTZ ring, which belongs to  $\pi$ - $\pi$ \* transition. The Gauss-Sum 2.2 Program [36] has been used to calculate the group contribution of molecular orbitals and to determine the density of states (DOS) of the molecule as shown in supplementary **Fig. S3**. DOS plot shows the population of orbital compositions with their contribution to chemical bonding and demonstrates a clear view of the character of the molecular orbitals in a certain energy range.

Fig. S2.

**Fig. S3.** 

Table S3

#### Molecular electrostatic potential (MEP) analysis

The MEP of a molecule is related to electron density (ED), which measures the reactivity of the molecule and determine the nature of the molecule [37]. The MEP, easily interpreted as a color spectrum, with red and blue as the lowest and highest electrostatic potential energy values respectively, employed to convey the varying intensities of the electrostatic potential energy values. The supplementary **Fig. S4** illustrates total density and electrostatic potential with its contour model of the compound **CZPTZA**, computed at the 0.002 a.u isosurface of the molecule.

From the MEP pictures, it could be observed that the color code of the maps is in the range between -0.111 (electrophilic attacking site) and 0.111 E (nucleophilic attacking sites), the areas of high potential (red), are characterized by an abundance of electrons. Oxygen has a higher electronegativity value than nitrogen and sulfur. Oxygen atom would consequently possess higher electron density around it than nitrogen and sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. However, the light yellow region spread on the MEP surface due to potential halfway between the two extreme regions and this confirms the existence of an intermolecular interaction.

#### Fig. S4.

#### Nuclear Magnetic Resonance spectral analysis

The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts calculation of compound CZPTZA have been made by B3LYP with 6-311++G(2d,p) basis set, compared with the experimental values and are presented in supplementary Table S4 and the experimental and theoretical spectra are furnished in supplementary Fig. S5. In the <sup>1</sup>H NMR, a sharp triplet appeared in the up field region at 0.87 ppm with three protons integral reveals the presence of methyl protons of hexyl side chain (H61, H62 and H63) and the experimental values are in good agreement with their computed chemical shifts (at 0.82, 0.84 and 1.10 ppm). There are five methylene groups present in the hexyl side chain. An eight protons multiplet appeared in the shielded region (1.33-1.94 ppm) corresponds to protons of four methylene groups (H53-H60) and a two protons triplet observed in the comparatively downfield region (4.35 ppm) corresponds to protons of other methylene group, directly attached to nitrogen atom of CZ moiety. All these methylene protons are matched well with their corresponding signals in computed one. A sharp singlet resonates in the extreme downfield region at 9.66 ppm with one proton integral corresponds to proton of aldehyde moiety and this value coincides with the computed one (9.34 ppm). A collection of signals obtained in low field region at 6.16-8.08 ppm corresponds to aromatic protons of CZ and PTZ moieties and these values are in harmony with the theoretical results.

#### Fig. S5.

In the <sup>13</sup>C-NMR, the aromatic carbon signals fall in overlapped areas of the spectrum with the chemical shifts ranging from 100 to 160 ppm in organic molecules [38]. The aromatic carbons appeared in the deshielded region from 109 to 150 ppm are in accordance with the calculated results. The shielded signals around 14.0-43.4 ppm are assigned to the hexyl side chain carbons (C30-C35) attached to the CZ ring, which are in good agreement with the calculated values of 13.7-42.5 ppm. A signal for carbonyl carbon of PTZ appeared in the extreme downfield region at 189.8 ppm. In the computed one, the characteristic signal appeared at 182.8 ppm is assigned to carbonyl carbon. The correlation coefficient values show a good agreement between the experimental and the calculated results as shown in supplementary **Fig. S6**.

#### Fig. S6.

#### Table S4

## Non-linear optical (NLO) properties

In order to investigate the relationship between molecular structure and non-linear optical properties (NLO), the polarizabilities and first order hyperpolarizabilities of the molecule was calculated. It is well known that molecules with high values of dipole moment, molecular polarizability, and first hyperpolarizability show more active NLO behaviours [39]. The first hyperpolarizability ( $\beta$ ) and the components of hyperpolarizability ( $\beta_x$ ,  $\beta_y$  and  $\beta_z$ ) of compound **CZPTZA** and the related properties ( $\mu_0$ ,  $\alpha_{total}$ , and  $\alpha_0$ ) are listed in supplementary **Table S5**.

The calculated value of total dipole moment is found to be 7.7134 Debye and average polarizability is 5.4894 x  $10^{-23}$  Debye-Ang. However, the average polarizability of the synthesized compound **CZPTZA** is greater than that of *p*-nitroaniline molecule which is a typical NLO material [40]. The magnitude of molecular hyperpolarizability ( $\beta$ ) is one of the important key factors for a NLO system. As can be seen from supplementary **Table S5**, the calculated first hyperpolarizability value ( $\beta$ ) of compound **CZPTZA** is 3.9046 x  $10^{-30}$  esu. Further, the first hyperpolarizability value is compared with the standard material, urea (0.372 x  $10^{-30}$  esu). The hyper-polarizability values ( $\beta$ ) of **CZPTZA** is nearly ten times greater than that of urea [41] and the dipole moment is also higher than that of urea (1.373 Debye). From the above results, it is concluded that the molecular polarizability and hyperpolarizability of the synthesized compound **CZPTZA** in all coordinates are active.

## Table S5

#### Conclusion

The title compound **CZPTZA** was synthesized by copper mediated Ullman type coupling reaction between 10*H*-phenothiazine-3-carbaldehyde and 9-hexyl-3-iodo-9*H*-carbazole in 1,2-dichlorobenzene under phase transfer catalytic condition. The scaled vibrational frequencies are in good agreement with the experimental results; the vibrational modes are assigned based on TED calculation. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values are in good harmony with the experimental results. The small HOMO-LUMO energy gap indicates the compound **CZPTZA** has potential applications in the field of OSCs. The predicted first hyperpolarizability value (β)

of molecule is nearly ten times greater than that of urea, which shows that the title chemical entity is an attractive object for future studies of nonlinear optical properties.

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Crystal data of CZPTZA.

10-(9-hexyl-9H-carbazol-3yl-)-1	0H-phenothiazine-3-carbaldehyde
Empirical formula	$C_{31}H_{28}N_2OS$
Formula weight	476.60
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
	$a = 11.9022(5) A$ $\alpha = 90^{\circ}$
Unit cell dimensions	$b = 9.2214(3) A$ $\beta = 100.096(2)^{\circ}$
	$c = 22.7176(8) A$ $\gamma = 90^{\circ}$
Volume	2454.76(16) A <sup>3</sup>
Z, Calculated density	4, 1.284 $Mg/m^3$
Absorption coefficient	$0.159 \text{ mm}^{-1}$
F(000)	1000
Theta range for data collection	1.815 to 28.898°
Limiting indices	-16 < h < 16, -12 < k < 12, -30 < l < 30
Reflections collected/unique	35686/6449 [R(int) = 0.0522]
Completeness to theta = $25.242$	100.0 %
Data/restraints/parameters	6449/0/327
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0915, $wR2 = 0.2685$
R indices (all data)	R1 = 0.1642, wR2 = 0.3327

nu. <u>s (all data,</u>

Selected structural parameters for CZPTZA.

Bond length	Calc.	Expt.	Bond length	Calc.	Expt.
C1-C2	1.391	1.376(7)	C17-C22	1.406	1.396(5)
C1-C6	1.393	1.358(6)	C18-C19	1.396	1.387(4)
C2-C3	1.393	1.379(5)	C19-C20	1.420	1.405(5)
C3-C4	1.402	1.396(5)	C19-C23	1.446	1.445(5)
C4-C5	1.406	1.395(5)	C20-C21	1.398	1.390(5)
C4-N7	1.424	1.412(4)	C20-N25	1.386	1.379(4)
C5-C6	1.393	1.396(5)	C21-C22	1.390	1.372(5)
C5-S10	1.779	1.744(4)	C23-C24	1.419	1.399(5)
N7-C8	1.406	1.388(4)	C23-C26	1.398	1.391(5)
N7-C17	1.444	1.444(4)	C24-N25	1.392	1.367(5)
C8-C9	1.411	1.408(4)	C24-C29	1.397	1.407(5)
C8-C11	1.410	1.402(5)	N25-C30	1.456	1.462(5)
C9-S10	1.780	1.753(4)	C26-C27	1.390	1.368(6)
C9-C14	1.388	1.364(5)	C27-C28	1.404	1.387(7)
C11-C12	1.384	1.366(5)	C28-C29	1.391	1.376(7)
C12-C13	1.400	1.388(5)	C30-C31	1.535	1.485(6)
C13-C14	1.400	1.387(5)	C31-C32	1.533	1.455(8)
C13-C15	1.472	1.445(5)	C32-C33	1.533	1.568(9)
C15-O16	1.214	1.202(5)	C33-C34	1.533	1.020(11)
C17-C18	1.390	1.378(5)	C34-C35	1.531	1.647(17)
Bond angle	Calc.	Expt.	Bond angle	Calc.	Expt.
C2-C1-C6	119.0	119.8(4)	C18-C17-C22	120.6	120.4(3)
C1-C2-C3	120.6	120.2(4)	C17-C18-C19	119.2	119.0(3)
C2-C3-C4	121.0	121.0(4)	C18-C19-C20	119.7	119.7(3)
C3-C4-C5	117.9	118.1(3)	C18-C19-C23	133.7	133.4(3)
C3-C4-N7	121.2	120.1(3)	C20-C19-C23	106.6	106.9(3)
C5-C4-N7	120.9	121.8(3)	C19-C20-C21	121.2	121.5(3)
C4-C5-C6	120.8	119.6(4)	C19-C20-N25	109.2	108.6(3)
C4-C5-S10	120.1	122.4(3)	C21-C20-N25	129.6	129.9(3)
C6-C5-S10	118.9	117.7(3)	C20-C21-C22	118.1	117.5(3)
C1-C6-C5	120.6	121.2(4)	C17-C22-C21	121.3	121.9(3)
C4-N7-C8	121.7	123.9(3)	C19-C23-C24	106.5	105.7(3)
C4-N7-C17	118.1	117.2(3)	C19-C23-C26	133.8	133.8(3)
C8-N7-C17	118.4	118.9(3)	C24-C23-C26	119.7	120.5(3)
N7-C8-C9	120.9	122.3(3)	C23-C24-N25	109.2	110.1(3)
N7-C8-C11	121.3	120.3(3)	C23-C24-C29	121.4	120.5(4)
C9-C8-C11	117.9	117.4(3)	N25-C24-C29	129.4	129.4(4)
C8-C9-S10	120.1	121.6(3)	C20-N25-C24	108.5	108.8(3)

C8-C9-C14	120.5	120.2(3)	C20-N25-C30	125.7	124.3(3)
S10-C9-C14	119.1	117.9(3)	C24-N25-C30	125.6	126.9(3)
C5-S10-C9	98.9	101.96(16)	C23-C26-C27	119.1	118.8(4)
C8-C11-C12	121.2	121.3(3)	C26-C27-C28	120.6	120.7(4)
C11-C12-C13	120.7	121.2(3)	C27-C28-C29	121.5	122.3(4)
C12-C13-C14	118.6	117.7(3)	C24-C29-C28	117.8	117.2(4)
C12-C13-C15	121.5	121.2(4)	N25-C30-C31	113.5	114.8(4)
C14-C13-C15	119.9	121.1(3)	C30-C31-C32	112.8	114.8(5)
C9-C14-C13	121.1	122.3(3)	C31-C32-C33	113.1	114.9(7)
C13-C15-O16	125.2	126.3(4)	C32-C33-C34	113.7	129.8(12)
N7-C17-C18	118.6	118.3(3)	C33-C34-C35	113.2	125.7(13)
N7-C17-C22	120.7	121.3(3)			
Dihedral angle	Calc.	Expt.	Dihedral angle	Calc.	Expt.
C6-C1-C2-C3	-1.0	1.0(7)	N7-C17-C18-C19	179.8	178.2(3)
C2-C1-C6-C5	-0.9	-2.8(7)	C22-C17-C18-C19	0.0	-0.1(5)
C1-C2-C3-C4	1.2	1.5(7)	N7-C17-C22-C21	-179.7	-178.4(3)
C2-C3-C4-C5	0.5	-2.2(6)	C18-C17-C22-C21	0.2	-0.2(5)
C2-C3-C4-N7	-179.9	176.4(4)	C17-C18-C19-C20	0.0	0.4(4)
C3-C4-C5-C6	-2.4	0.5(6)	C17-C18-C19-C23	-179.9	-179.1(3)
C3-C4-C5-S10	172.8	175.3(3)	C18-C19-C20-C21	0.0	-0.4(5)
N7-C4-C5-C6	178.0	-178.2(4)	C18-C19-C20-N25	179.7	179.8(3)
N7-C4-C5-S10	-6.9	-3.4(5)	C23-C19-C20-C21	179.8	179.2(3)
C3-C4-N7-C8	150.7	163.1(3)	C23-C19-C20-N25	-0.4	-0.6(3)
C3-C4-N7-C17	-13.7	-19.5(5)	C18-C19-C23-C24	179.7	179.5(3)
C5-C4-N7-C8	-29.6	-18.3(6)	C18-C19-C23-C26	-0.3	0.3(6)
C5-C4-N7-C17	166.0	159.2(3)	C20-C19-C23-C24	-0.1	-0.1(3)
C4-C5-C6-C1	2.6	2.1(7)	C20-C19-C23-C26	179.8	-179.2(4)
S10-C5-C6-C1	-172.6	-173.0(4)	C19-C20-C21-C22	0.2	0.2(5)
C4-C5-S10-C9	33.8	20.0(4)	N25-C20-C21-C22	-179.5	179.8(3)
C6-C5-S10-C9	-151.0	-165.1(3)	C19-C20-N25-C24	0.9	1.0(4)
C4-N7-C8-C9	28.7	16.8(6)	C19-C20-N25-C30	175.3	179.9(3)
C4-N7-C8-C11	-152.1	-164.2(4)	C21-C20-N25-C24	-179.5	-178.7(3)
C17-N7-C8-C9	-167.0	-160.6(3)	C21-C20-N25-C30	-5.0	0.2(6)
C17-N7-C8-C11	12.2	18.4(5)	C20-C21-C22-C17	-0.2	0.2(5)
C4-N7-C17-C18	-97.9	-85.1(4)	C19-C23-C24-N25	0.7	0.7(4)
C4-N7-C17-C22	82.0	93.1(4)	C19-C23-C24-C29	-179.7	-179.0(3)
C8-N7-C17-C18	97.2	92.5(4)	C26-C23-C24-N25	-179.3	180.0(3)
C8-N7-C17-C22	-82.9	-89.3(4)	C26-C23-C24-C29	0.4	0.3(5)
N7-C8-C9-S10	8.6	6.0(5)	C19-C23-C26-C27	179.9	178.8(4)
N7-C8-C9-C14	-177.4	178.7(3)	C24-C23-C26-C27	-0.2	-0.3(5)
C11-C8-C9-S10	-17/0.7	-173.0(3)	C23-C24-N25-C20	-0.9	-1.1(4)
CII-C8-C9-CI4	3.3	-0.3(5)	C23-C24-N25-C30	-175.4	-179.9(3)
N/-C8-C11-C12	1/9.4	-177.5(4)	C29-C24-N25-C20	1/9.4	1/8.6(4)
C9-C8-C11-C12	-1.3	1.6(6)	C29-C24-N25-C30	4.9	-0.2(6)
C8-C9-S10-C5	-34.7	-21.2(3)	C23-C24-C29-C28	-0.3	0.1(6)

C14-C9-S10-C5 C8-C9-C14-C13 S10-C9-C14-C13 C8-C11-C12-C13 C11-C12-C13-C14 C11-C12-C13-C14 C11-C12-C13-C15 C12-C13-C14-C9 C15-C13-C14-C9 C12-C13-C15-O16 C14-C13-C15-O16	151.2 -3.1 171.0 -1.0 1.3 -179.0 0.7 -179.0 0.1 179.9	$165.9(3) \\ -1.8(6) \\ 171.2(3) \\ -0.8(6) \\ -1.3(6) \\ 177.2(4) \\ 2.6(6) \\ -175.9(4) \\ 1.3(7) \\ 179.7(4)$		N25-C24-C29-C28 C20-N25-C30-C31 C24-N25-C30-C31 C23-C26-C27-C28 C26-C27-C28-C29 C27-C28-C29-C24 N25-C30-C31-C32 C30-C31-C32-C33 C31-C32-C33-C34 C32-C33-C34-C35	179.3 -87.0 86.6 0.0 0.1 179.8 -179.9 179.9 -180.0	-179.6(4) -77.5(5) 101.2(5) -0.1(6) 0.5(7) -0.5(7) -63.9(6) 177.0(6) 109(2) -6(4)
			C >		3	
			4			

Experimental and calculated vibrational frequencies values of CZPTZA with proposed assignment.

Mode	Expt Freq	Calc Freq	Calc Freq	Im	Assignment
No	(FT-IR)	(Unscaled)	(Scaled)	IR	Assignment
1		12	12	1.9	ГСССН (26)
2		16	15	1.34	$\Gamma CCCH(42) + \tau CCCC(20)$
3		22	21	1.64	ГСССН (32)
4		32	31	1.22	$\tau CCNC (35) + \Gamma CCCH (12)$
5		42	40	2.27	$\Gamma$ HCCH (20) + $\tau$ CCSC (32)
6		46	44	1.74	$\tau CCSC(24) + \tau CCCC(38)$
7		51	49	0.42	$\tau CCNC (22) + \beta CSC (15)$
8		70	67	1.19	$\tau CCNC (16) + \Gamma CCCH (26)$
9		93	89	5.51	τCCCC (28)
10		101	97	3.85	τCNCC (35)
11		103	99	3.37	τHCCH (18)
12		113	108	8.51	ГНССН (12)
13		128	123	7.46	$\tau CCCC(20) + \Gamma HCCH(32)$
14		133	128	3.7	τCCCC (33)
15		137	131	6.72	τCCCH (18)
16		145	139	2.72	$\tau CCCC(12) + \tau CCCH(20)$
17		153	147	2.36	ГНССН (26)
18		164	157	3.09	τCCCC (24)
19		199	191	5.9	τCCCC (22)
20		209	201	5.76	τCCNC (25)
21		235	226	9.67	τCCCH (28)
22		239	229	6.02	$\tau$ CCCH (18) + $\tau$ HCCH (12)
23		243	233	0.34	тСССН (32)
24		266	255	8.12	τCCCH (30)
25		272	261	8.3	τCCCH (38)
26		288	276	5.4	τCCCH (16) + ΓΗCCH (25)
27		292	280	10.43	$\tau$ CCCH (18) + $\Gamma$ HCCH (15)
28		314	301	11.92	$\Gamma CCCH(32) + \tau CCCC(10)$
29	$\rightarrow$	319	306	6.38	ГНССН (54)
30		332	319	5.92	$\tau CCCH (26) + \beta CCO (10)$
31		383	368	5.67	тСССН (20)
32		400	384	4.12	$\tau$ CCCH (18) + $\Gamma$ HCCC (20)
33		424	407	10.63	τCCCH (24)
34		434	417	6.41	$\beta$ CNC (22) + $\Gamma$ CCCH (15)

35		436	418	9.76	βCCN (25) + $Γ$ HCCH (10)
36		439	421	8.57	ГНССС (38)
37		440	422	3.72	βCCS (42)
38	430	452	434	8.76	$\tau$ CCCC (28) + $\beta$ CCS (14)
39		456	438	4.35	ГНССН (45)
40		465	446	10.43	ГНССН (38)
41	459	479	460	17.87	ГНССН (32)
42		522	501	11.8	ГСССН (22)
43		527	506	11.11	$\Gamma CCCH (40) + \Gamma HCCH (12)$
44		547	525	1.9	ГСССН (24)
45	546	571	548	11.08	ГСССН (28)
46		574	551	16.24	ГСССН (34)
47		584	561	10.08	$\Gamma CCCH (10) + \Gamma HCCH (46)$
48		617	592	20.26	ГСССН (42)
49	599	625	600	15.44	$\Gamma$ CCCH (38) + $\Gamma$ HCCH (32)
50		646	620	14.39	ГИССН (36)
51		657	631	10.67	ГСССН (32)
52	640	664	637	25.12	ГНССН (14)
53		681	654	9.53	ГНССН (26)
54		715	686	8.53	$\tau$ CCCH (64) + $\Gamma$ HCCH (18)
55		729	700	8.82	$\tau$ CCCH (26) + $\Gamma$ HCCH (40)
56		735	705	10	$\tau$ CCCH (32) + $\Gamma$ HCCH (28)
57		736	706	5.12	$\tau$ CCCH (44) + $\Gamma$ HCCH (16)
58		746	716	5.53	$\tau$ CCCH (22) + $\Gamma$ HCCH (34)
59		748	718	6.33	$\tau$ CCCH (30) + $\Gamma$ HCCH (10)
60		750	720	10.42	τCCCH (56)
61		752	722	38.18	τCCCH (48)
62		761	730	41.93	τCCCH (62)
63	735	767	736	18.55	$\beta$ CSC (18) + $\Gamma$ HCCH (30)
64		784	752	9.54	$\tau$ CCCH (28) + $\Gamma$ HCCH (44)
65		797	765	9.48	ГСССН (48)
66		811	778	27.19	ГСССН (32)
67	797	823	790	20.18	ГСССН (56)
68	813	844	810	22.63	ГСССН (52)
69	C	858	824	0.77	ГСССН (40)
70		865	830	2.01	$\beta$ CCC (28) + $\Gamma$ HCCH (64)
71		868	833	6.95	βHCO (72)
72	842	884	848	15.66	βHCC (40)
73		895	859	15.23	βHCC (64)
74		898	862	5.76	βHCC (58)
75		908	871	8.91	βHCC (36)
76		920	883	4.63	βHCC (68)
77		940	902	7.46	βHCC (48)

78		942	904	8.57	$\beta$ CSC (26) + $\Gamma$ HCCH (42)
79		944	906	12.61	$\beta$ CCO (34) + $\Gamma$ HCCH (16)
80	920	960	921	18.17	$\beta$ HCC (48) + ΓHCCH (32)
81		961	922	4.06	$\beta$ CCC (60) + $\tau$ CCCC (10)
82		979	940	0.33	$\beta$ CCC (36) + $\tau$ CCCC (22)
83		980	941	1.26	$\beta$ CCC (36) + $\tau$ CCCC (18)
84		985	945	3.67	βCCC (42)
85		1002	962	5.65	βCCC (58)
86		1012	971	5.78	$\beta$ CCC (48) + $\Gamma$ HCCH (10)
87		1030	989	3.05	$\beta$ CCC (62) + $\Gamma$ HCCH (18)
88		1031	990	6.43	βCCC (42)
89		1033	991	8.03	$\beta$ CCC (38) + $\tau$ CCCC (14)
90		1045	1003	15	ГСССН(46)
91		1048	1006	2.71	βCNC (22) + ΓCCCH (15)
92	1015	1062	1019	17.31	$\beta$ HCC (25) + $\beta$ CCC (10)
93		1064	1021	3.33	βCCO (38)
94		1074	1031	7.31	βCCC (42)
95		1077	1034	8.66	$\beta CCC(28) + \beta CCC(14)$
96		1089	1045	18.88	βCCN (40)
97	1072	1135	1089	14.08	$vCS(42) + \beta CCC(35)$
98		1145	1099	23.5	βHCC (33)
99		1151	1105	23.09	$\beta$ HCC (38) + $\beta$ CCC (35)
100		1161	1114	20.88	βHCC (25)
101		1167	1120	26.82	βHCC (26)
102		1173	1126	18.19	$\beta$ HCH (30) + $\beta$ CCC (19)
103	1134	1180	1133	26.87	$\beta$ HCH (23) + $\beta$ CCC (32)
104		1187	1139	8	$\beta$ HCC (38) + $\beta$ CCC (44)
105		1190	1142	11.94	βCCC (26)
106		1221	1172	74.93	βCCC (28)
107		1223	1174	22.88	$\beta$ CCC (38) + $\beta$ CCC (12)
108		1243	1193	18.88	$\beta$ CCN (32) + $\beta$ CCC (26)
109	1204	1255	1205	42.93	vNC $(35) + \beta$ HCC $(18)$
110	(	1261	1210	5.45	$\beta$ CCC (18) + $\beta$ HCC (10)
111		1267	1216	58.73	$\beta CCN(22) + \beta HCC(12)$
112		1276	1225	51.28	$\beta$ CCC (19) + $\beta$ HCC (21)
113		1289	1237	10.33	$\beta$ HCC (20) + $\beta$ CCC (20)
114	1245	1301	1249	23.29	$vCC(12) + vNC(48) + \beta CCH(20)$
115		1317	1264	24.29	$\beta$ HCC (25) + $\beta$ HCC (18)
116		1319	1266	35.26	$\beta$ CCC (28) + $\beta$ HCC (36)
117		1325	1272	25.26	$\beta CCC (26) + \beta HCC (10)$
118		1327	1274	14.52	$\beta$ CCC (32) + $\beta$ HCC (14)
119		1328	1275	81.31	$\beta CCN (25) + \beta HCC (12)$
120		1334	1280	5.96	$\beta$ CCC (28) + $\beta$ HCC (15)

121		1340	1286	8.7	$\beta$ CCC (32) + $\beta$ HCC (10)
122		1343	1289	9.2	$\beta$ CCC (30) + $\beta$ HCC (22)
123		1347	1293	21.21	$\beta CCN (38) + \beta HCC (10)$
124	1307	1365	1310	20.3	$\beta$ CCC (25) + $\beta$ HCC (12)
125		1374	1319	38.08	$\beta$ CCC (28) + $\beta$ HCC (15)
126		1382	1326	3.98	$\beta$ HCH (32) + $\beta$ HCC (10)
127		1401	1345	46.67	$\beta$ CCC (30) + $\beta$ HCH (22)
128		1404	1348	4.33	$\beta$ CCC (38) + $\beta$ HCH (10)
129		1407	1350	19.72	$\beta$ CCC (25) + $\beta$ HCH (12)
130		1411	1354	15.83	$\beta$ CCC (28) + $\beta$ HCH (15)
131	1369	1418	1361	7.74	βHCC (32) + $β$ HCH (10)
132		1441	1383	28	βHCC (30)
133	1402	1466	1407	14.73	βHCC (62)
134		1471	1412	36.77	βHCH (38)
135		1488	1428	35.43	$vCC(41) + \beta CCC(25)$
136		1489	1429	15.82	$vCC(42) + \beta CCC(24)$
137	1430	1491	1431	23.5	vCC ( 32) + $\beta$ CCC (48)
138		1497	1437	91.29	$vCC(28) + \beta CCC(16)$
139		1498	1438	11.56	$vCC(30) + \beta CCH(25)$
140		1502	1442	13.92	$vCC(52) + \beta CCH(28)$
141		1504	1444	21.38	$vCC(23) + \beta CCH(28)$
142		1509	1448	49.46	$\beta$ CCC (38) + $\beta$ CCH(10)
143		1512	1451	6.99	βHCH (73)
144		1518	1457	19.19	$vCC (66) + \beta HCH (58)$
145		1520	1459	44.69	$vCC (46) + \beta HCH (32)$
146	1463	1524	1463	31.53	vCC (60)
147		1586	1522	25.84	vCC (62)
148		1605	1540	22.15	$vCC(55) + \beta CCC(30)$
149		1611	1546	56.22	vCC (68)
150		1614	1549	3.35	vCC (75)
151		1616	1551	26.23	vCC (72)
152		1633	1567	39.59	vCC (78)
153	1570	1639	1573	55.67	vCC (75)
154		1661	1594	25.29	vCC (83)
155	1661	1758	1687	100	vCO (100)
156	2756	2878	2762	66.52	vCH <sub>aliphatic</sub> (98)
157	2805	2994	2874	7.53	$\nu CH_{aliphatic}$ (68)
158	2854	2999	2878	12.49	$\nu CH_{aliphatic}$ (75)
159		3010	2889	37.31	$\nu CH_{aliphatic}$ (86)
160		3013	2892	4.81	$\nu CH_{aliphatic}(82)$
161		3020	2899	30.37	$\nu CH_{aliphatic}(77)$
162		3024	2902	24.01	$\nu CH_{aldehyde}(94)$
163		3025	2903	6.07	$vCH_{aliphatic}(81)$

164		3044	2922	34.89	$vCH_{aliphatic}$ (68)
165	2928	3045	2923	27.33	$vCH_{aliphatic}(71)$
166		3058	2935	26.19	$vCH_{aliphatic}(92)$
167		3081	2957	37.97	$vCH_{aliphatic}$ (58)
168		3086	2962	32.28	$vCH_{aliphatic}(56) + vCH_{aromatic}(32)$
169	2957	3087	2963	34.01	vCH <sub>aliphatic</sub> (88)
170	3007	3160	3033	10.99	vCH <sub>aromatic</sub> (99)
171		3167	3040	3.05	vCH <sub>aromatic</sub> (82)
172		3170	3043	2.06	vCH <sub>aromatic</sub> (80)
173		3174	3046	11.51	vCH <sub>aromatic</sub> (88)
174		3177	3049	8.33	vCH <sub>aromatic</sub> (85)
175	3052	3178	3050	28.7	$\nu CH_{aromatic}$ (89)
176		3186	3058	11.53	$\nu CH_{aromatic}$ (91)
177		3187	3059	24.2	$\nu CH_{aromatic}$ (98)
178		3192	3064	2.95	$\nu CH_{aromatic}$ (74)
179		3193	3065	25.53	$\nu CH_{aromatic}$ (92)
180		3194	3066	16.94	vCH <sub>aromatic</sub> (96)
181		3195	3067	19.82	vCH <sub>aromatic</sub> (95)
182		3215	3086	7.75	$\nu CH_{aromatic}$ (88)
183		3216	3087	8.75	$vCH_{aromatic}$ (99)

v - stretching,  $\beta$  - in-plane bending,  $\tau$  - torsional vibrations,  $\Gamma$  - out of plane bending





Fig. 1. Structure of CZPTZA: a) ORTEP view and b) optimized structure.



Fig. 2. a) FT-IR spectrum of CZPTZA. b) Simulated FT-IR spectrum of CZPTZA.



Fig. 3. Mulliken charge distribution of CZPTZA indicated by color.



Fig. 4. Experimental and simulated UV-Vis spectra of CZPTZA.

# HIGHLIGHTS

- A novel **CZPTZA** has been synthesized by adopting multistep synthetic strategy.
- Experimental and theoretical studies are in harmony with each other.
- Small HOMO-LUMO band gap indicates that charge transfer occurs in the title compound.
- NLO analysis shows that the title compound would serve as an effective NLO material.

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