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studies

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Abstract

A series of pyrazole based D- π -A derivatives have been synthesized from 3-(4-nitrophenyl)-1-pheny-1H-pyrazole-3-carbaldehyde with series of active methylene compounds. The dyes were well characterized by FT-IR, ¹H NMR, ¹³C NMR, elemental analysis and mass spectroscopy. The synthesized dyes absorb in the range of 351 to 432 nm. Experimental absorption wavelengths for compounds are in good agreement with those predicted using the Time-Dependent Density Functional Theory (TD-DFT) [B3LYP/6-31G(d)]. Density Functional Theory calculations were performed to determine the static first hyperpolarizability (β_0) and related properties (μ , α , $\Delta \alpha$, β_0 and γ) for pyrazole based "donor- π -acceptor" dyes **3a-3f**, using B3LYP functional with 6-31G (d) basis sets at the ground state. The computed values for these dyes show high first order hyperpolarizability in the range $50.64 - 256.38 \times 10^{-30}$ esu and second hyperpolarizability (γ) in the range of 235.71 to 1580.81 x 10⁻³⁶ esu.

Keywords: Pyrazole, Synthesis, DFT, TDDFT, NLO study.

1. Introduction:

Pyrazole based dyes find applications in medicinal chemistry, agrochemicals and dye chemistry. Pyrazole has played a crucial role in the development of fused heterocyclic ring

systems, building block in biological and pharmacological intermediates [1–4], and they are widely used as intermediates in the dyestuff industry [5,6]. Pyrazole ring can act as an electron donor in a chromophoric system. The pyrazole ring has an electron-rich nitrogen atom which involves in conjugation by donating electron into the chromogenic molecule. Pyrazole containing molecules are known to show good electron-donating capacity and high hole transfer efficiency [7]. Pyrazole derivatives have been used as hole-transport materials in the electrophotography and electroluminescence fields [8]. Pyrazole derivatives are well known as blue emitters and can be used as blue electroluminescent materials in organic light-emitting diodes (OLEDs) [9,10]. *p*-Aryl-substituted pyrazole derivatives have also attracted considerable interest due to their wide range of applications in DSSCs [11], as well as second order nonlinear optical devices [12].

In recent decades, variety of chromophore have been studied as NLO materials. But several studies have demonstrated that donor chromophores bearing additional heteroatoms could dramatically increase the conjugation of the π -electron networks and the intramolecular charge transfer properties which could further influence the chromophores' first-order hyperpolarizability. The optical properties and NLO response can be tailored by i) by increasing λ_{max} , as increase in absorption wavelength leads to decrease in transition energy. For example near infrared active dyes are showing high hyperpolarizability values [13]. ii) Increase in transition dipole moment and increase in solvent polarity are also responsible for enhancing molecular hyperpolarizability [14,15]. iii) Molecules having twisted intramolecular charge transfer properties exhibits high values of hyperpolarizability [13,16,17]. iv) The β value might be properly influenced by adjusting the HOMO–LUMO energy gap of organic molecules [18–22].

In view of these findings, and in continuation of our previous studies [23,24] we have synthesized pyrazole based NLOphores. To synthesize pyrazole based dyes, a variety of

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active methylene compounds were used, such as malononitrile, methyl cyanoactetate, 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile, cyanomethylbenzthiazole, 3-methyl-1phenyl-1*H*-pyrazol-5(4*H*)-one and 2-(1-phenylethylidine) malononitrile. We have developed wide range of dyes which absorb from blue to yellow region. The newly synthesized derivatives of pyrazole contains electron rich pyrazole unit and strong acceptor group separated by π -conjugated bonds exhibiting high values of dipole moment and hyperpolarizability, which are desired properties for nonlinear optical materials.

2. Experimental Section

2.1. Computational Strategy

All the computations were performed on a HP workstation XW 8600 with Xeon processor, 4 GB RAM and Windows Vista as operating system. The software package used was Gaussian 09 [25]. DFT method with B3LYP functional and 6-31G(d) basis set was used for the ground state optimization. The hybrid functional namely B3LYP (Becke3-Lee-Yang-Parr hybrid functional) [26–29] was used. The 6-31G(d) basis set was used for all the atoms and later was ascertained in the literature [30]. The Polarizable Continuum Model (PCM) [31] was used to optimize the ground state geometries. The solvents used were toluene, tetrahydrofuran (THF), 1,4-dioxane (dioxane), chloroform (CHCl₃), dichloromethane (DCM), ethyl acetate (EtOAc), ethanol (EtOH), methanol (MeOH), *N*,*N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO). The excitation energies, oscillator strengths and orbital contribution for the lowest 20 singlet-singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set as for the geometry minimization in solvent environments.

2.2. Materials and Methods

1-(4-Nitrophenyl)ethanone, phenyl hydrazine, N,N-dimethylformamide, phosphorus oxychloride, sodium hydroxide and conc. H₂SO₄ were purchased from S. D. Fine Chemicals

Ltd, Mumbai, India and Sigma Aldrich. Solid reagents were characterized by melting point and used without further purification. Liquid reagents distilled at their boiling points and used thereafter. Synthetic grade solvent were used for synthesis and purification. Solvents were used after distillation at their boiling point and drying according to standard processes. All the reactions were monitored on precoated silica gel aluminium based plates kisel gel 60 F254 Merck, India. Purification of all the compounds were achieved by recrystallization and column chromatography whenever necessary. Melting points are uncorrected and were recorded on instrument from Sunder Industrial Product Mumbai. The absorption spectra of the compounds were recorded on a Perkin- Elmer Lamda 25 UV-visible spectrophotometer. The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ¹H NMR and ¹³C NMR spectra were recorded on a VARIEAN Inc. USA 500 MHz instrument. Chemical shifts (δ) are reported relative to tetramethylsilane ($\delta = 0.0$) as an internal standard. Mass spectra were recorded on Finnigan Mass spectrometer.

2.3. Synthesis and Characterization

2.3.1. Synthesis of (E)-1-(1-4-nitrophenyl)ethylidene)-2-phenylhydrazine (1) & 3-(4nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (2)

The compound **1** was prepared by condensation of *p*-nitroacetophenone and phenyl hydrazine in ethanol at reflux temperature using the reported procedure [32]. Compound **1** was further subjected to Vilsmeier-Haack reaction using DMF/POCl₃ to afford 3-(4-nitrophenyl)-1phenyl-1*H*-pyrazole-4-carbaldehyde (**2**) in good yield according to the procedure has been described by Kira *et al.* [33].

2.3.2. 2-((3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)malononitrile (3a)

3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and malononitrile (66 mg, 1 mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was stirred at RT for 2 h. After completion of the reaction, the

off white solid was filtered, washed with methanol, and dried. The dye obtained was purified

by column chromatography using silica gel 100-200 mesh and toluene as eluent system.

Color: Off white solid, Yield: 286 mg, 84%, M. P.: 196 – 198 °C.

FT-IR (KBr, cm⁻¹): 2224 (cyano stretching), 1528 (N-O), 1346 (N-O)

¹H NMR (500 MHz, CDCl₃) δ 7.48 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.76 (s, 1H),

7.77-7.86 (dd, *J* = 10.4, 8.6 Hz, 4H), 8.42 (d, *J* = 8.6 Hz, 2H), 9.10 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 80.2, 113.5, 115.0, 120.1, 124.4, 129.1, 129.7, 129.9, 130.0,

136.5, 138.3, 148.5, 149.7, 153.6.

MS (*m*/*z*): (M+H) Calcd for C₁₉H₁₂N₅O₂: 342.09 found 342.10.

Anal. Calcd. for C₁₉H₁₁N₅O₂: C, 66.86; H, 3.25; N, 20.52. Found: C, 66.80; H, 3.24; N, 20.44.

2.3.3. (E)-Methyl 2-cyano-3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)acrylate (3b)

3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and methyl-2cyanoacetate (100 mg, 1 mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was stirred at RT for 2 h. After completion of the reaction, the off white solid was filtered, washed with methanol, and dried. The dye obtained was purified by column chromatography using silica gel 100-200 mesh and toluene as eluent. Color: Off white solid, Yield: 314 mg, 84%, M. P.: 188 – 189 °C;

FT-IR (KBr, cm⁻¹): 2221 (cyano), 1726 (ester), 1526 (N-O), 1342 (N-O).

¹H NMR (500 MHz, CDCl₃) δ 3.92 (s, 3H), 7.37 (m, 1H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 4H), 8.24 (s, 1H), 8.39 (d, *J* = 8.9 Hz, 2H), 9.16 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 53.3, 100.9, 115.1, 116.2, 120.0, 124.2, 128.7, 129.7, 129.8(2), 129.9, 137.2, 138.6, 144.9, 148.3, 153.6, 162.8.

MS (*m*/*z*): (M+H) Calcd for C₂₁H₁₇N₄O₄: 375.11. Found 375.20.

Anal. Calcd. for C₂₀H₁₄N₄O₄: C, 64.17; H, 3.77; N, 14.97. Found: C, 64.12; H, 3.70; N, 14.92.

2.3.4. 2-(Benzo[d]thiazol-2-yl)-3-(1,3-diphenyl-1H-pyrazol-4-yl)acrylonitrile (3c)

3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and 2benzo[*d*]thiazol-2-yl)acetonitrile (174 mg, 1 mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was stirred at RT for 2 h. After completion of the reaction, the light yellow solid was filtered, washed with methanol and dried. The dye obtained was purified by column chromatography using silica gel 100-200 mesh and toluene as eluent system.

Color: Light yellow solid, Yield: 386 mg, 86%, M. P.: 284 – 285 °C;

FT-IR (KBr, cm⁻¹): 2218 (CN), 1600 (aromatic, C=C), 1529 (N-O), 1342 (N-O);

¹H NMR (500 MHz, CDCl₃) δ 7.44 - 7.45 (m, 2H), 7.52 - 7.58 (m, 3H), 7.89 (d, J = 7.8 Hz,

4H), 8.07 (s, 1H), 8.20 – 8.15 (m, 2H), 8.43 - 8.45 (d, *J* = 8.1 Hz, 2H), 9.17 (s, 1H).

¹³C NMR could not be recorded because of solubility problems.

MS (*m*/*z*): (M+H) Calcd for C₂₅H₁₆N₅O₂S: 450.10 found 450.40 (M+H).

Anal. Calcd. for C₂₅H₁₅N₅O₂S: C, 66.80; H, 3.36; N, 15.58; S, 7.13. Found: C, 66.84; H, 3.37; N, 15.51; S, 7.10.

2.3.5. 4-((1,3-Dipheny-1H-pyrazole-4-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)one (3d)

3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (174 mg, 1 mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was reflux for 12h. After completion of the reaction, the reaction mixture cooled to room temperature the orange solid was filtered, washed with methanol and dried. The dye obtained was purified by column chromatography using silica gel 100-200 mesh and toluene as eluent system.

Color: Orange Solid, Yield: 350 mg, 78%, M. P.: 251 – 252 °C

FT-IR (KBr, cm⁻¹): 1674 (amide), 1597 (aromatic, C=C), 1500 (N-O), 1338 (N-O);

¹H NMR (500 MHz, CDCl₃) δ 2.26 (s, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.35 (s, 1H), 7.438-7.47 (m, 3H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.89 (m, 4H), 7.96 (d, *J* = 7.9 Hz, 2H), 8.41 (d, *J* = 8.6 Hz, 2H), 10.27 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 12.9, 115.9, 119.2, 119.9, 124.1, 124.8, 125.0, 128.2, 128.9,

129.7, 130.1, 133.5, 134.4, 137.9, 138.3, 138.8, 148.2, 150.0, 154.4, 162.4.

MS (*m*/*z*): (M+H) Calcd for C₂₆H₂₀N₅O₃: 450.15 found 450.40.

Anal. Calcd. for C₂₆H₁₉N₅O₃: C, 69.48; H, 4.26; N, 15.58. Found: C, 69.43; H, 4.20; N, 15.56.

2.3.6. 2-(3-(1,3-Dipheny-1H-pyrazole-4-yl)-1-phenylallylidene)malononitrile (3e)

3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and 2-(1-phenylallylidene)malononitrile (168 mg, 1mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was reflux for 6h. After completion of the reaction, the reaction mixture cooled to room temperature the bright yellow solid was filtered, washed with methanol and dried. The dye obtained was purified by column chromatography using silica gel 100-200 mesh and toluene as eluent system.

Color: Yellow solid, Yield: 381 mg, 86%, M. P.: 230 – 232 °C.

FT-IR (KBr, cm⁻¹): 2224 (cyano), 1514 (N-O), 1342 (N-O);

¹H NMR (500 MHz, CDCl₃) δ 6.90 (d, *J* = 15.5 Hz, 1H), 7.36 – 7.40 (m, 2H), 7.41-7.44 (m, 1H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.52-7.61 (m, 5H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.81 (dd, *J* = 8.6, 1.1 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 8.47 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 81.5, 112.9, 113.3, 118.6, 119.6, 123.9, 124.8, 127.3, 128.2, 128.7, 129.1, 129.8, 131.4, 132.8, 138.0, 138.6, 147.9, 151.3, 171.0.

MS (*m*/*z*): (M+H) Calcd for C₂₇H₁₈N₅O₂: 444.14 found 444.40.

Anal. Calcd. for C₂₇H₁₇N₅O₂: C, 73.13; H, 3.86; N, 15.79. Found: C, 73.10; H, 3.82; N, 15.77.

2.3.7. 2-(3-(2(1,3-Dipheny-1H-pyrazole-4-yl)vinyl)5,5-dimethylcyclohex-2-en-1ylidene)malononitrile (3f)

3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (293 mg, 1 mmol) and 2-(3,5,5trimethylcyclohex-2-enylidene)malononitrile (186 mg, 1 mmol) were dissolved in dry methanol (15 mL). 0.1 mL of piperidine were added, and the solution was reflux for 8h. After completion of the reaction, the reaction mixture cooled to room temperature the red solid was filtered, washed with methanol and dried. The dye obtained was purified by column chromatography using silica gel 100-200 mesh and toluene as eluent system.

Color: Red solid, Yield: 369 mg, 80%, M. P.: 276 – 278 °C.

FT-IR (KBr, cm⁻¹): 2228 (cyano), 1516 (N-O), 1342 (N-O);

¹H NMR (500 MHz, CDCl₃) δ 1.09 (s, 6H), 2.41 (s, 2H), 2.61 (s, 2H), 6.81 (s, 1H), 6.91 (d, J

= 16.0 Hz, 1H), 7.01 (d, J = 16.0 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H),

7.80 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 2H), 8.32 (s, 1H), 8.39 (d, *J* = 8.8 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 28.0, 32.1, 38.9, 42.9, 78.9, 112.7, 113.4, 119.4, 119.8, 124.1,

125.8, 125.9, 127.8, 129.1, 129.7, 130.3, 138.9, 139.1, 147.7, 150.2, 153.5, 169.0.

HRMS m/z [M + H]+ Calcd for C₂₈H₂₄N₅O₂: 462.1930. Found: 462.2018.

Anal. Calcd. for C₂₈H₂₃N₅O₂: C,72.87; H, 5.02; N, 15.17. Found: C,72.82; H, 5.01; N, 15.24.

3. Result and Discussion

3.1. Chemistry

Herein, we have designed and synthesized a few nitro pyrazole based dyes featuring D- π -A molecular configuration. *N*-phenyl pyrazole bearing nitro group has unique function properties, Because of electron donating nature of pyrazole, we have introduced series of acceptor group on the pyrazole unit. These molecules behave as D- π -A type and hence it may

help to increase the optical properties. Compounds **1** and **2** were synthesized by using the reported method [32,33]. Malononitrile, methylcyanoacetate, isophorone, 2-aminothiophenol were available commercially. Active methylenes were synthesized by using the reported methods [34–37]. All the synthesized intermediates and final products were carefully purified and fully characterized by IR, ¹H NMR and ¹³C NMR, and mass spectroscopic technique.



3.2. Photophysical properties

3.2.1. Effect of solvent polarity on absorption spectra

In order to reveal the effect of multi-heteroatoms in electron donor moiety on the electronic structure of dipolar chromophores D- π -A, UV-Vis absorption spectra of the pyrazole substituted dyes were recorded in a series of nonpolar to polar solvents so that the solvatochromic behaviour of each chromophore could be investigated in a wide range of dielectric environments. The UV-Vis absorption spectra are shown in Fig. 1 and the data listed in Table 1. The dyes 3a-3f showed absorption bands in the range of 330 - 421 nm. The introduction of the nitro substituent into the aromatic portion of 3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole nucleus was expected to result in a bathochromic shift due to enhanced electron withdrawing ability of the chromophore. We have used various active methylenes to tune the absorption spectra. All the dyes exhibited a similar broad π - π intramolecular CT absorption band in the UV-Vis region with a continuous red-shift of the maximum absorption (λ_{max}) due to the gradually increasing acceptor strength. Compared with the dye 3a, the λ_{max} of the dyes **3e** and **3f** were shifted to a longer wavelength of 402 nm and 411 nm respectively in DMSO, which may be attributed to the additional double bond in acceptor moiety. In case of dye 3cthe absorption intensity was very low in methanol and ethanol solvents. This is due to less solubility of dye in respective solvent. The dyes **3a-3f** do not show any positive or negative solvotochromism as there was no linear trend observed from non-polar to polar solvents.

<< Please Insert: Fig. 1. Absorption spectra of dyes 3a-3f in solvent of varying polarities.>>

3.2.2. DFT Studies

3.2.2.1. Optimized Geometry

The ground state geometries of the dyes 3a-3f were optimized at B3LYP/6-31G(d) in various solvent of varying polarities. The optimized geometries of the dyes 3a-3f in DMF solvent are shown in Fig. 2. The optimized geometry of the dyes 3a-3f suggest that the two phenyl ring present on pyrazole core are shown twist in dihedral angle. The phenyl ring present on nitrogen of pyrazole core is twisted about 25.1° to 29.1° . Moreover the another phenyl ring

present on pyrazole core shows twist in the range of 34.8° to 40.9° . This result suggest that molecule possess twisted geometry.

<< Please Insert: Fig. 2. Optimized geometry of dyes 3a-3f in DMF solvent at the ground state using B3LYP/6-31G(d). >>

3.2.2.2. Vertical Excitation Spectra

In order to more understanding of the absorption properties of the synthesized pyrazole D- π bridge-A dyes, the ground state optimized geometries of the pyrazole dyes in solvents of various polarities were subjected to TD at least first 20 states in order to get vertical excitations using the B3LYP/6-31G(d) method and the results are collected in Table 1. The results of Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) also suggest there is less or negligible influence of the change in solvent polarity on the absorption of the pyrazole dyes **3a-3f** (Table 1). The vertical excitations are associated with the HOMO or HOMO-1 to LUMO or LUMO+1 transitions and strong oscillator strengths ranging from 0.2890 to 1.0813. Table 1 reveals that dye **3a** shows two absorption peak one in the range of 302-308 nm and other in 343-356 nm while computed vertical excitation shows closer value 347-352 with the oscillator strengths 0.2890-0.3069. Similar observation are found for the dyes 3c, 3e and 3f show two values which more closely match with the experimental values with comparable oscillator strength. Moreover, the dyes **3b** and **3d** show single absorption wavelength closer to the experimental absorption. The dye **3b** shows 3-16 nm deviation compared to the experimental value. The dye 3d shows more deviation of 30 to 46 nm.

<< Please Insert: Table 1 Photophysical data of the dyes 3a-3f in various solvents of varying polarities.>>

3.2.2.3. Frontier molecular orbitals

The absorption leading to the electronic excitation from the HOMO or HOMO-1 to the LUMO orbital can constitute the charge transfer from the *N*-phenyl pyrazole donor unit to the various acceptor units such as dicyanovinyl, carbomethoxy cyanovinyl, cyanobenzthiazolyl vinylene etc. In case of the dyes **3a**, **3b**, **3e**, **3f** the HOMOs are mainly located on *N*-phenyl pyrazole core and π bridge while the LUMOs are located on the acceptor unit like cyanovinylene and nitro phenyl ring (Table 2). However, for the dye **3c** the HOMO is mainly located on cyanovinyl benzthiazolyl unit and LUMO is spread all over the molecule, while for the dye **3e** the HOMO is located on methyl pyrazole unit and the LUMO is located on N-phenyl pyrazole unit and bridge bond.

<< Please Inset: Table 2 Frontier molecular orbitals of dyes 3a-3f in the ground state.>> The HOMO and LUMO energy level diagram gives quantitative idea of electronic structure and excitation properties. Fig. 3 reveals that the calculated HOMO-LUMO energy band gap of the dyes 3a-3f are in the range of 2.95-3.64 eV in DMF solvent. As shown in Fig. 3 the dye 3f shows lower energy gap as compared to the dyes 3a-3e while the dye 3a shows highest band gap of 3.64 eV (Table S1). This is because of the fact that the dye 3f shows more π conjugation as compared to the dye 3a. The results reveal that lengthening of the π systems and electron-donating and electron accepting ability of chromophore leads to lowering the HOMO-LUMO energy band gap.

<< Please Insert: Fig. 3. HOMO (H) – LUMO (L) energy level diagram of dyes 3a-3f in DMF solvent.>>

3.2.2.4. Non Linear Optical (NLO) property study by computational method.

The linear polarizability (α_0), first hyperpolarizability (β_0) and second hyperpolarizability (γ) values calculated using B3LYP/6-31G(d) on the basis of the finite field approach [38]. The results are gathered in Table 3. The detailed theory and essential formulae which describing the calculation of α_0 , β_0 and γ values are provided in supporting information. The schematic

representation for the first hyperpolarizability (β_0) and second hyperpolarizability (γ) values in various solvents for the dye **3f** are shown Fig. 4.

Herein, we have found out that all the dyes show lower value for α , β_0 and γ in 1,4-dioxane and higher value in DMSO. For example the dye **3f** shows lower β_0 value at 143.56 x 10⁻³⁰ esu in 1,4-dioxane and higher at 256.38 x10⁻³⁰ esu in DMSO. These values are 377 and 677 times greater than urea (0.38 x 10⁻³⁰ esu) respectively. The computed γ value for the dye **3f** in 1,4-dioxane is 811.56 and 1580.51 x 10⁻³⁶ esu in DMSO. These values are 1193 and 2324 times greater than urea (0.68 x 10⁻³⁶ esu). The trend in α , β_0 and γ values for dyes **3a-3f** are **3f** > **3c** > **3e** > **3d** > **3a** > **3b** (Table 4). We have also compared the β_0 value of dyes **3e** and **3f** with known analogue and we found that these dyes are showing greater β_0 value (Table 4)

<< Please Inset: Fig. 4. The static first (β_0) and second (γ) hyperpolarizability of dye 3f in various solvents in comparison with urea.>>

Theoretical calculations reproduce the expected optical behaviour in the studied set of pyrazole dyes. Increasing the length of conjugation in the set of pyrazole dyes **3a-3f** (Table S1) is accompanied by the decrease in HOMO-LUMO band gap, along with increase in oscillator strength that results into enhanced NLO response (larger α , β_0 and γ values). The hyperpolarizability values are markedly influenced by the solvent effects, from nonpolar to polar solvents hyperpolarizability values showing increasing tendency.

<< Please Insert: Table 3 Theoretically calculated nonlinear optical properties of the dyes 3a-3f in various solvents at B3LYP level using 6-31G(d) basis set.>>

<< Please Insert: Table 4 Comparison of first hyperpolarizability values of dyes 3e and 3f with known analogues. >>

4. Conclusion

A series of novel donor– π -bridge-acceptor pyrazole based dyes (**3a-3f**) have been synthesized and characterized by spectral technique. The simple and easy access to pyrazole dyes **3a-3f**

were carried out through the combination of Vilsmeier–Haack formylation and Knoevenagel condensation reaction. The synthesized dyes were optimized at B3LYP/6-31G(d) level in the ground state geometry. The synthesized pyrazole dyes were thoroughly investigated for their molecular nonlinear optical (NLO) properties at the theoretical level using density functional theory methods. A pronounced conformational effect on calculated hyperpolarizabilities for α , β_0 and γ were found for pyrazole derivatives (**3c**, **3e** and **3f**). All the dyes under investigation could be considered as efficient NLOphores due to their very large β_0 and γ values. Comparison of synthesized dyes with urea and known analogue showed the advantage in terms of nonlinear optical properties. In general, it was shown that inclusion of a π bridge-acceptor group on pyrazole ring substantially enhances the NLO response of the donor- π -acceptor systems.

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References

- Li X, Lu X, Xing M, Yang X-H, Zhao T-T, Gong H-B, et al. Synthesis, biological evaluation, and molecular docking studies of N,1,3-triphenyl-1H-pyrazole-4carboxamide derivatives as anticancer agents. Bioorg Med Chem Lett 2012;22:3589– 93.
- [2] Yu W-S, Cheng C-C, Cheng Y-M, Wu P-C, Song Y-H, Chi Y, et al. Excited-state intramolecular proton transfer in five-membered hydrogen-bonding systems: 2-pyridyl pyrazoles. J Am Chem Soc 2003;125:10800–1.
- [3] Moyano S, Barberá J, Diosdado BE, Serrano JL, Elduque A, Giménez R. Selfassembly of 4-aryl-1H-pyrazoles as a novel platform for luminescent supramolecular columnar liquid crystals. J Mater Chem C 2013;1:3119–28.
- [4] Sivakumar PM, Prabhu Seenivasan S, Kumar V, Doble M. Novel 1,3,5-triphenyl-2pyrazolines as anti-infective agents. Bioorg Med Chem Lett 2010;20:3169–72.

- [5] Karcı F, Karcı F. Synthesis and absorption spectra of some novel heterocyclic disazo dyes derived from pyridone and pyrazolone derivatives. Dye Pigment 2008;76:147–57.
- [6] Wang X, Li W, Zhang X, Liu D, Zhou X. A study on the synthesis and photophysical performances of some pyrazole and triazole fluorescent brightening agents. Dye Pigment 2005;64:141–6.
- [7] Barbera J, Clays K, Gimenez R, Houbrechts S, Persoons A, Luis Serrano J. Versatile optical materials: fluorescence, non-linear optical and mesogenic properties of selected 2-pyrazoline derivatives. J Mater Chem 1998;8:1725–30.
- [8] Wei X-Q, Yang G, Cheng J-B, Lu Z-Y, Xie M-G. Synthesis of novel light-emitting calix[4]arene derivatives and their luminescent properties. Opt Mater (Amst) 2007;29:936–40.
- [9] Ma CQ, Zhang LQ, Zhou JH, Wang XS, Zhang BW, Cao Y, et al. 1,3-Diphenyl-5-(9-phenanthryl)-4,5-dihydro-1H-pyrazole (DPPhP): structure, properties, and application in organic light-emitting diodes. J Mater Chem 2002;12:3481–6.
- [10] Chen X-L, Yu R, Zhang Q-K, Zhou L-J, Wu X-Y, Zhang Q, et al. Rational design of strongly blue-emitting cuprous complexes with thermally activated delayed fluorescence and application in solution-processed OLEDs. Chem Mater 2013;25:3910–20.
- [11] Xia J-B, Li F-Y, Yang H, Li X-H, Huang C-H. A novel quasi-solid-state dyesensitized solar cell based on monolayer capped nanoparticles framework materials. J Mater Sci 2007;42:6412–6.
- [12] Mishra A, Bhowmik AR, Thakur M. Synthesis and characterization of a new organic second-order optical material 4(2,2 dicyanoethenyl)-1-phenyl pyrazole (DCEPP). Lasers Electro-Optics, 1999 CLEO '99 Summ Pap Present Conf 1999:423.
- [13] Shi Y, Lou AJ-T, He GS, Baev A, Swihart MT, Prasad PN, et al. Cooperative coupling of cyanine and tictoid twisted π -systems to amplify organic chromophore cubic nonlinearities. J Am Chem Soc 2015;137:4622–5.
- [14] Deckers S, Vandendriessche S, Cornelis D, Monnaie F, Koeckelberghs G, Asselberghs I, et al. Poly(3-alkylthiophene)s show unexpected second-order nonlinear optical response. Chem Commun (Camb) 2014;50:2741–3.
- [15] Meyers F, Marder SR, Pierce BM, Bredas JL. Electric field modulated nonlinear optical properties of donor-acceptor polyenes: sum-over-States Investigation of the relationship between molecular polarizabilities (\$\alpha\s, \$\beta\s, and \$\gamma\s) and bond length alternation. J Am Chem Soc 1994;116:10703–14.
- [16] Kang H, Facchetti A, Jiang H, Cariati E, Righetto S, Ugo R, et al. Ultralarge hyperpolarizability twisted π-electron system electro-optic chromophores: Synthesis, solid-state and solution-phase structural characteristics, electronic structures, Linear and Nonlinear optical properties, and computational studies. J Am Chem Soc 2007;129:3267–86.

- [17] Kang H, Facchetti A, Zhu P, Jiang H, Yang Y, Cariati E, et al. Exceptional molecular hyperpolarizabilities in twisted π -electron system chromophores. Angew Chemie Int Ed 2005;44:7922–5.
- [18] Hales JM, Matichak J, Barlow S, Ohira S, Yesudas K, Brédas J-L, et al. Design of polymethine dyes with large third-order optical nonlinearities and loss figures of merit. Science 2010;327:1485–8.
- [19] Marder SR, Beratan DN, Cheng L-T. Approaches for optimizing the first electronic hyperpolarizability of conjugated organic molecules. Science (80-) 1991;252:103–6.
- [20] Bourhill G, Bredas J, Cheng L-T, Marder SR, Meyers F, Perry JW, et al. Experimental demonstration of the dependence of the first hyperpolarizability of donor-acceptorsubstituted polyenes on the ground-state polarization and bond length. J Am Chem Soc 1994;116:2619–20.
- [21] Chen W, Li Z-R, Wu D, Li Y, Sun C-C, Gu FL. The structure and the large nonlinear optical properties of Li@calix[4]pyrrole. J Am Chem Soc 2005;127:10977–81.
- [22] Oudar JL, Chemla DS. Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment. J Chem Phys 1977;66:2664.
- [23] Lanke SK, Sekar N. Aggregation induced emissive carbazole-based push pull NLOphores: Synthesis, photophysical properties and DFT studies. Dye Pigment 2016;124:82–92.
- [24] Lanke SK, Sekar N. Rigid coumarins: a complete DFT, TD-DFT and nonlinear optical property study. J Fluoresc 2015;25:1469–80.
- [25] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision C.01. Gaussian 09, Revis B01, Gaussian, Inc, Wallingford CT 2009.
- [26] Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J Phys Chem 1994;98:11623–7.
- [27] Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 1988;38:3098–100.
- [28] Becke AD. A new mixing of Hartree–Fock and local density-functional theories. J Chem Phys 1993;98:1372–7.
- [29] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 1988;37:785–9.
- [30] Saranya G, Kolandaivel P, Senthilkumar K. Optical absorption and emission properties of fluoranthene, benzo[k]fluoranthene, and their derivatives. A DFT study. J Phys Chem A 2011;115:14647–56.

- [31] Zhao Y, Truhlar D. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. Theor Chem Acc 2008;120:215–41.
- [32] Rector DL, Folz SD, Conklin RD, Nowakowski LH, Kaugars G. Structure-activity relationships in a broad-spectrum anthelmintic series. Acid chloride phenylhydrazones. I. Aryl substitutions and chloride variations. J Med Chem 1981;24:532–8.
- [33] Kira MA, Abdel-Rahman MO, Gadalla KZ. The vilsmeier-haack reaction III Cyclization of hydrazones to pyrazoles. Tetrahedron Lett 1969;10:109–10.
- [34] Elgemeie GH, Shams HZ, Elkholy YM, Abbas NS. Novel synthesis of pyrido[2,1-B]benzothiazoles and 1,3-benzothiazole derivatives. Phosphorus Sulfur Silicon Relat Elem 2000;165:265–72.
- [35] Weir MRS, Hyne JB. Some base-catalyzed condensation of systems of the form R1R2C=C(CN)2. Can J Chem 1965;43:772–82.
- [36] Massin J, Dayoub W, Mulatier J-C, Aronica C, Bretonnière Y, Andraud C. Nearinfrared solid-state emitters based on isophorone: Synthesis, crystal structure and spectroscopic properties. †. Chem Mater 2011;23:862–73.
- [37] Zhou S, Ren J, Liu M, Ren L, Liu Y, Gong P. Design, synthesis and pharmacological evaluation of 6,7-disubstituted-4-phenoxyquinoline derivatives as potential antitumor agents. Bioorg Chem 2014;57:30–42.
- [38] Vidya S, Ravikumar C, Hubert Joe I, Kumaradhas P, Devipriya B, Raju K. Vibrational spectra and structural studies of nonlinear optical crystal ammonium D, L-tartrate: a density functional theoretical approach. J Raman Spectrosc 2011;42:676–84.
- [39] Rizzo F, Cavazzini M, Righetto S, De Angelis F, Fantacci S, Quici S. A Joint Experimental and Theoretical Investigation on Nonlinear Optical (NLO) Properties of a New Class of Push-Pull Spirobifluorene Compounds. European J Org Chem 2010;2010:4004–16.
- [40] Gupta VD, Tathe AB, Padalkar VS, Umape PG, Sekar N. Red emitting solid state fluorescent triphenylamine dyes: Synthesis, photo-physical property and DFT study. Dye Pigment 2013;97:429–39.

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Table 1 Photophysical data of the dyes 3a-3f in various solvent of varying polarities.

		Ε	xperimental			Theoretical [B3LYP/6-31G(d)]				
D				Vertical		-	d			
Dye	Solvent	λ_{abs}	$\begin{bmatrix} \mathbf{v}_{\mathbf{E}} \\ \mathbf{v}_{\mathbf{I}} & 1 \end{bmatrix} = 1$	Excitation		Ч	μ_{ge}	Orbital		
		(nm)	(L moi cm)	(nm)	eV		(Debye)	contribution(%)		
	Toluene	356,	23449, 22465	377	3.2902	0.3790	5.52	H→L 98.7		
		308		347	3.5687	0.3016	4.72	H→L+1 90.2		
	Dioxane	346,	45272, 43806	376	3.3013	0.3716	5.46	H→L 98.7		
		305		347	3.5769	0.2899	4.63	H→L+1 92.0		
	THF	346,	30583, 29064	382	3.2492	0.3345	5.22	$H \rightarrow L 99.1$		
	CLICI	306	25424 22212	351	3.5320	0.2973	4.71	$H \rightarrow L+1.91.5$		
	CHCl ₃	352, 202	35434, 33212	380	3.2001	0.3502	5.32	$H \rightarrow L 98.9$		
	EtOA c	346	40364 38407	381	3.3404	0.3000	4.73	$H \rightarrow L + 1 92.0$		
3a	LION	303	-050-, 50-07	350	3 5383	0.3334	4 65	$H \rightarrow L + 1.91.3$		
	MeOH	345.	30917, 30306	383	3.2343	0.3082	5.01	$H \rightarrow L 99.2$		
		302		352	3.5239	0.2890	4.65	$H \rightarrow L+1 90.3$		
	EtOH	346,	38358, 37101	383	3.2336	0.3147	5.07	H→L 99.2		
		302		352	3.5235	0.2944	4.70	H→L+1 90.7		
	DMF	347	23617	384	3.2252	0.3229	5.14	H→L 99.1		
				352	3.5177	0.3069	4.80	H→L+1 91.1		
	DMSO	343,	32150, 30314	384	3.2251	0.3201	5.12	H→L 99.2		
		306		352	3.5180	0.3050	4.78	H→L+1 91.1		
	Toluene	347	21747	344	3.6068	0.3796	5.27	H→L+1 91.3		
	Dioxane	333	25829	343	3.6143	0.3678	5.18	H→L+1 90.8		
	THF	333	27527	345	3.5923	0.3521	5.09	H→L+1 89.6		
	CHCl ₃	339	14013	345	3.5953	0.3624	5.16	H→L+1 90.3		
3b	EtOAc	330	28638	345	3.5972	0.3470	5.05	H→L+1 89.5		
	MeOH	330	34027	345	3.5907	0.3333	4.95	H→L+1 88.2		
	EtOH	335	35164	345	3.5880	0.3403	5.00	H→L+1 88.6		
	DMF	330	33024	346	3.5827	0.3533	5.10	H→L+1 89.2		
	DMSO	330	28835	346	3.5834	0.3506	5.08	H→L+1 89.1		
	Toluene	383	13141	427	2.9046	1.0035	9.55	H→L 97.5		
				369	3.3564	0.1378	3.29	$H \rightarrow L+1 64.6$		
	Dioxane	379	21052	425	2.9152	0.9862	9.45	$H \rightarrow L 9/.6$		
				369	3.3621	0.1211	3.09	$H \rightarrow L+1\ 60.4$		
	THF	THF	378	378	23736	430	2.0020	0.9243	9.20	$\Pi \rightarrow L 97.7$ $\Pi \rightarrow L 1711$
						429	2.3293 2.8874	0.2104	934	$H \rightarrow L 97.6$
	CHCl ₃	382	32049	371	3.3364	0.1893	3.87	H L + 170.0		
•	EtOAc	075	25224	429	2.8903	0.9207	9.17	H→L 97.7		
3c		Ac 375	375 35234	372	3.3347	0.1951	3.93	H→L+1 69.0		
	MaOH			431	2.8778	0.8714	8.94	H→L 97.9		
	MeOH	-	-	373	3.3205	0.2392	4.36	H→L+1 70.8		
	FtOH	_	_	431	2.8755	0.8856	9.02	H→L 97.8		
	LIOH	-	-	373	3.3199	0.2392	4.36	H→L+1 71.7		
	DMF	376	24370	432	2.8663	0.9047	9.12	H→L 97.6		
		375	12448	374	3.3145	0.2507	4.47	$H \rightarrow L+173.7$		
	DMSO			432	2.8669	0.8989	9.09	$H \rightarrow L 9/./$		
	T. 1	264	07077	3/4	3.3143	0.2014	4.48	$\frac{\Pi \rightarrow L+1 / 3.4}{L+1 / 3.4}$		
	Toluene	364	27277	394	3.1506	0.4396	6.07	$H-1 \rightarrow L 95.9$		
	Dioxane	361	35120	392	3.1586	0.4314	6.00	H-1→L 96.2		
	THF	343	37978	396	3.1283	0.3887	5.73	H-1→L 94.9		

Tables All

3d	CHCl ₃	363	42436	396	3.1326	0.4046	5.84	H-1→L 95.3
	EtOAc	359	39127	396	3.1332	0.3870	5.71	H-1→L 95.3
	MeOH	360	33560	397	3.1265	0.3638	5.55	H-1→L 94.3
	EtOH	362	8626	396	3.1246	0.3705	5.59	H-1→L 94.3
	DMF	361	38657	397	3.1195	0.3801	5.67	H-1→L 93.9
	DMSO	364	43969	397	3.1203	0.3772	5.65	H-1→L 93.9
		20.6	272.44	421	0.7362	0.7362	8.13	H→L 94.3
	l'oluene	396	3/341	386	0.2447	0.2447	4.49	H→L+1 91.2
	Diovane	301	41651	419	2.9602	0.7194	8.01	H→L 93.7
	DIOXAIIC	571	41051	385	3.2214	0.2384	4.42	H→L+1 90.5
	THF	394	25983	426	2.9077	0.6480	7.67	H→L 94.4
		07.	20700	392	3.1589	0.2823	4.85	$H \rightarrow L+1 89.4$
	CHCl ₃	397	39784	425	2.9180	0.6808	7.85	$H \rightarrow L 94.4$
	5			391	3.1742	0.2687	4.73	$H \rightarrow L+1 90.2$
3e	EtOAc	390	43665	425	2.9184	0.6454	/.64	$H \rightarrow L 93.9$
				391	3.1080	0.2740	4.78	$H \rightarrow L+1 89.1$
	MeOH	391	48224	428	2.8930	0.5881	7.32	$H \rightarrow L 94.1$
				393 420	5.1504 2.8010	0.5078	5.09 7.42	$\Pi \rightarrow L+1 0/./$
	EtOH	393	38250	429	2.0919	0.0055	7.43	$\Pi \rightarrow L 94.3$ $\Pi \rightarrow L + 1.99.4$
				430	2 8805	0.3000	7.55	$H \rightarrow L + 1 00.4$
	DMF	399	20475	396	2.8805	0.0229	7.33 5.14	$H \rightarrow I + 1.89.4$
				430	2.8807	0.5150	7 52	$H \rightarrow L 94 9$
	DMSO	402	23906	396	3.1307	0.3139	5.15	$H \rightarrow L+1 89.2$
	T. 1	410	25212	454	2.7314	1.0813	10.23	H→L 92.5
	l'oluene	413	35312	417	2.9677	0.3638	5.68	H→L+1 91.6
	Diovono	411	21029	451	2.7472	1.0535	10.06	H→L 91.5
	Dioxaile	411	21958	416	2.9789	0.3677	5.71	H→L+1 90.5
	THF	THF 414 195	19525	462	2.6817	0.8589	9.91	H→L 89.8
			1)525	426	2.9079	0.5543	7.09	H→L+1 87.6
	CHCl ₃	CHCl ₃ 415 3258	32588	460	2.6960	0.9410	9.60	H→L 90.9
			52500	424	2.9232	0.4854	6.62	H→L+1 89.9
3f	EtOAc	OAc 410	34314	460	2.6945	0.8599	9.18	$H \rightarrow L 89.2$
01	Lione		0.001.	425	2.9189	0.5403	6.99	H→L+1 86.9
	MeOH EtOH DMF	411	31073	466	2.6593	0.7169	8.44	H→L 87.9
			01070	429	2.8907	0.6710	7.63	$H \rightarrow L+1 84.8$
		415	31238	466	2.6587	0.7496	8.63	$H \rightarrow L 88.8$
				429	2.8891	0.6509	7.71	$H \rightarrow L+1 85.8$
		421	61108	468	2.6462	0.7856	8.85	$H \rightarrow L 90.5$
	DMSO	DMSO 422		431	2.8/18	0.041/	/.08	$H \rightarrow L+1 \delta/./$
			33001	469	2.6458	0.7715	8.78	$H \rightarrow L 90.2$
				431	2.8778	0.0314	1.15	$H \rightarrow L+1 \delta/.4$

 ${}^{a}\lambda_{abs}$ = absorption wavelength maxima (nm), ${}^{b}\varepsilon$ = molar extinction coefficient at conc. 25 x 10⁻⁶ mol L⁻¹, ${}^{c}f$ = oscillator strength, ${}^{d}\mu_{ge}$ = transition dipole moment.

Tables All

LUMO номо HOMO-1 LUMO+1 Dye 3a 3b **3**c 3d 3e 3f

Table 2 Frontier molecular orbitals of dyes 3a-3f in the ground state.

Tables All

Dye	Solvent	μ ^a Debye	a_0^{b} 10 ⁻²⁴ (esu)	Δα ^c 10 ⁻²⁴ (esu)	$\beta_0^{\rm d}$ 10 ⁻³⁰ (esu)	γ ^e 10 ⁻³⁶ (esu)	$\frac{\mu\beta_0}{10^{-48}(\text{esu})}$
	Toluene	8.7	45.28	3351.37	50.64	235.71	440.57
	THF	9.3	49.99	4027.08	72.61	347.48	675.27
	Dioxane	8.6	44.87	3289.31	50.20	226.94	431.72
3 a	EA	9.2	49.32	3948.96	69.74	331.31	641.61
	DCM	9.3	50.46	4089.10	74.74	359.62	695.08
	CHCl ₃	9.1	48.52	3824.69	65.97	310.38	600.33
	MeOH	9.5	52.28	4315.80	83.13	408.52	789.74
	EtOH	9.5	52.05	4289.42	82.08	402.31	779.76
	DMF	9.5	52.37	4326.22	83.55	411.01	793.73
	DMSO	9.5	52.51	4341.23	84.16	414.67	799.52
	Toluene	3.7	48.99	3434.43	54.83	236.66	202.87
	THF	4.1	53.85	4049.60	73.35	338.98	300.74
	Dioxane	3.7	48.57	3374.77	53.24	228.42	196.99
	EA	4.0	53.19	3972.97	70.79	324.17	283.16
21	DCM	4.1	54.34	4104.74	75.24	350.06	308.48
30	CHCl ₃	4.0	52.32	3867.01	67.43	305.05	269.72
	MeOH	4.2	56.26	4303.42	82.67	394.86	347.21
	EtOH	4.2	56.02	4280.37	81.74	389.14	343.31
	DMF	4.2	56.36	4312.49	83.04	397.16	348.77
	DMSO	4.2	56.50	4325.64	83.59	400.54	351.08
	Toluene	8.8	66.83	11636.57	116.93	919.44	1028.98
	THF	9.5	73.85	13929.88	153.96	1328.59	1462.62
	Dioxane	8.8	66.21	11421.32	113.67	886.30	1000.30
	EA	9.4	72.91	13642.98	149.08	1299.47	1401.35
2	DCM	9.5	74.55	14135.79	157.51	1371.49	1496.35
50	CHCl ₃	9.3	71.67	13255.12	142.69	1196.21	1327.02
	MeOH	9.8	77.28	14894.37	171.11	1542.86	1676.88
	EtOH	9.8	76.93	14802.90	169.42	1521.05	1660.32
	DMF	9.8	77.42	14930.38	171.79	1551.62	1683.54
	DMSO	9.8	77.62	14983.01	172.77	1564.49	1693.15
	Toluene	4.5	62.23	6006.76	63.01	365.24	283.55
	THF	4.7	68.40	6888.79	84.52	516.81	397.24
	Dioxane	4.5	61.68	5921.03	61.17	352.87	275.27
	EA	4.7	67.56	6784.39	81.59	495.43	383.47
24	DCM	4.7	69.01	6961.35	86.66	532.60	407.30
Su	CHCl ₃	4.6	66.47	6638.79	77.74	467.67	357.60
	MeOH	4.7	71.40	7204.72	94.97	595.17	446.36
	EtOH	4.7	71.10	7179.89	93.95	587.36	441.57
	DMF	4.7	71.53	7217.91	95.42	598.59	448.47
	DMSO	4.7	71.70	7228.79	95.99	602.98	451.15
	Toluene	7.6	65.37	5391.30	90.76	468.97	689.78
	THF	8.5	72.97	6687.12	130.47	711.07	1109.00
	Dioxane	7.6	64.71	5277.80	87.59	450.63	665.68
30	EA	8.5	71.92	6513.40	124.74	674.72	1060.29
JE	DCM	8.6	73.74	6813.80	134.75	738.46	1158.85
	CHCl ₃	8.2	70.55	6283.80	117.37	628.69	962.43
	MeOH	8.9	76.83	7304.39	152.14	852.32	1354.05
	EtOH	8.8	76.44	7243.44	149.90	837.46	1319.12

 Table 3 Theoretically calculated nonlinear optical properties of the dyes 3a-3f in various

solvents at B3LYP level using 6-31G(d) basis set.

Tables All

	DMF	8.9	76.99	7328.77	153.04	858.33	1362.06
	DMSO	8.9	77.22	7364.45	154.37	867.27	1373.89
	Toluene	8.2	74.80	9968.58	148.91	845.16	1221.06
	THF	9.0	83.74	12647.35	215.97	1291.38	1943.73
	Dioxane	8.1	74.03	9744.61	143.56	811.56	1162.84
	EA	8.9	82.51	12275.14	206.27	1224.15	1835.80
3f	DCM	9.0	84.65	12921.19	223.24	1342.08	2009.16
	CHCl ₃	8.7	80.90	11789.45	193.82	1139.14	1686.23
	MeOH	9.3	88.28	13997.95	252.61	1553.02	2349.27
	EtOH	9.3	87.82	13861.89	248.81	1525.29	2313.93
	DMF	9.3	88.47	14051.84	254.14	1564.13	2363.50
	DMSO	9.3	88.74	14130.71	256.38	1580.51	2384.33

^aStatic dipole moment (μ), ^bmean polarizability (α_0), ^cpolarizability anisotropy ($\Delta \alpha$), ^dfirst hyperpolarizability (β_0) and ^esecond hyperpolarizability (γ).

 Table 4 Comparison of first hyperpolarizability values of dyes 3e and 3f with known analogues.

Sr. No.	Dye	β	μβ	Reference
1	N-C-NO2	65	689	[39]
2	N-C-NO2	138	1642	[39]
3		65	540	[39]
4		196	-	[40]
Зе		867	1373	This work
3f	$\begin{array}{c} O_2 N \\ & &$	1580	2384	This work

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- 1. Fig. 1. Absorption spectra of dyes 3a-3f in solvent of varying polarities.
- Fig. 2. Optimized geometry of dyes 3a-3f in DMF solvent at the ground state using B3LYP/6-31G(d).
- 3. Fig. 3. HOMO (H) LUMO (L) energy level diagram of dyes 3a-3f in DMF solvent.
- 4. Fig. 4. The static first (β_0) and second (γ) hyperpolarizability of dye 3f in various solvents in comparison with urea.

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Fig. 1. Absorption spectra of dyes 3a-3f in solvent of varying polarities.

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Fig. 2. Optimized geometry of dyes **3a-3f** in DMF solvent at the ground state using B3LYP/6-31G(d).



Fig. 3. HOMO (H) – LUMO (L) energy level diagram of dyes 3a-3f in DMF solvent.

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Fig. 4. The static first (β_0) and second (γ) hyperpolarizability of dye 3f in various solvents in comparison with urea.

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Highlights

- Novel pyrazole based push-pull dyes were synthesized and characterized.
- Photophysical properties estimated using experimental method are in good agreement with the theoretical results.
- DFT computation were performed for determination of nonlinear optical (NLO) properties.
- Pyrazole based dyes exhibited large second order hyperpolarizabilities.