Microwave assisted synthesis, Spectroscopic and photophysical properties of novel Pyrazol-3-one containing push -pull chromophore

Mohie E.M. Zayed, Parveen Kumar, Salman A. Khan

PII:	S0022-2860(19)31209-8
DOI:	https://doi.org/10.1016/j.molstruc.2019.127103
Reference:	MOLSTR 127103
To appear in:	Journal of Molecular Structure
Received Date:	13 April 2019
Accepted Date:	19 September 2019

Please cite this article as: Mohie E.M. Zayed, Parveen Kumar, Salman A. Khan, Microwave assisted synthesis, Spectroscopic and photophysical properties of novel Pyrazol-3-one containing push -pull chromophore, *Journal of Molecular Structure* (2019), https://doi.org/10.1016/j.molstruc. 2019.127103

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.





Mohie E. M. Zayed^{1,*}, Parveen Kumar², Salman A. Khan*

¹Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Saudi Arabia

²Department of Chemistry, DAV college Faridabad, Haryana, India

* Corresponding author e-mail: mohiem@yahoo.com (M. E. M. Zayed), sahmad_phd@yahoo.co.in (S. A. Khan)



Microwave assisted synthesis, Spectroscopic and photophysical properties of novel Pyrazol-3-one containing push -pull chromophore

Mohie E. M. Zayed^{1,*}, Parveen Kumar², Salman A. Khan*

¹Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Saudi Arabia

²Department of Chemistry, DAV college Faridabad, Haryana, India

* Corresponding author e-mail: <u>mohiem@yahoo.com</u> (M. E. M. Zayed), <u>sahmad phd@yahoo.co.in</u> (S. A. Khan)

Abstract: The present work deals with synthesis of pyrazole-3-one containing Schiff base as a push-pull chromophore and its photophysical studies. The title compound 4-((9-ethyl-9H-carbazol-3-yl) methylene) amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (EDPO) derived from the reaction of 9-ethyl-3-carbazole carboxaldehyde with 4-amino phenazone under microwave irradiation for 4 min achieving 94.8 % yield. The structure of chromophore (EDPO) was established on the basis of elemental analysis and spectroscopic techniques. Photophysical properties such as transition dipole moments, stokes shift, oscillator strength and fluorescence quantum yields was investigated in ten different solvents. It was observed that the intensity of the absorbance and emission of EDPO increased on the basis of the solvent polarity (n-Hexane to DMSO). In addition the effect of the surfactants CTAB and SDS on the EDPO were also studied to determine the critical micelle concentration of the cationic and anionic surfactants CTAB and SDS.

Keywords: Pyrazole-3-one, Schiff base; Stokes shift; Surfactants; CMC

1. Introduction

Within the last few decades, organic compounds functionalized with nitrogen atoms became enormously investigated and growing area of organic chemistry [1]. Due to the presence of nitrogen atoms, organic compounds possess strange and unique properties, which applicable in many branches of contemporary life sciences [2]. Nitrogen containing heterocyclic organic molecules play major role in the field of agriculture [3], biological and pharmaceutical [4] and additional in recent times were also used as ionic liquid [5], organocatalysts [6], and polymeric materials [7]. Pyrazol-3-one is 5-membered nitrogen containing heterocyclic compound with carbonyl group present at number two position have received significant consideration [8]. It is commendable of note that pyrazol-3-one compounds have been reported to show a broad range of bioactive molecule, like anticancer, antitumor, antifungal, anti-HIV, and antidepressant [9-11]. Since last two decades, pyrazol-3-one derivatives are used as metal sensors such as Pd (II) sensor, Hg (II) sensor Cu (II) sensor, Zn (II) sensor, organic light emitting diodes sensing of DNA and live cell sensor [12]. Pyrazol-3-one framework have oxygen atom joined with carbon by the double bond we can say oxygen use as acceptor (A), has synthesized by one pot-synthesis. Many one-pot reactions have been reported for the synthesis of various heterocyclic compounds [13]. If donor (D) group such as NR₂, OR, containing long pi (π) bond conjugated system joined with the pyrazol-3-one ring is known as donor acceptor chromophore [14]. Donor (D) acceptor (A) containing compounds are applicable in the field of material sciences such as multifunctional, optoelectronic materials [15], electroluminescent [16], photovoltaic devices [17], light emitting diodes [18], and electroluminescent [19]. Intramolecular electron transfer processes from the donor group to acceptors group are playing important role to determine the photophysical and photochemical properties of organic molecules constituting π -donor-acceptor

conjugated system such as transition dipole moments, stokes shift, oscillator strength and fluorescence quantum yields [20]. Interaction of D-D-A chromophore with the cationic and anionic surfactants such as cetyltrimethylammonium bromide (CTAB) and Sodium dodecyl sulphate (SDS) have been studied by the enhancement or quenched of the emission spectra to determine the critical micelle concentration (CMC) of the surfactants are also important application of the D-D-A chromophore. Various mane reactions have been reported such as Perkin condensation [21], Knoevenagel condensation [22], Cross-coupling reactions [23], Aldol condensation [24], Suzuki cross-coupling reaction [25] and Erlenmeyer-Plochl reaction [26] for the synthesis of such type of chromophores. Condensation reaction is also applicable for the synthesis of push -pull chromophores. Azomethine generally prepare by the condensation of amine and aldehyde or ketone. Reaction of push and pull group containing aldehyde and amine generally synthesized the push -pull Schiff base. During the literature review, we found lot of work have been made on the optical properties of donor (D)-π- acceptor (A) chromophores with their photophysical and physicochemical properties, but very rare examples reported optical properties of push and pull group containing heterocyclic Schiff base. In the present manuscript we synthesized push -pull chromophores by the reaction of 9-ethyl-3-carbazolecarboxaldehyde with 4aminophenazone under microwave irradiation. Physicochemical and parameters such as extinction coefficient, oscillator strength, transition dipole moment, stokes shift and fluorescence quantum yield of the EDPO were calculated in the different solvents to see the effect of the solvents with EDPO on the basis of solvents polarity. EDPO was also applicable for determination of critical micelle concentration (CMC) of cationic and anionic surfactant such as cetyltrimethyl ammonium bromide (CTAB) and sodium dodecylsulfate (SDS).

2. Experimental

2.1. Reagents and chemicals

Require reagents and solvents for the present work are of analytical grade purchased from Acros Organic and used directly. Carbazole, ethyl iodine, 4-amino phenazone, cetyl trimethylammonium bromide (CTAB) and sodium dodeyl sulfate (SDS) were pursed from Sigma-Aldrich. The stock solution of EDPO was prepared in DMSO and stock solution of CTAB and SDS was prepared in double distilled water. Absorbance and fluorescence was recorded at room temperature. 9-Ethyl-3-carbazole carboxaldehyde was prepared according to the published methods [27].

2.2. Equipment

The purity of the EDPO was confirmed by the 0.2 mm 60F-254 silica gel coated TLC plate and the melting point of the chromophore was recorded by Sturat Scientific Co. Ltd. apparatus. IR spectrum of chromophore was recorded with Perkin-Elmer 100-FT-IR spectrometer. ¹H & ¹³C-NMR signal of the compound was recorder in DMSO-d6 at 600/ 125 MHz on a Bruker AVANCE. The UV-Vis absorption and emission spectra of the EDPO was recorded with Shimadzu UV-1650 PCUV/VIS spectrophotometer and Shimadzu RF 5301PC spectrofluorophotometer.

2.3. Synthesis of 4-((9-ethyl-9H-carbazol-3-yl) methylene) amino)-1,5-dimethyl-2phenyl-1,2-dihydro-3H-pyrazol-3-one (EDPO)

Title compound EDPO was synthesized by the equimolar reaction of ethyl-3-carbazole carboxaldehyde (0.011 mol, 2.50 g) and 4-amino phenazone (0.011 mol, 2.27 g) in the minimum amount of (10 ml) EtOH and in 50 ml conical flask one drop of HCl was added in the reaction mixture, then the conical flask was taken in a domestic microwave oven. The reaction was irradiated under 210 watt microwave irradiation for 4 min. After completion the reaction,

4

mixture was allowed to cool and obtained solid was recrystalized in chloroform and ethanol (8:2) [28]

Yellow solid; % yield: 94.8%; m.p: 191 °C; IR ν_{max} cm⁻¹: 2977 (C-H), 1658 (C=N), 1679 (C=O), 1626 (C=C), 1148 (N-N); ¹H-NMR (DMSO-d₆) δ : 10.08 (s, 1H, CH_{Azomethine}), 8.69 (s, H3, CH_{Aromatic}), 8.26 (dd, H1, CH_{Aromatic}, J = 7.80 Hz), 8.18 (dd, H2, CH_{Aromatic}, J = 7.0 Hz), 7.68 - 7.32 (m, 5H, CH_{Aromatic}), 7.18 (d, 1H, CH_{Aromatic}, J = 7.2Hz), 7.06 (d, 1H, CH_{Aromatic}, J = 7.0 Hz), 6.96 (d, 1H, CH_{Aromatic}, J = 7.6Hz), 4.51 (q, 2H, N-CH₂-CH₃, J = 7.4 Hz), 3.12 (s, 3H, N-CH₃), 2.62 (s, 3H, -CH₃), 1.54 (t, 3H, N-CH₂-<u>CH₃</u>, J = 6.8Hz); ¹³C-NMR (DMSO-d₆): 163.07 (C=O), 152.33 (C=N), 142.52, 138.10, 136.47, 135.32, 134.93, 129.22, 129.02, 127.98, 125.87, 124.45, 123.09, 122.08, 120.18, 119.32, 118.88, 109.17 (Ar-C), 37.88 (N-CH₃), 36.18 (N-CH₂-CH₃), 14.87 (CH₃), 10.29 (N-CH₂-CH₃); EI-MS (m/z, %): 409.35 (M+1, 38); Anal. Calc for C₂₆H₂₄A₄O: C, 76.45; H, 5.92; N, 13.72; Found C, 76.35; H, 5.85; N, 13.64.

3. Results and Discussion

3.1. Characterization of EDPO

4-((9-ethyl-9H-carbazol-3-yl) methylene) amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3Hpyrazol-3-one (EDPO) was synthesized by reaction of 9-ethyl-3-carbazolecarboxaldehyde with 4-aminophenazone under microwave irradiation (Scheme 1). Structure of EDPO was characterized by the FT-IR, ¹H-NMR, ¹³C-NMR, EI-MS m/z (rel. int.%), and elemental analysis. Structure of EDPO was confirmed by the IR spectra due to characteristic band at 1688 cm⁻¹ of the v (C=O), peak for aldehyde is shifted to a lower frequency of 1656 cm⁻¹ for C=N conformed aldehyde converted to azomethine. Further evidence for the formation of EDPO was obtained from the ¹H NMR spectra, which provide diagnostic tools for the positional elucidation of the

protons. Assignments of the signals are based on the chemical shifts and intensity patterns. The aromatic protons of EDPO is shows multiplets in the range 7.32-7.68 ppm for 5 aromatic protons. A singlet signal is due to CH=N, azomethine proton in the EDPO was observed at 10.08 ppm respectively and other two singlets at 3.22 and 2.62 ppm for the N-CH₃ and C-CH₃ protons. ¹³C-NMR (CDCl₃) spectrum of EDPO was recorded in CDCl₃and spectral signals are in good agreement with the suggested functional groups. The carbonyl carbon of the EDPO generally appears at δ 163.07 in ¹³C NMR spectra. The azomethine carbon give rise to characteristic signal at δ 152.33 for C=N carbon. Details of ¹³C-NMR spectra of EDPO have presented in the experimental section. Finally, characteristic peaks were observed in the EI-MS mass spectra of EDPO as well as the molecular ion peak. The mass spectrum of EDPO shows a molecular ion peak (M⁺.) at m/z 409.35.

3.2. Absorption and fluorescence spectral behavior of EDPO in different solvents The absorptions and emission spectra of the EDPO has been recorded in ten different solvent on the basis of polarity such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), chloroform (CHCl₃), dicholoro methane (CH₂Cl₂), acetonitrile (CH₃CN), 1,4-dioxane, tetrahydrofuran (THF), n-Hexane at room temperature. As shown in the **Figure 1.** Maximum absorption band of the EDPO was significantly affected on the polarity of the solvents. The absorption maxima of the EDPO shifted to longer wavelength red shift 13 nm from n-hexane (332 nm) to DMSO (345 nm) (bathochromic shift) and intensity of the absorption increased (hyperchromic shift) when polarity of the solvent increased indicating the EDPO chromophore has more polar nature in ground state. The molar absorption coefficient (ε) also effected with the polarities of the solvents its value were presented in **Table 1**. As expected bathochromic shift (red shift) when increase the polarity of the solvents like n-Hexane to DMSO is due to

intramolecular charge transfer (ICT) from push group (carbazole) to pull group (carbonyl group) [29].

On excitation at 350 nm, the fluorescence spectrums of the EDPO were strongly correlates with the polarities of the solvents. As shown in **Figure 2** the EDPO chromophore displayed one broad band which characterized electronic transition from S_1 to S_0 . It was examined that the bathochromic shift in the emission maxima with the polarity of the solvent increases 26 nm from n-Hexane (419 nm) to DMSO (445 nm) were more than the bathochromic shift in the absorption maxima (Table 1). The excited state energy of EDPO chromophore was more affected with solvent polarities as compared to the ground state energy of the EDPO indicated due to the π - π * transition [30].

The empirical Dimroth polarity parameters $E_T(30)$ of the different solvent correlate with the absorption energy (E_a) and emission energy (E_f) of the EDPO in various solvent as mention in **Figure 3.** One dimensional correlation between different polarity of solvent and absorption, emission energy were acquired by the following equations [31].

$$E_a = 87.60 - 0.067 \text{ x } E_T(30) \tag{1}$$

 $E_f = 72.54 - 0.092 \text{ x } E_T(30)$

3.3. Determination of transition dipole moment and oscillator strength

(2)

The solvatochromic behavior of EDPO enable to determine the different dipole moments between the singlet excited state and ground state $\Delta \mu = \mu_e - \mu_g$.

Lippert-Mataga equation can be used to obtain these variations on the optical properties of EDPO [32].

$$\Delta \overline{V}_{st} = V_{abs} - V_{em} = \frac{2\Delta\mu^2}{h\,c\,a^3} \Delta f + Const. \tag{3}$$

where, $\Delta \overline{v}_{st}$ is represent the stokes shift as mention in the table 1, the value of stokes shift increasing with increasing the polarity of the solvents (n-Hexane to DMSO), signifying strong stabilization of excited state in polar solvent, h is the plank constant, a is the raids cavity, c is the velocity of light and Δf is the orientation polarizability of the different solvents have explained by following equation (eq. 4).

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\eta^2 - 1}{2\eta^2 + 1} \tag{4}$$

where η and ε are the refractive index of the solvents and dielectric constant correspondingly. The plot of stokes shift $(\Delta \bar{v}_{st})$ versus orientation polarizability (Δf) as showed **Figure 4.** The linear associations between orientation polarizability versus stokes shift identified that stokes shift was dependent on the polarity of the solvents' or polarizability. The dipole moments ($\Delta \mu$) different between ground and excited state of EDPO was calculated by using Lippert – Mataga equation (3). At the Equation 3 the a is the cavity radius of the EDPO was estimated by the following equation (5)

$$a = \left(\frac{3M}{4N\pi d}\right)^{1/3} \tag{5}$$

Where N is the Avigadro number, M is molecular mass and d is the assumed density of the chromophore of 1g / cm³. The dipole moment different of EDPO was found 7.68 Debye (Figure 4). Positive vale indicated that excited state is more polar than ground state [33].

The transition dipole moments of the EDPO chromophore between ground state and excited state in different solvent were calculates as following equation (eq. 6) [34]. The values were listed in Table 1.

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} E_{\text{max}}}$$
(6)

where f is the oscillator strength and E_{max} is the maximum energy of the absorption in cm⁻¹. The oscillator strength (f) of the EDPO chromophore in different solvent were calculated by the following equation (7)

$$f = 4.32 \times 10^{-9} \int \varepsilon(\overline{\nu}) d\overline{\nu} \tag{7}$$

Where \mathcal{E} is the dielectric constant (M⁻¹cm⁻¹) and $\overline{\nu}$ is the wavenumber (cm⁻¹). The calculated values of the oscillator strength (f) in different solvent were present in the Table 1. The oscillator strength of the EDPO was directly dependent to the polarity of the solvent.

3.4. Fluorescence quantum yields of EDPT

The fluorescence quantum yields (ϕ_f) of the EDPO in different solvents were calculated with the reference of the standard dye (Quinine sulphate $\phi_r = 0.55$ in 0.1 M H₂SO₄ solution). The flowing equation was applied for the calculation of fluorescence quantum yields (ϕ_f) for the EDPO [35].

$$\Phi_f = \Phi_r \frac{I x A_r x n^2}{Ir x A x n^2_r}$$
(8)

Where ϕ_f is the calculated fluorescence quantum yields of the EDPO in different solvent, ϕ_r is the fluorescence quantum yield of the Quinine sulphate as standard dye, I is the integrated emission intensity, A is the absorbance of EDPO and reference dye at the excited wave length and n is the refractive index of the solvent.

The fluorescence quantum yield (ϕ_f) of EDPO depending on the polarity of the solvents, because the fluorescence spectra have an effected on solvent polarity. The value ϕ_f in different solvents were listed in Table 1. In addition the relationship between of value

fluorescence quantum yield of the EDPO in different solvents and $E_T(30)$ of the different solvent were shown in **Figure 5**, where $E_T(30)$ is the solvent polarity parameter identified by Reichardt [37]. The obtained data displayed that significantly dependent to the solvent properties such as polarizability and hydrogen bonding. The fluorescence quantum yield increased when solvent polarity increased (0.05 in n-Hexane to 0.12 in DMSO). This phenomenon can be explained by the negative solvatokinetic effects. On the other, the fluorescence quantum yield of EDPO in highly polar solvent such as EtOH, and MeOH showed week as comparing to the other solvents having less polarity due the hydrogen bonding between the solutes and alcoholic solvents.

3.5. Effect of surfactant on fluorescence spectra of EDPO

The effect of the cationic and anionic surfactants such ascetyl trimethyl ammonium bromide (CTAB) and Sodium dodecyl sulphate (SDS) on the fluorescence spectrum of EDPO dye. The chosen of these two specific surfactants due to the ionic charged obsessed by the EDPO can be prejudiced by the positively charged and negatively charged surfactant. Thus, the emission behavior of the EDPO dye was based on the charge interaction between EDPO dye with CTAB or SDS. The fluorescence emission spectrum of the EDPO was measured in the absence of the CTAB and SDS. The fluorescence intensity of the EDPO increases with increase the concentration of the both type of the surfactants. The emission intensity of the EDPO increase with increase the concentration of CTAB (1 x 10^{-4} to 1.8×10^{-3} M) and as same the fluorescence intensity of the EDPO increases with increases the concentration of CTAB (1 x 10^{-4} to 1.8×10^{-3} M) and as same the fluorescence intensity of the EDPO increases with increases the concentration of the fluorescence strength of 1×10^{-5} M of EDPO at unchanging molar concentration with an increase the concentration of the CTAB and SDS as presented in the **Figure 6 & Figure 7**. The fluorescence band maximum observed at 430 nm in water and red

shifted 55 nm and 50 nm on adding the CTAB and SDS, respectively. This shift is accompanied by a uniform increasing the emission intensity. The spectral shift and enhancement of the fluorescence intensity can be rationalized is due to the enrolment of polar, conformationally relaxed intramolecular charge transfer states, whose stability is expected to be influenced by changing the micropolarity of the micelle domains. In addition to polarity, hydrogen-boning effect also plays a role at the binding site. So it is clear that EDPO in the surfactants CTAB and SDS can be located in interfacial regions with 4-((9-ethyl-9H-carbazol-3-yl) methylene) amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (EDPO) fragment inside hydrophobic alkyl chains to ward polar environment favoring efficient hydrogen bonding. In the Present of different concentration of the CTAB and SDS with sudden change the intensity of the fluorescence spectra of EDPO taking place at surfactant concentration 8.96 x 10⁻⁴ and 6.38 x 10⁻ ³mol dm⁻³, which are very near to critical micelle concentration of the CTAB and SDS surfactant **Figure 8** and **Figure 9** [38]. Thus the molecules EDPO can be use as probe analyzes the CMC of the cationic and anionic surfactants.

4. Conclusion

The pyrazole-3-one containing push-pull chromophore (EDPO) has been synthesized by the reaction of 9-ethyl-3-carbazole carboxaldehyde with 4-amino phenazone under microwave irradiation, obtained higher yield 94.8 % in a less reaction time by a simple and usual workup. The structure of EDPO was established on the basis of IR, ¹H-NMR, ¹³C-NMR and EI-MS spectroscopic techniques and elemental analysis. The photophysical behavior of the EDPO was described in ten solvents on the basis of the different polarity. The chromophore EDPO showed good photophysical properties depending on the solvent polarity it showed bathochromic shift when the polarity of the solvent increased n-Hexane to DMSO. The

11

emission intensity, transition dipole moments, stokes shift, oscillator strength and fluorescence quantum yields of the chromophore EDPO increased when the polarity of solvents increased. In addition the effect of the surfactants CTAB and SDS on the EDPO were also studied and it can be use as probe to determine the critical micelle concentration (CMC) of the cationic and anionic surfactants CTAB and SDS.

Acknowledgments

This project was funded by the deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant no. G-480-130-38. The authors, therefore, acknowledge with thanks DSR for technical and financial support.

References

- [1].M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes. Nature, 510 (2014) 485-496.
- [2]. Y. Hoshino, N. Ohtsuka, T. Okada, K. Honda, One-pot synthesis of primary amines from carboxylic acids through rearrangement of in situ generated hydroxamic acid derivatives. Tetrahedran Lett., 57 (2016) 5304-5307.
- [3].X. Liu, J. Zhu, A. Zhou, B. Song, H. Zhu, L. Bai, P. S. Bhadury, C. X. Pan, Synthesis, structure and antibacterial activity of new 2-(1-(2-(substituted-phenyl)-5-methyloxazol-4-yl)-3-(2-substitued-phenyl)-4,5-dihydro-1*H*-pyrazol-5-yl)-7-substitued-1,2,3,4-tetrahydroisoquinoline derivatives. Bioorg. Med. Chem. 17 (2009)1207-1213.
- [4]. D. Zampieri, M. G. Mamolo, E. Laurini, G. Scialino, E. Banfi, L. Vio, Antifungal and antimycobacterial activity of 1-(3,5-diaryl-4,5-dihydro-1*H*-pyrazol-4-yl)-1*H*-imidazole derivatives. Bioorg. Med. Chem., 16 (2008) 4516-4522.

- [5].H. B. Alhanash, A. K. Brisdon, Quaternary ammonium ionic liquids containing fluorous ponytails: Competitive alkylation and elimination reactions of $I(CH_2)_n R_f (n = 2, 3)$ with tertiary amines. J. Fluorine Chem. 156 (2013) 152-157.
- [6].P. Lu, Y. Yu, Z. Chen, G. Hou, Y. Chen, D. Ma, J. Gao, X. Gong, Syntheses, structures, catalytic and antitumor activities of a series of pyrimidine derivatives coordination complexes. Synth. Met. 203 (2015) 164-173.
- [7].M. S. Zakerhamidi, S. G. Sorkhabi, S. Ahmadi-Kandjani, E. Ortyl, S. Shahabadi, Substituent and solvent effects on the dipole moments and photo-physical properties of a group of polymeric azo sulfonamide substances. J. Mol. Struct.1048 (2013).441-447.
- [8].E. Lakontseva, M. Krasavin, Diversity-oriented pyrazol-3-one synthesis based on hydrazinodipeptide-like units prepared via the Ugi reaction. Tetrahedron Lett., 51 (2010) 4095-4099.
- [9].R. S. Balaskar, S. N. Gavade, M. S. Mane, B. B. Shingate, M. S. Shingare, D. V. Mane, Greener approach towards the facile synthesis of 1,4-dihydropyrano[2,3-c]pyrazol-5-yl cyanide derivatives at room temperature. Chin. Chem. Lett. 21 (2010) 1175-1179.
- [10]. H. B. Mehta, B. C. Dixit, R. B. Dixit, L-Proline catalyzed one-pot multi-component synthesis of 2-(1,3-diphenyl-1*H*-pyrazol-4-yl)quinazolin-4(3*H*)-one derivatives and their biological studies. Chin. Chem. Lett. 25 (2014) 741-744.
- [11]. M. S. Jourshari, M. Mamaghani, F. Shirini, K. Tabatabaeian, M. Rassa, H. Langari, An expedient one-pot synthesis of highly substituted imidazoles using supported ionic liquid-like phase (SILLP) as a green and efficient catalyst and evaluation of their antimicrobial activity. Chin. Chem. Lett. 24 (2013) 993-996.

- [12]. S. Choi, S. Nayab, J. Jeon, S. H. Park, H. Lee, Cobalt(II) complexes containing N'-substituted N,N',N-bis((1H-pyrazol-1-yl)methyl)amine ligands: The formation of four-coordinate or five-coordinate complexes as a function of the N'-substitution group in N,N',N-bis((1H-pyrazol-1-yl)methyl)amine. Inorganica Chim. Acta. 438 (2015) 118-127.
- [13]. M. S. Singh, A. Nagaraju, G. K. Verma, G. Shukla, R. K. Verma, A. Srivastava, K. Raghuvanshi, Eco-efficient, regioselective and rapid access to 4,5-disubstituted 1,2,3-thiadiazoles *via* [3 + 2] cycloaddition of α-enolicdithioesters with tosyl azide under solvent-free conditions. Green Chem., 15 (2013) 954-962.
- [14]. V. Ramkumar, P. Kannan, Novel heterocyclic based blue and green emissive materials for opto-electronics. Opt. Mater. 46 (2015) 314-323.
- [15]. C. Liao, A. H. Shelton, K. Y. Kim, K. S. Schanze, Organoplatinum Chromophores for Application in High-Performance Nonlinear Absorption Materials. ACS Appl. Mater. Interfaces, 3 (2011) 3225–3238.
- [16]. A. Danel, B. Jarosz, P. Karasiński, B. Sahraoui, P. Armatys, Synthesis, photophysical and electroluminescent properties of 1,3-diphenyl-1*H*benzo[g]pyrazolo[3,4–b]quinoxaline. Mater. Lett.138 (2015) 9-12.
- [17]. Akçay, H. T., Bayrak, R., Şahin, E., Karaoglu, K., Demirbas, Experimental and computational studies on 4-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methoxy]phthalonitrile and synthesis and spectroscopic characterization of its novel phthalocyanine magnesium(II) and tin(II) metal complexes. Spectrochim. Acta A: 114 (2013) 531-540.
- [18]. V. Cherpak, P. Stakhira, S. Khomyak, D. Volynyuk, Z. Hotra, L. Voznyak, G. Dovbeshko, O. Fesenko, V. Sorokin, A. Rybalochka, O. Oliynyk, Properties of 2,6-ditert.-butyl-4-(2,5-diphenyl-3,4-dihydro-2H-pyrazol-3-yl)-phenol as hole-transport

material for life extension of organic light emitting diodes. Opt. Mater. 33, (2011) 1727-1731.

- [19]. X. Shang, D. Han, D. Li, S. Guan, Z. Wu, Theoretical study on the electronic structures and photophysical properties of a series of Ir(III) complexes based on substituted 2-(pyrazol-3-yl)pyridine ligand Chem. Phys. Lett. 588, (2013) 68-75.
- [20]. M. S. Singh, K. Raghuvanshi, Recent advances in InCl₃-catalyzed one-pot organic synthesis. Tetrahydron, 68 (2012) 8683-8697.
- [21]. D. Ray, A. Nag, A. Jana, D. Goswami, P. K. Bharadwaj, Coumarin derived chromophores in the donor–acceptor–donor format that gives fluorescence enhancement and large two-photon activity in presence of specific metal ions. Inorganica Chim. Acta 363 (2010) 2824-2832.
- [22]. A. M. Asiri, H. M. Marwani, S. A. Khan, Spectroscopic investigation of novel donor–acceptor chromophores as specific application agents for opto-electronics and photonics. J. Saudi Chem., 18 (2014) 392-397.
- [23]. M. Manuela, M. Raposo, A. M. C. Fonseca, G. Kirsch, Synthesis of donor-acceptor substituted oligothiophenes by Stille coupling. Tetrahedron, 18 (2004) 4071-4078.
- [24]. B. Liu, X. Hu, J. Liu, Y. Zhao, Z. Huang, Synthesis and photophysical properties of novel pyrimidine-based two-photon absorption chromophores. Tetrahedron Lett., 48, (2007) 5958-5962
- [25]. S. Kotha, K. Lahiri, D. Kashinath, Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis. Tetrahedron, 58 (2002) 9633-9695

- [26]. A. M. Asiri, S. A. El-Daly, S. A. Khan, Spectral characteristics of 4-(p-N,Ndimethyl-aminophenylmethylene)-2-phenyl-5-oxazolone (DPO) in different media. Spectrochim. Acta A: 95 (2013) 679-684.
- [27]. S. Bal, J. D. Connolly, Synthesis, characterization, thermal and catalytic properties of a novel carbazole derived Azo ligand and its metal complexes. Arabian J Chem. 10 (2017) 761-768.
- [28]. A. M. Asiri, S. A. Khan, H. M. Marwani, K. Sharma, Synthesis, spectroscopic and physicochemical investigations of environmentally benign heterocyclic Schiff base derivatives as antibacterial agents on the bases of *in vitro* and density functional theory J. Photochem. Photobiol.120 (2013) 82-89.
- [29]. F. Lu, N. Kitamura, T. Takaya, K. Iwata, T. Nakanishi, Y. Kurashige, Experimental and theoretical investigation of fluorescence solvatochromism of dialkoxyphenyl-pyrene molecules. Phys. Chem. Chem. Phys., 20 (2018)3258-3264
- [30]. S. Jana, S. Dalapati, S. Ghosh, S. Kar, N. Guchhait, Excited State Charge Transfer reaction with dual emission from 5-(4-dimethylamino-phenyl)-penta-2,4-dienenitrile:
 Spectral measurement and theoretical density functional theory calculation. J. Mol. Struct. 998 (2011)136-143.
- [31]. S. A. Khan, Green Synthesis, Spectrofluorometric Characterization and Antibacterial Activity of Heterocyclic Compound from Chalcone on the Basis of in Vitro and Quantum Chemistry Calculation. J. Fluoresc., 27(2017) 929-937.
- [32]. B. Siddlingeshwar, S. M. Hanagodimath, Estimation of the ground and the first excited singlet-state dipole moments of 1,4-disubstituted anthraquinone dyes by the solvatochromic method. Spectrochim. Acta A, 75 (2010)1203-1210

- [33]. S. Gandhimathi, C. Balakrishnan, R. Venkataraman, M. A. Neelakantan, Crystal structure, solvatochromism and estimation of ground and excited state dipole moments of an allyl arm containing Schiff base: Experimental and theoretical calculations J. Mol. Liq. 219 (2016) 239-250.
- [34]. M. S. Tunuli, M. A. Rauf, Farhataziz, Dimroth's $E_T(30)$ as parameters of solvent polarity: a caveat. J. Photochem. 24 (1984) 411-413
- [35]. Y. Suwa, M. Yamaji, H. Okamoto, Synthesis and photophysical properties of difluoroboronated β-diketones with the fluorene moiety that have high fluorescence quantum yields. Tetrahedron Lett. 57 (2016)1695-1698.
- [36]. Z. Zhang, P. Xue, P. Gong, G. Zhang, J. Peng, R. Lu, Mechanofluorochromic behaviors of β-iminoenolate boron complexes functionalized with carbazole. J. Mater. Chem. C, 2 (2014) 9543-9551.
- [37]. A. K. Vasu, S. Kanvah, Red-emitting cationic fluorophore as a probe for anionic surfactants. Dyes Pigm. 142 (2017) 230-236
- [38]. A. M. Asiri, N. S. M. Al-Gamdi, H. D. Cancar, P. Kumar, S. A. Khan, Physicochemical and Photophysical investigation of newly synthesized carbazole containing pyrazolinebenzothiazole as fluorescent chemosensor for the detection of Cu²⁺, Fe³⁺ & Fe²⁺ metal ion. J.



Mole. Stru.1195 (2019) 670-680.

Scheme 1: Schematic diagram for the synthesis of EDPO

Solvent	Δf	E_T^N	E _T (30) Kcal mol ⁻¹	λ _{ab} (nm)	λ _{em} (nm)	ε M ⁻¹ cm ⁻¹	f	μ ₁₂ Debye	$\Delta \overline{\nu}$ (cm ⁻¹)	Φ_f
DMSO	0.263	0.441	54.1	345	445	26390	0.68	7.04	6514	0.12
DMF	0.274	0.404	43.8	342	444	23800	0.63	6.75	6717	0.11
EtOH	0.288	0.654	51.9	337	445	24000	0.69	7.01	7202	0.082
MeOH	0.308	0.762	55.4	337	447	23900	0.69	7.01	7302	0.100
CHCl ₃	0.208	0.259	39.1	338	428	21400	0.53	6.16	6221	0.105
CH_2Cl_2	0.255		40.7	336	428	21500	0.55	6.25	6397	0.104
Acetonitrile	0.304	0.472	45.6	338	439	23780	0.64	6.76	6806	0.059
Dioxan	0.021	0.164	36	336	437	23000	0.63	6.69	6878	0.11
THF	0.10	0.210	37.4	336	426	17600	0.44	5.58	6287	0.057
n-Hexane	0.0014	0.006	31.1	332	419	13400	0.33	4.81	6254	0.051

Table 1: Spectral data of EDPO in different solvents



Figure 1: Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of EDPO in different solvents.



Figure 2: Emission spectra of 1×10^{-5} mol dm⁻³ of EDPO in different solvents.



Figure 3: Plot of energy absorption (E_a) and emission (E_f) versus $E_T(30)$ of different solvents



Figure 4: Plot of Δf versus Stokes shift ($\Delta \upsilon$).



Figure 5: Plot of ϕ_f versus E_T (30) of different solvents.



Figure 6: Emission spectrum of 1×10^{-5} mol dm⁻³ of EDPO at different concentrations of CTAB, the concentrations of CTAB at increasing emission intensity are 0.0, 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 10×10^{-4} , 12×10^{-4} , 16×10^{-4} and 18×10^{-4} mol dm⁻³.



Figure 7: Emission spectrum of 1×10^{-5} mol dm⁻³ of EDPO at different concentrations of SDS, the concentrations of SDS at increasing emission intensity are 0.0, 2 x 10⁻³, 4 x 10⁻³, 6 x 10⁻³, 8 x 10⁻³, 10 x 10⁻³, 12 x 10⁻³, 16 x 10⁻³ and 18 x 10⁻³ mol dm⁻³.



Figure 8: Plot of I_f versus the concentration of CTAB



Figure 9: Plot of I_f versus the concentration of SDS

- ► 4-((9-ethyl-9H-carbazol-3-yl) methylene) amino-1,5-dimethyl-2-phenyl-1,2dihydro-3H-pyrazol-3-one (EDPO)
- ▶ Physicochemical and Photophysical investigations of EDPO dye
- ► Determine the critical micelle concentration (CMC) of CTAB and SDS

Journal