

Contents lists available at ScienceDirect

# Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstr

# Synthesis of Novel D- $\pi$ -A chromophores: Effect of structural manipulations on photophysical properties, viscosity and DFT study



Mahesh Jachak, Sushil Khopkar, Khushbu Patel, Yogesh Patil, Ganapati Shankarling\*

Department of Dyestuff Technology, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai - 400019, Maharashtra, India

#### ARTICLE INFO

Article history: Received 1 December 2020 Revised 28 January 2021 Accepted 4 February 2021 Available online 8 February 2021

Keywords: Fluorescent styryl dyes N-pyridin-(2-ylpyridin)-2-amine Fluorescence molecular rotors (fmrs) Positive emission solvatochromism DFT

# ABSTRACT

Four novel *push-pull* D- $\pi$ -A type chromophores namely (E)-2-cyano-3-(4-(di(pyridin-2-yl)amino) phenyl)acrylic acid (**BECA**), (E)-2-(5-(4-(di(pyridin-2-yl)amino)benzylidee)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (**BERA**), (E)-2-cyano-3-(5-(di(pyridin-2-yl)amino)thiophen-2-yl)acrylic acid (**THCA**) and (E)-2-(5-((5-(di(pyridin-2-yl)amino)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (**THCA**) were synthesized. The dyes synthesize were characterized by HR-MS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopies. The synthesized dyes show absorption and emission wavelength in the range of 362–499 nm and 471–557 nm respectively. The chromophores **BECA** and **BERA** show a large stroke shift (63–130 nm) as compared to chromophores **THCA** and **THRA** (38–62 nm). Oscillator strengths (f), transition dipole moments ( $\mu_{eg}$ ), and different solvent polarity plots have been investigated for understanding intramolecular charge transfer (ICT) characteristics from donor to the acceptor. Interestingly, the viscosity induced emission for all four chromophores were observed in ethanol: polyethylene - 400 solvent mixtures. The computational study of these chromophores was carried out by using density functional theory (DFT) along with time-dependent density functional theory (TD-DFT).

© 2021 Elsevier B.V. All rights reserved.

# 1. Introduction

Organic dyes containing donor-acceptor with extended  $\pi$ conjugation compounds attracted attention in current years. As the donor-acceptor form  $\pi$ -conjugated compounds possess a good intramolecular charge transfer process from donor to acceptor via  $\pi$ -bridge. The photophysical properties of these compounds can be optimized by changing their electron donor to acceptor moiety and extend the length of the  $\pi$ -conjugated bridge [1–4]. Due to easy modification at donor, acceptor, and  $\pi$ -spacers, many donoracceptor compounds have been reported for various applications including dye-sensitized solar cells (DSSC's) [5,6], biological imaging [7], metal sensors [8], luminescent polymer [9], organic fieldeffect transistors devices (OFET's) [10], optical data processing and storage [11], organic electronics [12] and organic photovoltaics [13].

Styryl dyes are widely used in donor-acceptor type compounds. As the styryl dyes show extended  $\pi$ -conjugated structures as well as good intramolecular charge transfer (ICT) characteristics. The advantages of styryl dyes over other classes of dyes are ease of synthesis, the scope of different donor and acceptors which can cover the spectrum from the UV to near-infrared region, and good photostability [14,15]. Up to date, various styryl dyes with different

Corresponding author.
E-mail address: gsshankarling@gmail.com (G. Shankarling).

electron donors such as carbazole, phenothiazine, triphenylamine, etc., as well as electron acceptors such as quinaxalines, cyanovinyl, pyridine, etc. were reported for various properties and applications [16]. Styryl dyes are extensively used as additives in photographic industry [17], laser dyes [18], flexible dyes [19], viscosity sensor [20] and optical sensitizers [21].

FMRs are  $\pi$ -conjugated fluorescent molecules, in which fluorescence intensity changes as the degree of intramolecular rotation of the rotators affected by environmental viscosity therefore its act as viscosity and temperature probes in different media. As the viscosity of medium is low, the fast rotation of the rotators causing non-radiative thermal relaxation of the excitation energy resulting in quenching of the fluorescence lifetime but as the viscosity of medium increase, the rotation of rotators get inhibited resulting in increases in fluorescence intensity as decreases in non-radiative thermal relaxation of the excitation energy. It has applications such as in biomedical imaging [22] and measuring microviscosity of specific cellular organelles and biomolecules [23]. It has also been used in measuring intra channel viscosity [24] and measuring temperature-sensitive responses in microfluidic devices [25].

The chromophores containing a N-pyridin-(2-ylpyridin)–2amine as donor and chelating group used in many areas such as metal sensor [26,27], metal complex formation [28], homogeneous catalysis [29], and photoluminescent materials [30]. As well as, the chromophores containing a carboxylic acid or 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid group usage as an electron-withdrawing group and anchoring group in DSSC [31,32]. Also carboxylic acid substituted BODIPYs are used for bioimaging [33] and coumarins as profluorophores for nucleic acid detection [34]. Reactive dyes containing carboxylic acid group uses for dying on cellulose fibers [35]. The 2-(4-oxo-2-sulfanylidene-1,3thiazolidin-3-yl)acetic acid group uses in ratiometric fluorescent chemosensor for Ag<sup>+</sup> [36], also use in anticancer and antibacterial activity derivatives [37,38].

N-pyridin-(2-ylpyridin)–2-amine as a common electrondonating with a 2-cyanoacetic acid or 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid group as a strong acceptor group with different  $\pi$ -bridge make good intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) acceptordonor (A-  $\pi$  -D) system. As a result, the system affects HOMO-LUMO energy band gap changes in spectroscopic properties [39]. The changes in different groups with different  $\pi$ -bridge also affect thermal properties and heat of fusion or heat of crystallization [40]. Therefore it is creating more interest to study the effect of N-pyridin-(2-ylpyridin)–2-amine as a common donor with 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid or 2cyanoacetic acid group as a strong acceptor baring chromophores with different  $\pi$ -bridge.

In this research work, we designed and synthesized four  $D-\pi$ -A styryl dyes having N-pyridin-(2-ylpyridin)—2-amine as a common donor with 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid or 2-cyanoacetic acid as a common acceptor with phenyl or thiophene as  $\pi$ -bridge. Also, we did a comparison study of different groups on their photophysical as well as thermal properties. Finally, we also study the effect of viscosity induced emission for all four chromophores in ethanol: polyethylene - 400 system and results of a DFT study.

# 2. Experimental section

#### 2.1. Materials and instruments

The synthetic grade chemicals were procured from Sigma-Aldrich Ltd., Spectrochem Pvt. Ltd., and Oxford Lab Fine Chem LLP. All the chemical reactions were monitored on a Merck aluminum TLC plate (coated with silica gel 60 with fluorescent indicator  $F_{254}$ ). The NMR <sup>1</sup>H (400 MHz) and <sup>13</sup>C (126 MHz) analysis of synthesized dyes was performed on an Agilent instrument with TMS as an internal standard and CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as a solvent (Supporting Information **S1-S14**). The High-resolution mass spectra (HR-MS) were recorded on Agilent technologies quadrupole time of flight instrument (Supporting Information S15-S18). A Jasco V-750 Uvvis spectrophotometer was used to record the absorption spectra of all the chromophores and a Jasco FP-8200 spectrofluorometer was used to record the fluorescence spectra of all chromophores with freshly prepared solutions. Thermogravimetric and differential scanning calorimetric (DSC-TGA) analyses of synthesized dyes were recorded on a Perkin Elmer instrument.

#### 2.2. Experimental methods

All the photophysical studies were carried with quartz cuvettes of 1 cm path length. The slit width of 5 nm is used for the measurement of excitation and emission spectra. The experimental conditions used for analysis were kept continuous in all the experiments. All dyes were excited at their maximum absorbance value ( $\lambda_{max}$ ) in corresponding solvents to found out the emission value. All dyes stock solution formulated in chloroform. The photophysical data of dyes were measured in seven different solvents by an increase in polarities with the concentration of ~5 × 10<sup>-6</sup> mol/L.

The fluorescein ( $\phi = 0.79$ ) in 0.1 mol/L NaOH solution was used as a standard to determine the quantum yield of the dye.

# 2.3. Synthesis and characterization of intermediates and styryl dyes

#### 2.3.1. N-pyridin-(2-ylpyridin)-2-amine (3)

In a THF (50 mL), 2-amino pyridine (1) (1.88 g, 0.02 mole) was dissolved completely. After the dissolution of starting reagents, sodium hydride (60% dispersion in mineral oil) (1.2 g, 0.03 mole) was put in portion-wise to it and the blend was mixed for 30 min at 30 °C. Later, 2-bromopyridine (2) (2.10 g, 0.022 mole) was added and further heated to 70 °C for 18 h in a nitrogen atmosphere. Once completion of the reaction, the brown-colored solution was obtained. Then, the solvent was evaporated on a rotary evaporator and the resulting crude sticky gel mass obtained was rinse with water and further 2-3 times extracted with ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (*n*-hexane: ethyl acetate = 9:1). Off white colored solid. Yield: 2.291 g (67%), Melting point = 90 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  8.28 (ddd, J = 5.0, 1.8, 0.8 Hz, 2H), 8.01 (s, 1H), 7.62 - 7.55 (m, 4H), 6.86 -6.83 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.1, 147.7, 137.7, 116.3, 111.7.

#### 2.3.2. 4-(di(pyridin-2-yl)amino)benzaldehyde (4)

In a microwave reaction vial, N-pyridin-(2-ylpyridin)-2-amine (3) (0.291 g, 0.0017 mole) and 4-bromobenzaldehyde (0.368 g, 0.0020 mole) were dissolved in N-methyl-2-pyrrolidone (NMP) (12 mL) and after that potassium carbonate (0.276 g, 0.0020 mole) and copper (I) iodide (0.065 g, 0.00034 mole) were added. This reaction mixture was then exposed to microwave radiation for 1 hour at 10 bar pressure at 200 °C. When the reaction completion occurs, the yellow-colored precipitation was obtained. Once the reaction was completed, it was drowned in ice water and the solid product collected, further solid dissolved in ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (*n*-hexane: ethyl acetate = 9:1). Light yellow colored solid. Yield: 0.258 g (55%), Melting point = 105 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  9.92 (s, 1H), 8.39 (dd, J = 5.0, 2.0 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.65 (td, J = 7.8, 2.0 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.07 - 7.04 (m, m)4H).

 $^{13}{\rm C}$  NMR (126 MHz, CDCl\_3)  $\delta$  190.9, 157.5, 150.7, 149.1, 138.1, 132.2, 131.1, 124.7, 119.7, 118.4.

# 2.3.3. 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5)

In a 20 mL microwave reaction vial, N-pyridin-(2-ylpyridin)-2amine (3) (0.291 g, 0.0017 mole) with 5-bromo thiophene-2carboxaldehyde (0.380 g, 0.0020 mole) were dissolved in Nmethyl-2-pyrrolidone (NMP) (12 mL) and after that potassium carbonate (0.276 g, 0.0020 mole) and copper(I) iodide (0.065 g, 0.00034 mole) were added. This reaction mixture was then exposed to microwave radiation for 90 min at 10 bar pressure at 200 °C. As the reaction was completed, the yellow-colored precipitate was obtained. The reaction mixture drowned into ice water and the solid product was obtained, further solid dissolved in ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (n-hexane: ethyl acetate = 9:1). Dark brown colored solid. Yield: 0.215 g (45%), Melting point = 135 °C, <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS)  $\delta$  9.73 (s, 1H), 8.60 (dd, J = 5.0, 1.8 Hz, 2H), 7.91 (td, J = 7.8, 2.0 Hz, 2H), 7.68 (d, J = 4.5 Hz, 1H), 7.36 (dd, J = 7.2, 1H)5.0 Hz, 2H), 6.97 (d, J = 8.2 Hz, 2H), 6.02 (d, J = 4.5 Hz, 1H).

 $^{13}\mathrm{C}$  NMR (126 MHz, DMSO–d\_6)  $\delta$  184.1, 154.8, 153.9, 149.2, 140.1, 137.3, 133.4, 121.7, 118.1, 114.0.

# 2.3.4. (E)–2-cyano-3-(4-(di(pyridin-2-yl)amino)phenyl)acrylic acid (BECA)

In acetonitrile (50 mL), 2-cyanoacetic acid (0.132 mL, 0.0020 mol) was added and mix. To this reaction mixture, 2–3 drops of piperidine were added and stirred for 10 min in a nitrogen atmosphere. After 10 min, added 4-(di(pyridin-2-yl)amino)benzaldehyde (4) (0.275 g, 0.0010 mole) and stirred for 4 h at 85 °C. As the reaction was completed, the pale yellow colored precipitation was obtained, which was extracted with ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (*n*-hexane: ethyl acetate = 9:1). Pale yellow-colored solid. Yield: 0.281 g (82%), Melting point = 180 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS)  $\delta$  8.31 (dd, *J* = 4.8, 1.2 Hz, 2H), 8.23 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.76 (td, *J* = 8.2, 1.9, 2H), 7.12–7.16 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H).

 $^{13}\text{C}$  NMR (126 MHz, DMSO–d\_6)  $\delta$  164.1, 157.3, 153.8, 149.7, 149.1, 139.0, 138.4, 132.6, 126.8, 124.8, 120.4, 118.8, 117.0.,

+ ESI-MS: m/z calcd for  $C_{20}H_{14}N_4O_2$  ( $M^+$ ): 343.1117, found: 343.1120.

# 2.3.5. (E)-2-(5-(4-(di(pyridin-2-yl)amino)benzylidene)-4-oxo-2thioxothiazolidin-3-yl)acetic acid (**BERA**)

In acetic acid (60 mL), 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid (0.161 g, 0.00084 mole) was added and mix. Further ammonium ethanoate (0.054 g, 0.0007 mole) was added and stirred for 5 min in a nitrogen atmosphere. After 5 min, added 4-(di(pyridin-2-yl)amino) benzaldehyde (4) (0.193 g, 0.0007 mole) and stirred for 3 h at 120 °C. As completion of the reaction, the yellow-colored precipitate was obtained. After the completion of the reaction, the reaction mass was extracted with ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (nhexane: ethyl acetate = 9:1). Yellow-colored solid. Yield: 0.263 g (84%), Melting point = 245 °C. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , TMS)  $\delta$  8.30 (d, J = 3.6 Hz, 2H), 7.83 (s, 1H), 7.75 (td, J = 8.2, 1.7 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.19 - 7.10 (m, 4H), 7.03 (d, J = 8.2 Hz, 2H), 4.72 (s, 2H).

<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 193.5, 167.8, 166.9, 157.4, 149.1, 148.0, 138.9, 134.0, 132.6, 128.5, 125.7, 120.2, 118.6, 45.5.

+ ESI-MS: m/z calcd for  $C_{22}H_{16}N_4O_3S_2$  ( $M^+$ ): 449.0864, found: 449.0885.

# 2.3.6. (E)-2-cyano-3-(5-(di(pyridin-2-yl)amino)thiophen-2-yl)acrylic acid (THCA)

In acetonitrile (50 mL), 2-cyanoacetic acid (0.132 mL, 0.0020 mole) was added. To this reaction mixture, 2-3 drops of piperidine were added and stirred for 10 min in a nitrogen atmosphere. After 10 min, added 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5) (0.281 g, 0.0010 mole) and stirred for 4 h at 85 °C. As completion of the reaction, the pale orange colored precipitate was obtained. After the completion of the reaction, extracted with ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (*n*-hexane: ethyl acetate = 9:1). Light orange colored solid. Yield: 0.271 g (78%), Melting point = 145 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS)  $\delta$  8.61 (dd, J = 4.7, 1.0 Hz, 2H), 8.33 (s, 1H), 7.95 (td, J = 8.2, 1.8 Hz, 2H), 7.69 (d, J = 4.7 Hz, 1H), 7.42 (dd, J = 7.0, 5.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.07 (d, I = 4.7 Hz, 1H).

 $^{13}\text{C}$  NMR (126 MHz, DMSO–d\_6)  $\delta$  161.7, 157.5, 153.1, 149.2, 140.5, 126.4, 122.5, 121.7, 118.4, 116.4, 115.9, 114.6, 67.3.,

+ ESI-MS: m/z calcd for  $C_{18}H_{12}N_4O_2S$  ( $M^+$ ): 349.0411, found: 349.0415.

# 2.3.7.(E)-2-(5-((5-(di(pyridin-2-yl)amino)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (**THRA**)

In acetic acid (60 mL), 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid (0.161 g, 0.00084 mole) was added. Further ammonium ethanoate (0.054 g, 0.0007 mole) was added and stirred for 5 min in a nitrogen atmosphere. After 5 min, added 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5) (0.197 g, 0.0007 mole) and stirred for 3 h at 120 °C. As completion of the reaction, the yellow-colored precipitation was obtained. Then, the obtained mass was extracted using ethyl acetate. The collected organic phase was dried with anhydrous sodium sulfate and further evaporator on rotavap. The purification of sticky residue was done by column chromatography on silica gel (*n*-hexane: ethyl acetate = 9:1). Orange colored solid. Yield: 0.254 g (80%), Melting point = 210 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, TMS)  $\delta$  8.60 (d, J = 3.2 Hz, 2H), 8.03 (s, 1H), 7.90 (t, J = 7.3 Hz, 2H), 7.54 (d, J = 3.7 Hz, 1H), 7.38 – 7.28 (m, 2H), 6.98 (d, J = 7.9 Hz, 2H), 6.11 (d, J = 4.1 Hz, 1H), 4.69 (s, 2H).

 $^{13}\text{C}$  NMR (126 MHz, DMSO–d<sub>6</sub>)  $\delta$  192.2, 167.9, 166.3, 154.9, 153.7, 149.2, 140.1, 136.4, 129.3, 128.6, 121.7, 118.0, 115.7, 113.6, 45.6.,

+ ESI-MS: m/z calcd for  $C_{20}H_{14}N_4O_3S_3$  ( $M^+$ ): 455.0428, found: 455.0441.

# 3. Results and discussion

#### 3.1. Design and synthesis

The synthesis protocol for four D- $\pi$ -A structured styryl dyes coded as BECA, BERA, THCA, and THRA having common Npyridin-(2-ylpyridin)–2-amine donor, different  $\pi$ -bridge and different acceptor units and intermediate represented in Scheme 1. The nucleophilic substitution reaction between 2-amino pyridine (1) with 2-bromo pyridine (2) in presence of NaH (60%) in THF at 70 °C for 18 h gave N-pyridin-(2-ylpyridin)-2-amine (3). Further intermediate 4-(di(pyridin-2-yl)amino)benzaldehyde (4) or 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5) were synthesized by Ullmann-type nucleophilic substitution reaction between N-pyridin-(2-ylpyridin)-2-amine (3) and 4-bromo benzaldehyde or 5-bromo thiophene-2-carboxaldehvde respectively in N-methyl-2-pyrrolidone (NMP) in presence of potassium carbonate and copper(I) iodide irradiated with a microwave at 200 °C. The chromophores BECA and THCA were synthesized by Knoevenagel condensation of intermediate 4-(di(pyridin-2-yl)amino)benzaldehyde (4) and 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5) respectively with 2-cyanoacetic acid in acetonitrile in presence of piperidine for 4 h at 85 °C. The chromophores BERA and THRA were synthesized by Knoevenagel condensation of intermediate 4-(di(pyridin-2-yl)amino)benzaldehyde (4) and 5-(di(pyridin-2-yl)amino)thiophene-2-carbaldehyde (5) respectively with 2-(4oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid in acetic acid in presence of ammonium ethanoate for 3 h at 120 °C. The synthesized dyes were characterized by standard spectroscopic techniques. (Supporting Information S1- S18)

## 3.2. Absorption and fluorescence properties

To correlate the impact of different  $\pi$  spacers with common donor and acceptor, we compared the photophysical properties of **BECA** against **THCA** and **BERA** against **THRA**. Also, to correlate the



Scheme 1. Synthetic route of synthesized dyes BECA, THCA, BERA and TERA.

impact of different acceptor with common donor and  $\pi$  spacer, we compared **BECA** against **BERA** and **THCA** against **THRA** Fig. 1.

From non-polar solvents to polar solvents, the polarity of solvent increases, which can affect the absorption and emission wavelengths of molecules, thus we carried out photophysical experiments of four chromophores in seven various solvents of different polarities. Fig. 2, shown the absorption as well as emission spectra of four dyes whereas, In Table 1, the obtained experimental photophysical data in various solvents is compiled. From Fig. 2, it

is observed that dyes show a bathochromic shift in the absorption and emission maxima as the polarity of aprotic solvents increases. In the case of methanol, a polar protic solvent they show a hypsochromic shift in absorption maxima as compared to aprotic solvent (Toluene) in all four chromophores. The chromophores **BECA** and **BERA** show different absorption and emission properties as they have the same donor and  $\pi$ -bridge but different acceptor based dye, **BERA** show red-shifted absorption maxima (432 nm) and emission maxima (495 nm) as compared to **BECA** absorption



Fig. 1. Structures of synthesized styryl dyes.

Table 1				
Experimental photophysica	al data of BECA. BERA	. THCA. at	nd THRA in	different solvents.

		$\lambda_{max}^{a}$	$\varepsilon^b$ × 10 <sup>5</sup>	FWHM <sup>c</sup>	$\lambda_{onset}^{d}$	$\Delta E_{opt}^{e}$	λ <sub>exc</sub>	$\lambda_{em}^{g}$	$\Delta \lambda_s^h$			$\mu_{\rm eg}^{k}$
Comp.	solvent	(nm)	$(M - {}^{1}cm^{-1})$	(nm)	(nm)	(eV)	(nm)	(nm)	(nm)	$\Phi^i$	f <sup>j</sup>	(Debye)
BECA	Toluene	394	0.687	62.3	443	2.80	396	471	77	0.028	1.206	10.060
	THF	403	0.780	61.6	450	2.76	405	487	84	0.022	1.474	11.247
	Chloroform	410	0.649	60.6	457	2.71	413	497	87	0.015	1.262	10.496
	DMF	362	0.714	59.5	431	2.88	365	493	131	0.016	1.614	11.156
	DMSO	374	0.726	64.3	431	2.88	376	500	126	0.010	1.591	11.256
	Acetonitrile	374	0.741	61.0	427	2.90	377	502	128	0.008	1.682	11.576
	Methanol	367	0.641	60.8	431	2.88	369	497	130	0.010	1.761	11.733
THCA	Toluene	451	0.771	50.7	482	2.57	453	489	38	0.026	1.163	10.570
	THF	451	0.864	51.1	485	2.56	454	493	42	0.019	1.299	11.171
	Chloroform	457	0.866	49.7	490	2.53	459	497	40	0.011	1.181	10.720
	DMF	457	0.861	53.3	495	2.51	460	502	45	0.011	1.369	11.542
	DMSO	460	0.833	54.1	498	2.49	463	505	45	0.016	1.343	11.470
	Acetonitrile	452	0.910	53.4	490	2.53	455	500	48	0.006	1.480	11.937
	Methanol	450	0.825	54.7	490	2.53	452	497	47	0.006	1.386	11.526
BERA	Toluene	432	0.494	70.6	482	2.57	435	495	63	0.034	1.449	11.545
	THF	436	0.566	73.4	491	2.53	439	513	77	0.027	1.557	12.025
	Chloroform	438	0.549	70.2	490	2.53	440	516	78	0.023	1.559	12.060
	DMF	431	0.475	75.9	492	2.52	433	538	107	0.015	1.629	12.229
	DMSO	440	0.483	79.1	504	2.47	443	548	108	0.012	1.617	12.310
	Acetonitrile	434	0.516	75.8	496	2.08	437	546	112	0.005	1.717	12.597
	Methanol	418	0.546	74.6	480	2.58	421	541	123	0.005	1.749	12.479
THRA	Toluene	487	0.572	76.0	533	2.33	490	530	43	0.032	1.438	12.213
	THF	492	0.605	70.7	540	2.30	495	539	47	0.029	1.463	12.380
	Chloroform	494	0.635	78.6	547	2.27	496	548	54	0.023	1.333	11.841
	DMF	489	0.602	78.6	543	2.28	492	550	61	0.019	1.518	12.572
	DMSO	499	0.583	79.4	553	2.24	503	557	58	0.014	1.505	12.648
	Acetonitrile	493	0.646	75.9	548	2.26	496	554	61	0.010	1.510	12.590
	Methanol	479	0.650	88.8	541	2.29	482	541	62	0.011	1.523	12.463

<sup>a</sup> absorption maxima at molar concentration of  $c = -5 \times 10^{-6}$  mol/L.

<sup>b</sup> molar extinction coefficient calculated from the absorbance at  $c = -5 \times 10^{-6}$  mol/L.

<sup>c</sup> full width at half maximum (FWHM).

<sup>d</sup> onset absorption edge.

 $^{e}$  optical band gap calculated from the equation,  $\Delta E_{opt}$  = 1240/ $\lambda_{onset}.$ 

<sup>f</sup> excitation maxima.

 $^{\rm g}\,$  emission maxima at molar concentration of c = ~5  $\times$  10  $^{-6}\,$  mol/L.

<sup>h</sup> Stokes shift.

<sup>i</sup> fluorescence quantum yield calculated using fluorescein as a standard ( $\phi = 0.79$  in 0.1 mol/ L NaOH.) [44].

<sup>j</sup> oscillator strength.

<sup>k</sup> transition dipole moment.

maxima (394 nm) and emission maxima (471 nm) in toluene. This is attributed due to 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid as a strong acceptor than 2-cyanoacetic acid. The same trend was observed in the case of **THCA** and **THRA**, **THRA** show red-shifted absorption maxima (487 nm) and emission maxima (530 nm) in toluene as compared to **THCA** absorption maxima (451 nm) and emission maxima (489 nm) in toluene, due to presence of 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid as strong acceptor than 2-cyanoacetic acid. As compared to chromophores **BECA** and **THCA**, they have the same donor and acceptor but different  $\pi$ -bridge. **THCA** show red-shifted absorption maxima (451 nm) and emission maxima (489 nm) as compared to **BECA** absorption maxima (394 nm) and emission maxima (471 nm) in toluene due to the presence of thiophene as  $\pi$ -bridge.



Fig. 2. Absorption spectra of BECA (A), BERA (C), THCA (E), THRA (G) and emission spectra of BECA (B), BERA (D), THCA (F), THRA (H) in various solvents ( $c = -5 \times 10^{-6} \text{ mol}/L$ ).

The same trend was observed with chromophores **BERA** and **THRA**, as they have the same donor and acceptor but different  $\pi$ -bridge. **THRA** shows red-shifted absorption maxima (487 nm) and emission maxima (530 nm) as compared to **BERA** absorption maxima (432 nm) and emission maxima (495 nm) in toluene, as it contains thiophene as  $\pi$ -bridge. Experimental results show a red shift in absorption maxima, from **BECA**<**BERA**<**THCA**<**THRA** in all studied solvents, from which it can be concluded that there is a good

charge transfer within the dyes from **BECA**<**BERA**<**THCA**<**THRA**. As with the increase in solvent polarity from non-polar to a polar solvent, in the excited state stabilization energy increase in the polar solvent which showed a red-shifted emission wavelength from **BECA**<**THCA**<**BERA**<**THRA**. The dyes **BERA** and **THRA** show full-width Half-maximum (FWHM) from 70–88 nm which provides a scope for the application of dyes in the field of photonics. [41]. The large Stokes shift observed in dyes **BECA** and **BERA** (63–130 nm)

as compared to **THCA** and **THRA** (38–62 nm) from non-polar solvent to polar solvent which indicates a fast relaxation from the initial to emissive state, which may due to good intramolecular energy transfer within the molecule when phenyl used as a  $\pi$ -bridge as compared to thiophene in a molecule. The obtained experimental data, from Table 1, the highest quantum yield was observed in a non-polar solvent in toluene (0.028 for **BECA**, 0.026 for **THCA**, 0.034 for **BERA**, and 0.032 for **THRA**) as compared to polar solvent (methanol). Moreover, it was observed that low quantum yield in methanol as compared to toluene which leads to an assumption that the presence of intramolecular and twisted intramolecular charge transfer [42].

With the help of transition dipole moments ( $\mu_{eg}$ ) and oscillator strengths (f), we can study the charge transfer characteristic of dyes towards the emissive state. As "oscillator strength" is a dimensionless quantity which states that the possibility of several electromagnetic radiation transitions from the ground state to the excited state in energy levels during the absorption to emission process in atom or molecule. The transition dipole moment is the transition. It evaluates the possibility of radiative transitions in molecules between the initial state and final state in various solvents. By knowing the oscillator strength of molecule in various solvents from the Eq. (1), we further find out the transition dipole moment of molecule in various solvents from the Eq. (2), [43]

$$f = 4.32 \times 10^{-9} \int \varepsilon(v) dv \tag{1}$$

$$\mu_{eg}^{2} = \frac{f}{(4.32 \times 10^{-7} \times \nu)}$$
(2)

In Eqs. (1 and 2),  $\varepsilon$  is molar absorptivity and  $\nu$  is wave number in cm<sup>-1</sup>.

From Table 1, The oscillator strengths as well as transition dipole moments were found in toluene for all four dyes (f = 1.206,  $\mu_{eg} = 10.060$  for **BECA**, f = 1.163,  $\mu_{eg} = 10.570$  for **THCA**,

f = 1.449,  $\mu_{eg} = 11.545$  for **BERA** and f = 1.438,  $\mu_{eg} = 12.213$  for **THRA**). From the obtained data, it was observed that **BECA** and **BERA** show high oscillator strengths as compared to **THCA** and **THRA**, which shows that donor and acceptor  $\pi$ -bridge by phenyl ring created high oscillator strengths as compared to thiophene  $\pi$ -bridge. Similar to this **BERA** and **THRA** show high oscillator strengths as compared to thiophene  $\pi$ -bridge. Similar to this **BERA** and **THRA** show high oscillator strengths as compared to **BECA** and **THCA**, which shows that 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid created high oscillator strengths as compared to 2-cyanoacetic acid.

Similarly, **BERA** and **THRA** show high transition dipole moments as compared to **BECA** and **THCA**, which shows that 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid created high transition dipole moments as compared to 2-cyanoacetic acid. Similar to this **THCA** and **THRA** show high transition dipole moments as compared to **BECA** and **BERA**, which shows that donor and acceptor  $\pi$ -bridge by thiophene ring created high transition dipole moment as compared to phenyl  $\pi$ -bridge.

From the data observed from Table 1, it appeared that the oscillator strength and transition dipole moment of all four dyes were increased as solvent polarity increased, which specifies that from non-polar to polar solvent, the intramolecular charge transfer increases. For example (dye **BECA** showed f = 1.206 and  $\mu_{eg} = 10.060$  in toluene, upon increase of solvent polarity, f = 1.761 and  $\mu_{eg} = 11.733$  increased in methanol)

#### 3.3. Solvent polarity functions plots

The optical properties such as Stokes shift and emission wavelength of the synthesized chromophores increased towards the polar solvents due to the increase in the stabilization of the excited state in polar solvents of the chromophores as compared to the ground state in polar solvents (positive solvatochromism). The excited state of dyes was stabilized in polar solvents by polarizability of the surrounding medium, dipole-dipole interactions, and hydrogen bonding.

The solvatochromic behavior of the chromophores was studied using the aid of Lippert-Mataga, E<sub>T</sub> (30), and McRae solvent polarity plots. Lippert-Mataga function describes the relationship between Stokes shift of the dye with solvent parameters such as refractive index, a radius of the solvent cage, and dipole moment [45]. Fig. 3A denotes the Lippert-Mataga solvent polarity plot which consists of Stokes shift of the BECA, THCA, BERA, and **THRA** dyes against orientation polarizability ( $\Delta f_{LM}$ ) of the solvents. From Fig. 3A, linear regression coefficient ( $R^2 = 0.6594$  for BECA,  $R^2$  = 0.7584 for  $\mbox{BERA},\ R^2$  = 0.8348 for THCA and  $R^2$  = 0.5445 for THRA) are obtained, suggesting that redshift in emission spectra is due to influences of the refractive index of solvents, Onsager radius of dyes and dielectric constant. The McRae solvent function is the developed form of the Lippert-Mataga function, where the solute together with solvent polarizability factors has been taken into consideration [46]. Fig. 3B graph denote McRae function which consists of Stokes shift of the BECA, THCA, BERA, and THRA dyes against McRae polarity parameter ( $\Delta f_{MR}$ ). From Fig. 3B, a linear regression coefficients were as follows,  $R^2 = 0.7404$  for **BECA**,  $R^2 = 0.8116$  for **BERA**,  $R^2 = 0.8434$  for **THCA** and  $R^2 = 0.5493$  for THRA. The linear relationship in Fig. 3B indicates the solute polarity originating in between N-pyridin-(2-ylpyridin)-2-amine as a donor and 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid or 2-cyanoacetic acid as an acceptor of the dyes as well added to the positive emissive solvatochromic shift. The Dimroth-Reichardt presented solvent polarity parameters which introduced the acidic character of solvent as well as negative solvatochromic dye [47]. Fig. 3C graph denotes Dimroth-Reichardt  $E_T$  (30) plot which consists of Stokes shift of the BECA, THCA, BERA, and THRA dyes against  $E_T$  (30) polarity parameter [48]. For Fig. 3C, a line regression coefficients ( $R^2 = 0.6290$  for **BECA**,  $R^2 = 0.7594$  for **BERA,**  $R^2 = 0.7639$  for **THCA** and  $R^2 = 0.8938$  for **THRA**) were observed, which signifies that observed positive emissive solvatochromic shift of dyes in the polar solvent has due to the influence of dielectric solute-solvent interaction.

# 3.4. Relationship between intramolecular charge transfer characteristics and dipole moment

From the photo-physical data, the fast relaxation of dye molecule results in bathochromic shift obtained in emission spectra in a polar solvent which may due to increases in ICT characteristic in the dye. For the BECA and THCA chromophores, the charge transfer occurs from N-pyridin-(2-ylpyridin)-2-amine donor to the 2-cyanoacetic acid acceptor and for BERA and THRA from Npyridin-(2-ylpyridin)-2-amine donor to 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid acceptor. As there some limitations of the Lippert-mataga function as it considers only local excitation, so with the help of Rettig as well as Weller's plots, we can explain the relationship between bathochromic shift in emission state with ICT characteristic. As in Weller's plot, excited state charge transfer characteristics of the chromophores were determined. It consists of the maximum emissive wave number of the chromophore in a particular solvent in cm<sup>-1</sup> against Weller's function ( $\Delta f_w$ ). Fig. 4A, denote Weller's plot, which consists of the maximum emissive wave number of BECA, BERA, THCA, and THRA against Weller's function values in respective solvents. In the Fig. 4A, a linear regression coefficient ( $R^2 = 0.7179$  for **BECA**,  $R^2 = 0.7409$  for **BERA**,  $R^2 = 0.5417$ for **THCA** and  $R^2 = 0.6945$  for **THRA**) was obtained, which signifies that ICT characteristics influence the bathochromic emissive shift obtained from non-polar to polar solvents [49]. As in polar protic



Fig. 3. (A) Lippert-Mataga solvent polarity plots (B) McRae solvent polarity plots and (C) E<sub>T</sub> (30) function of BECA, BERA, THCA and THRA.



Fig. 4. (A) Weller's plot and (B) Rettig plot of BECA, BERA, THCA and THRA.

#### Table 2

Relationship between intramolecular charge transfer and dipole moment.

Compound	Solvent	f <sup>a</sup>	$\mu_{eg}{}^{b}$	$a^{c}~(cm^{-1})\times10^{-8}$	m(LM) <sup>d</sup>	$(\mu_e - \mu_g)^e$ Debye	$\mu_{g}{}^{f}$ (Debye)	$\mu_{e}{}^{g}$ (Debye)
BECA	Toluene	1.206	10.060	10.980	10,718.64	3.756	12.051	15.807
	THF	1.474	11.247	10.972		3.752	14.006	17.758
	Chloroform	1.262	10.496	10.973		3.753	13.352	17.105
	DMF	1.614	11.156	10.972		3.752	15.070	18.822
	DMSO	1.591	11.256	10.972		3.752	15.079	18.831
	Acetonitrile	1.682	11.576	10.972		3.752	15.083	18.835
	Methanol	1.761	11.733	10.972		3.752	15.029	18.781
THCA	Toluene	1.163	10.570	10.910	1180.39	1.235	10.512	11.747
	THF	1.299	11.171	10.907		1.234	12.675	13.909
	Chloroform	1.181	10.720	10.908		1.234	11.963	13.197
	DMF	1.369	11.542	10.904		1.234	13.937	15.171
	DMSO	1.343	11.470	10.906		1.234	13.897	15.131
	Acetonitrile	1.480	11.937	10.904		1.234	13.745	14.978
	Methanol	1.386	11.526	10.908		1.234	13.631	14.866
BERA	Toluene	1.449	11.545	11.077	2125.35	1.695	4.499	6.194
	THF	1.557	12.025	11.075		1.695	5.210	6.904
	Chloroform	1.559	12.060	11.077		1.695	4.975	6.670
	DMF	1.629	12.229	11.073		1.694	5.620	7.314
	DMSO	1.617	12.310	11.073		1.694	5.650	7.344
	Acetonitrile	1.717	12.597	11.073		1.694	5.615	7.309
	Methanol	1.749	12.479	11.073		1.694	5.573	7.267
THRA	Toluene	1.438	12.213	11.007	1200.27	1.272	5.543	6.815
	THF	1.463	12.380	11.005		1.271	6.944	8.215
	Chloroform	1.333	11.841	11.008		1.272	6.301	7.572
	DMF	1.518	12.572	11.003		1.271	7.710	8.981
	DMSO	1.505	12.648	11.002		1.271	7.641	8.912
	Acetonitrile	1.510	12.590	11.003		1.271	7.773	9.044
	Methanol	1.523	12.463	11.002		1.271	7.680	8.951

<sup>a</sup> oscillator strength.

<sup>b</sup> transition dipole moment.

<sup>c</sup> Onsager radius determined from DFT.

<sup>d</sup> slope determined from Lippert-Mataga plot.

<sup>e</sup> ground and excited state dipole moment difference determined by Lippert-Mataga plot.

<sup>f</sup> ground state dipole moment determined from DFT.

<sup>g</sup> excited state dipole moment.

solvents, blue shift observed in absorption spectra as compared to polar aprotic solvent. The observed bathochromic shift is due to the TICT phenomena also playing the role along with ICT phenomena. Fig. 4**B**, denote the Rettig plot, which consists of the maximum emissive wave number of **BECA**, **BERA**, **THCA**, and **THRA** against Rettig function values in respective solvents. In Fig. 4**B**, a linear regression coefficient ( $R^2 = 0.9275$  for **BECA**,  $R^2 = 0.6232$  for **BERA**,  $R^2 = 0.6592$  for **THCA** and  $R^2 = 0.7054$  for **THRA**) was obtained, which signifies that TICT phenomena also influence with the aid of ICT phenomena in existing chromophores **BECA**, **BERA**, **THCA**, and **THRA** [50].

It is renowned that the charge distribution characteristics, as well as induced dipole moment, generates in a molecule during the transfer of electron charge while absorption and emission of photons in the molecule were elucidated from dipole moments generate in the molecule [51]. Table 2 contains the slope found from the Lippert-Mataga equation (m) and the oscillator strength as well as transition dipole moment ( $\mu_{eg}$ ) found from photo-physical data. To find out the dipole moment  $(\mu_e - \mu_g)$  generates during the absorption and emission process, we find out the Onsager radius (a) of all four chromophores in seven different solvents from DFT optimized geometry. It was calculated from N-pyridin-(2-ylpyridin)-2amine as a donor to conjugated 2-cyanoacetic acid or 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid ring as an acceptor. By knowing the Onsager radius (a) and Lippert-Mataga slope (m), the value of the difference between emission and absorption dipole moment ( $\mu_e$ - $\mu_g$ ) was calculated.

The ground state dipole  $(\mu_g)$  of chromophores were calculated from DFT carried out by using B3-LYP as a function with triple zeta def2-TZVP as the basis set. The excited state dipole moment  $(\mu_e)$  found out from ground state dipole  $(\mu_g)$  and the difference between emission and absorption dipole moment  $(\mu_e)$ 

 $\mu_{\rm g}$ ) (Table 2). The obtained values of excited-state dipole moment ( $\mu_{\rm e}$ ) and ground-state dipole moment ( $\mu_{\rm g}$ ), Table 2, it is indicated that ground-state dipole moment ( $\mu_{\rm e}$ ) are lower than excited state dipole moment ( $\mu_{\rm g}$ ), which indicate that ground state (S<sub>0</sub>) is less polar than excited-state (S<sub>1</sub>). Also, the value of excited-state dipole moment ( $\mu_{\rm e}$ ) of all the chromophores increases from non-polar solvent to the polar solvent, which signifies that the ICT phenomena increase in the excited-state from non-polar to polar solvent [52].

#### 3.5. Viscosity sensitivity study

Viscosity sensitivity study of our synthesized chromophores was carried out in ethanol: PEG 400 system. From Fig. 5, fluorescence spectra, as the viscosity of the system increases, the fluorescence intensity of the four chromospheres in the medium also gradually increases. In a medium with a composition of 99% PEG 400 and 1% ethanol, THRA shows more enhancement in fluorescence intensity as compared to other chromospheres. In the composition of 99% PEG 400 and 1% ethanol, THRA, BECA, BERA, and THCA shows 16.23, 9.42, 7.30, 5.34 fold increase in emission intensity respectively in comparison with pure ethanol. These chromophores show a remarkable viscosity dependent enhanced emission as compared to reported styryl dyes [53]. The restriction of TICT state in a more viscous medium as compare to low viscous medium results in maximum fluorescence enhancement in a more viscous medium. (Fig. 5) [54]. By using Forster-Hoffmann Eq. (3) [55], the quantitative measurement of viscosity sensitivity in a high viscous system of fluorescence molecular rotors (FMR) was explained.

$$\log I = C + x \log \eta \tag{3}$$



Fig. 5. Fluorescence spectra of (A) (B)BECA, (C) (D) BERA, (E) (F) THCA, and (G) (H) THRA in Ethanol: PEG 400 (100: 0) to and Ethanol: PEG 400 (1:99) system at molar concentration of  $\sim 1 \times 10^{-5}$  mol/L.



Fig. 6. Frontier molecular orbitals of BECA, BERA, THCA and THRA in chloroform.

Where, I = emission intensity of the rotors, x = viscosity sensitivity of the rotors,  $\eta =$  viscosity of the system, C = constant.

From Fig. 5, the viscosity sensitivity parameter (x) values for FMRs **BECA**, **BERA**, **THCA**, and **THRA** were as follows 0.28, 0.29, 0.25, and 0.42 respectively. From the above-observed data, dye **THRA** shows good FMR properties than the other three synthesized FMRs **BECA**, **BERA**, and **THCA**.

# 3.6. Theoretical study

From the theoretical study, we can find a relationship between photophysical properties and molecular structures of dye. The theoretical study was done by using Turbomole software (Version 6.5) [56]. Zych et al. [57] have studied similar molecules, with cyanoacrylic acid as the acceptor group and substituted 1,2,3triazole motif as the donor group, in B3LYP, CAM-B3LYP, M06, and wb97XD exchange-correlation functional in combination with the 6-31G(d,p) basis set. The theoretical results were in good agreement with experimental results when the computations were carried out with B3LYP exchange-correlation functional in combination with 6-31G(d,p) basis set. Therefore, we have used B3LYP [58,59] as functional and def2-TZVP as the basis set [60] for geometry optimization of our synthesized molecules. The vertical electronic excitation (VEE), oscillator strengths (f), and molecular orbital contributions aimed at the first five singlet transitions in seven different solvents of all four dyes were determined by the aid of time dependent-density functional theory (TD-DFT), where the same method was used which we had previously used in geometry optimization.

The frontier molecular orbital energy gap amongst HOMO and LUMO level in chloroform are shown in Fig. 6 to elaborate the electronic transitions and charge distribution within the molecules. The non-planar conformations were found from the DFT optimized geometry of dyes. The optimized geometries of **BECA**, **BERA**, **THCA**, and **THRA** are shown in **Figure S19**.

The HOMO-LUMO band gap, transition dipole moment, oscillator strengths, vertical electronic excitation (VEE), and orbital contribution of **BECA**, **BERA**, **THCA**, and **THRA** dyes in different polarity solvents were performed with the aid of TD-DFT and the obtained results are tabulated in Table 3.

From Table 3, The **BERA** show red-shifted vertical electronic excitation maxima (474 nm) as compared to **BECA** vertical electronic excitation maxima (424 nm) in toluene. This is attributed due to 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid as a strong acceptor than 2-cyanoacetic acid. The same trend was observed in the case of **THCA** and **THRA**, **THRA** show red-shifted vertical electronic excitation maxima (494 nm) as compared to **THCA** vertical electronic excitation maxima (444 nm) in toluene, due to presence of 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid as strong acceptor than 2-cyanoacetic acid.

As compared to chromophores **BECA** and **THCA**, **THCA** show red-shifted vertical electronic excitation maxima (444 nm) as compared to **BECA** vertical electronic excitation maxima (424 nm) in toluene due to the presence of thiophene as  $\pi$ -bridge. The same trend was observed with chromophores **BERA** and **THRA**, **THRA** show red-shifted vertical electronic excitation maxima (494 nm) as compared to **BERA** vertical electronic excitation maxima (474 nm) in toluene, as it contains thiophene as  $\pi$ -bridge.

#### Table 3

Comparative experimental and computational data of BECA, BERA, THCA, and THRA.

Dye	solvent	$\lambda_{max}^{a}$ (nm)	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	Eg <sup>b</sup> (eV)	VEE <sup>c</sup> (nm)	f <sup>d</sup>	Orbital contribution <sup>e</sup>	$\mu_{\rm eg}^{f}$ (Debye)
BECA	Toluene	394	-5.84	-2.54	3.30	424	0.872	H→L (98.4)	8.867
	THF	403	-5.82	-2.60	3.22	430	0.876	H→L (98.4)	8.946
	Chloroform	410	-5.83	-2.58	3.25	428	0.875	H→L (98.4)	8.926
	DMF	362	-5.82	-2.64	3.18	435	0.887	H→L (98.5)	9.060
	DMSO	374	-5.82	-2.64	3.18	438	0.890	H→L (98.5)	9.099
	Acetonitrile	374	-5.82	-2.64	3.18	433	0.866	H→L (98.4)	8.928
	MeOH	367	-5.82	-2.64	3.18	432	0.861	H→L (98.4)	8.896
BERA	Toluene	432	-5.66	-2.70	2.96	474	1.024	H→L (98.8)	10.159
	THF	436	-5.65	-2.75	2.90	481	0.988	H→L (98.9)	10.048
	Chloroform	438	-5.66	-2.74	2.92	479	1.002	H→L (98.9)	10.103
	DMF	431	-5.65	-2.78	2.87	486	0.988	H→L (98.9)	10.106
	DMSO	440	-5.65	-2.78	2.87	488	0.998	H→L (98.9)	10.177
	Acetonitrile	434	-5.65	-2.78	2.87	483	0.965	H→L (98.9)	9.962
	MeOH	418	-5.65	-2.78	2.87	483	0.959	H→L (98.9)	9.925
THCA	Toluene	451	-5.74	-2.60	3.14	444	0.774	H→L (97.7)	8.548
	THF	451	-5.74	-2.61	3.13	442	0.817	H→L (97.6)	8.761
	Chloroform	457	-5.73	-2.60	3.13	443	0.812	H→L (97.6)	8.742
	DMF	457	-5.75	-2.64	3.11	444	0.834	H→L (97.7)	8.877
	DMSO	460	-5.76	-2.66	3.10	449	0.822	H→L (97.8)	8.858
	Acetonitrile	452	-5.76	-2.67	3.09	446	0.778	H→L (97.6)	8.591
	MeOH	450	-5.76	-2.67	3.09	447	0.759	H→L (97.6)	8.496
THRA	Toluene	487	-5.55	-2.72	2.83	494	0.924	H→L (98.1)	9.847
	THF	492	-5.54	-2.76	2.78	498	0.934	H→L (98.1)	9.943
	Chloroform	494	-5.55	-2.75	2.80	497	0.917	H→L (98.1)	9.848
	DMF	489	-5.54	-2.78	2.76	503	0.947	H→L (98.2)	10.063
	DMSO	499	-5.55	-2.79	2.76	505	0.949	H→L (98.2)	10.099
	Acetonitrile	493	-5.54	-2.78	2.76	500	0.932	H→L (98.1)	9.949
	MeOH	479	-5.54	-2.78	2.76	499	0.923	H→L (98.0)	9.895

<sup>a</sup> experimental absorption.

<sup>b</sup> HOMO-LUMO energy band gap obtained from DFT.

<sup>c</sup> computational vertical electronic excitation.

<sup>d</sup> computational oscillator strength.

<sup>e</sup> major electronic transition.

<sup>f</sup> computed transition dipole moment.

Theoretical results show a red shift in absorption maxima, from **BECA**<**THCA**<**BERA**<**THRA** in all studied solvents, from which it can be concluded that there is a good charge transfer within the dyes from **BECA**<**THCA**<**BERA**<**THRA**. As with the increase in solvent polarity from non-polar to a polar solvent, in the excited state stabilization energy increase in the polar solvent which showed a red-shifted emission wavelength from **BECA**<**THCA**<**BERA**<**THRA**.

From Table 3, the theoretically obtained oscillator strengths and transition dipole moment were found in toluene for all four dyes (f = 0.872,  $\mu_{eg} = 8.867$  for BECA, f = 0.774,  $\mu_{eg} = 8.548$  for THCA, f = 1.024,  $\mu_{eg} = 10.159$  for BERA and f = 0.924,  $\mu_{eg} = 9.847$  for THRA). From the obtained data, it was observed that BECA and BERA show high oscillator strengths as compared to THCA and THRA, which shows that donor and acceptor  $\pi$ -bridge by phenyl ring created high oscillator strengths as compared to thiophene  $\pi$ -bridge. Similar to this BERA and THRA show high oscillator strengths as compared to thiophene strengths as compared to BECA and THCA, which shows that 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid created high oscillator strengths as compared to 2-cyanoacetic acid.

Similarly, **BERA** and **THRA** show high transition dipole moments as compared to **BECA** and **THCA**, which shows that 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid created a high transition dipole moment as compared to 2-cyanoacetic acid. Similar to this **BECA** and **BERA** shows high transition dipole moment as compared to **THCA** and **THRA**, which shows that donor and acceptor  $\pi$ -bridge by phenyl ring created high transition dipole moment as compared to thiophene  $\pi$ -bridge.

From Table 3, it shows that obtained theoretical results show good congruence experimental results, which strengthen the results obtained in practical experiments with theoretical study.

From Fig. 6, it is observed that HOMOs of BECA, BERA, THCA, and THRA dyes are generally placed on N-pyridin-(2-ylpyridin)-2amine donor and  $\pi$ -bridge as compared to the acceptor group. When the excitation of chromophores occurs, the electron density from the donor system is transferred to 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid or 2-cyanoacetic acid acceptor. The electron cloud of LUMO +1 of BECA and THCA chromophores are more distributed on N-pyridin-(2-ylpyridin)-2-amine donor and in the case of BERA and THRA chromophores were mostly distributed on 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid. From Fig. 6, In the transfer of electron density from HOMO to LUMO from N-pyridin-(2-ylpyridin)-2-amine to 2-(4-oxo-2sulfanylidene-1,3-thiazolidin-3-yl)acetic acid or 2-cyanoacetic acid acceptors through the conjugated  $\pi$ -bridge, as outcomes in a strong interface of intramolecular charge transfer from acceptor to the donor. Moreover, results in a decrease in the HOMO-LUMO bandgap. The theoretically observed band gaps of HOMO-LUMO orbitals for BECA, BERA, THCA, and THRA in different solvents are plotted in Fig. 7.

The **BERA** shows a lower HOMO-LUMO band gap (2.93 eV) as compared to **BECA** (3.25 eV). Similarly, **THRA** shows a lower HOMO-LUMO band gap (2.80 eV) as compared to **THCA** (3.13 eV). This is because of the strong association between donors and 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid acceptor compared to 2-cyanoacetic acid as an acceptor via  $\pi$ -bridge. Moreover, the energy band gap observed in HOMO-LUMO orbitals for **THCA** and **THRA** was lower as compared to **BECA** and **BERA**, due to the thiophene ring as  $\pi$ -bridge, which decreases the bandgap by good transport of electron density from donor to acceptor. From Table 3, it was observed that the maximum orbital contribution (97–99%) to electronic transitions was attributed to the HOMO to LUMO energy bandgap.



Fig. 7. HOMO-LUMO energy level band gap plots of BECA, BERA, THCA and THRA in different solvents.



Fig. 8. Thermogravimetric analysis (TGA) of synthesized dyes.

# 3.7. Thermal properties

The changes in physical properties of **BECA**, **BERA**, **THCA**, and **THRA** dyes as a function of temperature were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) from the temperature range of 30 to 600 °C with a purge of nitrogen gas and linear controlled heating rate of 20 °C/minute. Fig. 8, denotes the thermogravimetric analysis graph, from it was observed that less amount of weight loss in dyes below tempera-

ture 250 °C. The dyes **BECA**, **THCA**, **BERA**, and **THRA** showed thermal decomposition temperature (Td) at 250 °C by a reduction in 2.5% of total weight, at 271 °C by a reduction in 2% of total weight, at 295 °C by a reduction in 4% of total weight and at 262 °C by a reduction in 2.5% of total weight respectively. These results demonstrated that all the four chromospheres are thermally stable over 250 °C. From Fig. 8, the decomposition temperatures of dyes are high which indicates that these dyes possess good thermal stability [61]. In DSC analysis, for **THCA**, **BECA**, **THRA**, and **BERA**, a small endothermic peak was observed at 151 °C, 184 °C, 225 °C.



Fig. 9. Differential scanning calorimetric analysis (DSC) of synthesized dyes.

and 270 °C respectively, which is typically for the fusion point [62]. Fig. 9, shows that **THCA** has a low melting point than **BECA** and **THRA** has a low melting point than **BERA** due to the presence of the thiophene ring as a  $\pi$ -bridge, which shows that donor and acceptor  $\pi$ -bridge by phenyl ring increases the latent heat of melting than the  $\pi$ -bridge by thiophene ring. Also, the rhodamine-3-acetic acid group increases the fusion point of dyes. For example, **THRA** has a high melting point than **BECA**, and **BERA** has a high melting point than **THCA** and **BERA** has a high melting point than **BECA**, which shows that 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid as an acceptor increases the latent heat of melting than the 2-cyanoacetic acid as an acceptor.

## 4. Conclusions

In this article, we have examined the photophysical properties of BECA, BERA, THCA, and THRA novel styryl chromophores. The above chromophores exhibited a comprehensive  $\pi$ - $\pi$ \* system with ICT and TICT phenomena. They display absorption and emission wavelength from a range of 362-499 nm and 471-557 nm respectively with Stokes shift of 38-130 nm from non-polar to polar solvents. Furthermore, BECA, THCA, BERA, and THRA dyes indicated red emission spectra by an intensification of solvent polarity from aprotic to a protic solvent which was investigated with the aid of solvent polarity plots (Lippert-Mataga,  $E_T$  (30) and McRae plot). As well as the intramolecular and twisted intramolecular charge transfer phenomena of the dyes were figured out with the aid of solvent polarity plots (Weller's and Rettig plot) and dipole moment in solute-solvent interaction. Which makes these dyes potent applicants in the field of organic non-linear optical materials. These BECA, BERA, THCA, and THRA dyes display viscosity sensitive characteristics in PEG 400: ethanol system, so these FMR dyes can be applied for measuring microviscosity of specific cellular organelles and biomolecules. Besides, the observed experimental data demonstrated parallel co-relation with the computed data from DFT and TD-DFT study. The substitution of phenyl ( $\pi$ bridge) by thiophene ring and 2-cyanoacetic acid by 2-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)acetic acid acceptor causes reduction of HOMO-LUMO energy bandgap with an increase in thermal stability. Thus the experimental, as well as the theoretical study of styryl dyes indicates that the dye BERA and THRA are the most promising candidates for potential application in organic photonics and electronics.

We believe that the presented work will be an inspiration for other styryl dyes researchers to perform a further study of this molecule for suitable applications.

#### **Declaration of Competing Interest**

None.

#### **CRediT** authorship contribution statement

Mahesh Jachak: Conceptualization, Methodology, Software. Sushil Khopkar: Visualization, Formal analysis. Khushbu Patel: Investigation, Writing – original draft, Writing – review & editing. Yogesh Patil: Writing – original draft, Writing – review & editing. Ganapati Shankarling: Supervision, Funding acquisition.

#### Acknowledgements

Authors are thankful to UGC-CAS and AICTE for financial support.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130086.

# References

- T.-.Y. Wu, M.-.H. Tsao, F.-.L. Chen, S.-.G. Su, C.-.W. Chang, H.-.P. Wang, et al., Synthesis and characterization of organic dyes containing various donors and acceptors, Int. J. Mol. Sci. 11 (2010) 329–353, doi:10.3390/ijms11010329.
- [2] Y. Kutuvantavida, G.V.M. Williams, M.D.H. Bhuiyan, S.G. Raymond, A.J. Kay, Effects of Chromophore Conjugation Length and Concentration on the Photostability of Indoline-Based Nonlinear Optical Chromophore/Polymer Films, J. Phys. Chem. C 119 (2015) 3273–3278, doi:10.1021/jp509293m.
- [3] D. Zych, A. Slodek, Acceptor-π-Acceptor-Acceptor/Donor systems containing dicyanovinyl acceptor group with substituted 1,2,3-triazole motif – synthesis, photophysical and theoretical studies, J. Mol. Struct. 1204 (2020) 127488, doi:10.1016/j.molstruc.2019.127488.
- [4] D. Zych, A. Slodek, M. Matussek, M. Filapek, G. Szafraniec-Gorol, S. Maślanka, et al., 4'-Phenyl-2,2':6',2"-terpyridine derivatives-synthesis, potential application and the influence of acetylene linker on their properties, Dye Pigment 146 (2017) 331–343, doi:10.1016/j.dyepig.2017.07.030.
- [5] D. Patil, M. Jadhav, K. Avhad, T.H. Chowdhury, A. Islam, I. Bedja, et al., A new class of triphenylamine-based novel sensitizers for DSSCs: a comparative study of three different anchoring groups, New J. Chem. 42 (2018) 11555–11564, doi:10.1039/C8NJ01029C.
- [6] A. Slodek, D. Zych, G. Szafraniec-Gorol, P. Gnida, M. Vasylieva, E. Schab-Balcerzak, Investigations of New Phenothiazine-Based Compounds for Dye-Sensitized Solar Cells with Theoretical Insight, Mater 13 (2020), doi:10.3390/ ma13102292.
- [7] B. Dumat, G. Bordeau, E. Faurel-Paul, F. Mahuteau-Betzer, N. Saettel, M. Bombled, et al., N-phenyl-carbazole-based two-photon fluorescent probes: strong sequence dependence of the duplex vs quadruplex selectivity, Biochimie 93 (2011) 1209–1218, doi:10.1016/j.biochi.2011.05.035.
- [8] S.S. Deshpande, M.A. Jachak, S.S. Khopkar, G.S. Shankarling, A simple substituted spiropyran acting as a photo reversible switch for the detection of lead (Pb2+) ions, Sensors Actuators B Chem. 258 (2018) 648–656, doi:10.1016/j.snb. 2017.11.138.
- [9] V. Joseph, K.R.J. Thomas, S. Sahoo, M. Singh, D.K. Dubey, J.-.H. Jou, Vinyl-Linked Cyanocarbazole-Based Emitters: effect of Conjugation and Terminal Chromophores on the Photophysical and Electroluminescent Properties, ACS Omega 3 (2018) 16477–16488, doi:10.1021/acsomega.8b02198.
- [10] K.N. Shivananda, I. Cohen, E. Borzin, Y. Gerchikov, M. Firstenberg, O. Solomeshch, et al., Sequence-Independent Synthesis of  $\pi$ -conjugated Arylenevinylene Oligomers using Bifunctional Thiophene Monomers, Adv. Funct. Mater. 22 (2012) 1489–1501, doi:10.1002/adfm.201101897.
- [11] H. Mustroph, M. Stollenwerk, V. Bressau, Current Developments in Optical Data Storage with Organic Dyes, Angew Chemie Int Ed 45 (2006) 2016–2035, doi:10. 1002/anie.200502820.
- [12] D. Zych, A. Kurpanik, A. Slodek, A. Maroń, M. Pająk, G. Szafraniec-Gorol, et al., NCN-Coordinating Ligands based on Pyrene Structure with Potential Application in Organic Electronics, Chem. – A Eur. J. 23 (2017) 15746–15758, doi:10. 1002/chem.201703324.
- [13] D.W. Chang, S.-J. Ko, J.Y. Kim, S.-.M. Park, H.J. Lee, L. Dai, et al., Multifunctional Conjugated Polymers with Main-Chain Donors and Side-Chain Acceptors for Dye Sensitized Solar Cells (DSSCs) and Organic Photovoltaic Cells (OPVs), Macromol. Rapid Commun. 32 (2011) 1809–1814, doi:10.1002/marc.201100447.
- [14] D. Patil, M. Jadhav, K. Avhad, Y. Gawale, N. Sekar, NIR emitting new N, Ndiethylaniline based NLOphoric D-π-A and D-A'-π-A dyes: photophysical properties, viscosity sensitivity and DFT studies, J. Lumin. 204 (2018) 436–447, doi:10.1016/j.jlumin.2018.08.031.
- [15] P.R. Bohländer, H.-.A. Wagenknecht, Synthesis and evaluation of cyanine-styryl dyes with enhanced photostability for fluorescent DNA staining, Org. Biomol. Chem. 11 (2013) 7458–7462, doi:10.1039/C30B41717D.
- [16] T. Deligeorgiev, A. Vasilev, S. Kaloyanova, J.J. Vaquero, Styryl dyes synthesis and applications during the last 15 years, Color. Technol. 126 (2010) 55–80, doi:10.1111/j.1478-4408.2010.00235.x.
- [17] B.N. Jha, J.C. Banerji, Chromophoric chain  $\beta$ -aryl-substituted styryl cyanines: effect of substituents on visible absorption spectra and photosensitisation properties, Dye Pigment 6 (1985) 213–226, doi:10.1016/0143-7208(85)80018-8.
- [18] A. Costela, I. García-Moreno, M. Pintado-Sierra, F. Amat-Guerri, M. Liras, R. Sastre, et al., New laser dye based on the 3-styryl analog of the BODIPY dye PM567, J. Photochem. Photobiol. Chem. 198 (2008) 192–199, doi:10.1016/j. jphotochem.2008.03.010.
- [19] Z.-E. Chen, Q.-L. Qi, H. Zhang, Linear donor with multiple flexible chains for dye-sensitized solar cells: inhibition of dye aggregation and charge recombination, Synth. Met. 267 (2020) 116473, doi:10.1016/j.synthmet.2020.116473.
- [20] M. Jachak, S. Khopkar, A. Chaturvedi, A. Joglekar, G. Shankarling, Synthesis of novel viscosity sensitive pyrrolo-quinaldine based styryl dyes: photophysical properties, electrochemical and DFT study, J. Photochem. Photobiol. Chem. 397 (2020) 112557, doi:10.1016/j.jphotochem.2020.112557.
- [21] W.A. Dhafina, M.Z. Daud, H. Salleh, The sensitization effect of anthocyanin and chlorophyll dyes on optical and photovoltaic properties of zinc oxide based dye-sensitized solar cells, Optik (Stuttg) 207 (2020) 163808, doi:10.1016/j.ijleo. 2019.163808.
- [22] G. Hong, A.L. Antaris, H. Dai, Near-infrared fluorophores for biomedical imaging, Nat. Biomed. Eng. 1 (2017) 10, doi:10.1038/s41551-016-0010.
- [23] M. Peng, J. Yin, W. Lin, Development of a two-photon fluorescent probe to monitor the changes of viscosity in living cells, zebra fish and mice, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 224 (2020) 117310, doi:10.1016/ j.saa.2019.117310.

- [24] R. Kotani, H. Sotome, H. Okajima, S. Yokoyama, Y. Nakaike, A. Kashiwagi, et al., Flapping viscosity probe that shows polarity-independent ratiometric fluorescence, J Mater. Chem. C 5 (2017) 5248–5256, doi:10.1039/ C7TC01533J.
- [25] T. Xia, L. Wang, Y. Qu, Y. Rui, J. Cao, Y. Hu, et al., A thermoresponsive fluorescent rotor based on a hinged naphthalimide for a viscometer and a viscosity-related thermometer, J Mater Chem C 4 (2016) 5696–5701, doi:10. 1039/C6TC01241H.
- [26] R. Joseph, B. Ramanujam, H. Pal, C.P. Rao, Lower rim 1,3-di-amide-derivative of calix[4]arene possessing bis-{N-(2,2'-dipyridylamide)} pendants: a dual fluorescence sensor for Zn2+ and Ni2+, Tetrahedron Lett. 49 (2008) 6257–6261, doi:10.1016/j.tetlet.2008.08.049.
- [27] H.G. Lee, K.B. Kim, G.J. Park, Y.J. Na, H.Y. Jo, S.A. Lee, et al., An anthracenebased fluorescent sensor for sequential detection of zinc and copper ions, Inorg. Chem. Commun. 39 (2014) 61–65, doi:10.1016/j.inoche.2013. 10.049.
- [28] A. Chatterjee, G. Kaur, M. Joshi, A.R. Choudhury, R. Ghosh, pH dependent catecholase activity of Fe(II) complexes of type [Fe(L)]X2 [L = N-(phenylpyridin-2-yl-methylene)-ethane-1,2-diamine; X = CIO4- (1), PF6- (2)]: role of counter anion on turnover number, Inorganica. Chim. Acta 513 (2020) 119933, doi:10.1016/j.ica.2020.119933.
- [29] V. Mishra, J.M. Thomas, S. Chinnappan, N. Thirupathi, Homoleptic cis- and trans-palladium(II) bis(guanidinato) complexes derived from N-aryl-N',N''di(pyridin-2-yl)- and N-aryl-N',N''-bis(6-methylpyridin-2-yl)guanidines: catalysts for Heck-Mizoroki coupling reactions, J. Organomet. Chem. 892 (2019) 1–17, doi:10.1016/j.jorganchem.2019.04.009.
- [30] C. Seward, J. Pang, S. Wang, Luminescent Star-Shaped Zinc(II) and Platinum(II) Complexes Based on Star-Shaped 2,2'-Dipyridylamino-Derived Ligands, Eur. J. Inorg. Chem. 2002 (2002) 1390–1399 doi:10.1002/1099-0682(200206)2002:6<1390::AID-EJIC1390>3.0.CO;2-E.
- [31] K. Avhad, M. Jadhav, D. Patil, T.H. Chowdhury, A. Islam, I. Bedja, et al., Rhodanine-3-acetic acid containing D-π-A push-pull chromophores: effect of methoxy group on the performance of dye-sensitized solar cells, Org. Electron. 65 (2019) 386–393, doi:10.1016/j.orgel.2018.11.041.
- [32] D.S. Patil, K.K. Sonigara, M.M. Jadhav, K.C. Avhad, S. Sharma, S.S. Soni, et al., Effect of structural manipulation in hetero-tri-aryl amine donor-based D-A'- $\pi$ -A sensitizers in dye-sensitized solar cells, New J. Chem. 42 (2018) 4361–4371, doi:10.1039/C7NJ04620K.
- [33] Y. Ni, L. Zeng, N.-Y. Kang, K.-W. Huang, L. Wang, Z. Zeng, et al., meso-Ester and Carboxylic Acid Substituted BODIPYs with Far-Red and Near-Infrared Emission for Bioimaging Applications, Chem. – A Eur. J. 20 (2014) 2301–2310, doi:10. 1002/chem.201303868.
- [34] R.M. Franzini, E.T. Kool, 7-Azidomethoxy-Coumarins as Profluorophores for Templated Nucleic Acid Detection, ChemBioChem 9 (2008) 2981–2988, doi:10. 1002/cbic.200800507.
- [35] P.O. Nkeonye, Reactive Dyes Containing Phosphonic and Carboxylic Acid Reactive Groupings and Their Reactions with Cellulose, J. Soc. Dye Colour 102 (1986) 384–391, doi:10.1111/j.1478-4408.1986.tb01050.x.
- [36] B. Zhang, J. Sun, C. Bi, G. Yin, L. Pu, Y. Shi, et al., A highly selective ratiometric fluorescent chemosensor for Ag+ based on a rhodanineacetic acid-pyrene derivative, New J. Chem. 35 (2011) 849-853, doi:10.1039/ C0NJ00958J.
- [37] S. Ali Muhammad, S. Ravi, A Thangamani, Synthesis and evaluation of some novel N-substituted rhodanines for their anticancer activity, Med. Chem. Res. 25 (2016) 994–1004, doi:10.1007/s00044-016-1545-7.
- [38] J. Niao, C.-.J. Zheng, L-P Sun, M.-.X. Song, L-L Xu, H.-.R. Piao, Synthesis and potential antibacterial activity of new rhodanine-3-acetic acid derivatives, Med. Chem. Res. 22 (2013) 4125–4132, doi:10.1007/s00044-012-0417-z.
- [39] A. Slodek, M. Filapek, G. Szafraniec, I. Grudzka, W.A. Pisarski, J.G. Malecki, et al., Synthesis, Electrochemistry, Crystal Structures, and Optical Properties of Quinoline Derivatives with a 2,2'-Bithiophene Motif, Eur. J. Org. Chem. 2014 (2014) 5256–5264, doi:10.1002/ejoc.201402241.
- [40] A. Slodek, M. Matussek, M. Filapek, G. Szafraniec-Gorol, A. Szlapa, I. Grudzka-Flak, et al., Small Donor-Acceptor Molecules Based on a Quinoline-Fluorene System with Promising Photovoltaic Properties, Eur. J. Org. Chem. 2016 (2016) 2500–2508, doi:10.1002/ejoc.201600318.
- [41] S. Kedia, R. Vijaya, A.K. Ray, S. Sinha, Laser emission from self-assembled active photonic crystal matrix, J. Nanophotonics 4 (2010) 1–7, doi:10.1117/1.3506524.

- [42] D. Nagaraja, R.M. Melavanki, N.R. Patil, R.A. Kusanur, Solvent effect on the relative quantum yield and fluorescence quenching of 2DAM, Spectrochim. Acta – Part A Mol. Biomol. Spectrosc. 130 (2014) 122–128, doi:10.1016/j.saa.2014.03. 063.
- [43] R.D. Telore, N. Sekar, Carbazole-containing push-pull chromophore with viscosity and polarity sensitive emissions: synthesis and photophysical properties, Dye Pigment 129 (2016) 1–8, doi:10.1016/j.dyepig.2016.02.012.
- [44] A.M. Brouwer, Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report), Pure Appl. Chem. 83 (2011) 2213–2228, doi:10.1351/pac-rep-10-09-31.
- [45] E. Lippert, Spektroskopische Bestimmung des Dipolmomentes aromatischer Verbindungen im ersten angeregten Singulettzustand. Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys Chemie 61 (1957) 962–975, doi:10.1002/bbpc.19570610819.
- [46] C.R. Yonker, R.D. Smith, Solvatochromism: a Dielectric Continuum Model Applied To Supercritical Fluids, J. Phys. Chem. 92 (1988) 235–238, doi:10.1021/ j100312a050.
- [47] J.P. Cerõn-Carrasco, D. Jacquemin, C. Laurence, A. Planchat, C. Reichardt, K. Sraïdi, Solvent polarity scales: determination of new ET(30) values for 84 organic solvents, J. Phys. Org. Chem. 27 (2014) 512–518, doi:10.1002/poc.3293.
- [48] C. Reichardt, Empirical Parameters of Solvent Polarity as Linear Free-Energy Relationships, Angew. Chemie. Int. Ed. English 18 (1979) 98-110, doi:10.1002/ anie.197900981.
- [49] A. Weller, Innermolekularer Protonenübergang im Angeregten Zustand (Intramolecular proton transfer in excited states), Z Elktrochem Angew P 60 (1956) 1144–1147, doi:10.1002/bbpc.19560600938.
- [50] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Structural Changes Accompanying Intramolecular Electron Transfer: Focus on Twisted Intramolecular Charge-Transfer States and Structures, Chem. Rev. 103 (2003) 3899–4032, doi:10.1021/ cr9407451.
- [51] S.K. Patil, M.N. Wari, C.Y. Panicker, S.R. Inamdar, Determination of ground and excited state dipole moments of dipolar laser dyes by solvatochromic shift method, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 123 (2014) 117– 126, doi:10.1016/j.saa.2013.12.031.
- [52] I. Georgieva, A.J.A. Aquino, F. Plasser, N. Trendafilova, A. Köhn, H. Lischka, Intramolecular Charge-Transfer Excited-State Processes in 4-(N, N – Dimethylamino)benzonitrile: the Role of Twisting and the  $\pi\sigma^*$  State, J. Phys. Chem. A 119 (2015) 6232–6243, doi:10.1021/acs.jpca.5b03282.
- [53] P.K.M. Lokhande, D.S. Patil, N. Sekar, Viscosity sensitive red shifted novel D-π-A carbazole chromophore with chlorine in π-spacer: synthesis, photophysical properties, NLO study and DFT approach, J. Lumin. 211 (2019) 162–175, doi:10. 1016/j.jlumin.2019.03.028.
- [54] F. Zhou, J. Shao, Y. Yang, J. Zhao, H. Guo, X. Li, et al., Molecular Rotors as Fluorescent Viscosity Sensors : molecular Design, Polarity Sensitivity, Dipole Moments Changes, Screening Solvents, and Deactivation Channel of the Excited States, Eur. J. Org. Chem. (2011) 4773–4787, doi:10.1002/ejoc.201100606.
- [55] Th Förster, G. Hoffmann, Die viskositätsabhängigkeit der fluoreszenzquantenausbeuten einiger farbstoffsysteme, Zeitschrift für Physikalische Chemie 75 (no. 1\_2) (1971) 63–76.
- [56] TURBOMOLE V6.5, A development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH. 1989-2007, TURBOMOLE GmbH (2013) since 2007available from http://www.turbomole.com.
- [57] D. Zych, A. Slodek, Sensitizers for DSSC containing triazole motif with acceptor/donor substituents – Correlation between theoretical and experimental data in prediction of consistent photophysical parameters, J. Mol. Struct. 1207 (2020) 127771, doi:10.1016/j.molstruc.2020.127771.
- [58] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648, doi:10.1063/1.464913.
- [59] G. Rauhut, P. Pulay, Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields, J. Phys. Chem. 99 (1995) 3093-3100, doi:10. 1021/j100010a019.
- [60] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (2005) 3297–3305, doi:10.1039/B508541A.
- [61] M.E.M. Emam, Thermal Stability of Some Textile Dyes, J. Therm. Anal. Calorim. 66 (2001) 583–591, doi:10.1023/A:1013185422100.
- [62] B. Demirel, A. Yaraş, H ELÇİÇEK, Crystallization Behavior of PET Materials, Balıkesir Üniversitesi Fen Bilim Enstitü Derg 13 (2011) 26–35.