ORIGINAL ARTICLE



# Study on Synthesis and Fluorescence of Novel Benzofused Phenazine $\pi$ -Conjugated Skeleton with Coumarin and Isophoron Cores

Amol S. Choudhary<sup>1</sup> · Sharad R. Patil<sup>1</sup> · Nagaiyan Sekar<sup>1</sup>

Received: 6 February 2015/Accepted: 15 June 2015/Published online: 3 July 2015 © Springer Science+Business Media New York 2015

Abstract The novel benzofused phenazine  $\pi$ -conjugated skeleton with a coumarin and isophoron core was synthesized, characterized, and condensed with suitably substituted active methylene compounds by classical Knoevenagel condensation reaction to obtain novel mono-styryl dyes 6a-6d. These novel styryl dyes have hue varying from yellow to violet. The geometries of the styryl dyes were optimized at B3LYP/6-31G (d) level of theory, and their electronic excitation properties were evaluated using density functional theory.

Keywords Phenazines  $\cdot$  Isophoron  $\cdot$  Styryl dyes  $\cdot$  DFT  $\cdot$  Fluorescence  $\cdot$  TDDFT

### Introduction

In recent years, the development of organic  $\pi$ -conjugated molecules for organic electronic, such as organic light emitting diode (OLEDs) [1], organic field effect transistor (OFETs) [2], environment-sensitive fluorescence [3] and organic photovoltaic (OPVs) [4] remain a key objective. Organic materials have distinct advantage of their structure diversity, which can be achieved by versatile synthetic protocol in organic chemistry. It is important to tailor the electronic structure of

**Electronic supplementary material** The online version of this article (doi:10.1007/s10895-015-1597-y) contains supplementary material, which is available to authorized users.

Nagaiyan Sekar n.sekar@ictmumbai.edu.in; nethi.sekar@gmail.com

<sup>1</sup> Tinctorial Chemistry Group, Department of dyestuff and intermediate Technology, Institute of Chemical Technology, Mumbai, Nathalal Parekh Marg, Matunga, Mumbai 400 019, India  $\pi$ -conjugated molecules and control the solid-state structure to obtained appropriated intermolecular interaction in an intelligent way.

Consequently, recent advance in exploring  $\pi$ -conjugated molecules involved the extension of  $\pi$ -conjugation between the donor (D) motif such as carbazole, biphenyl amine, quinoxaline or N,N,-diethylamide and acceptor group (A) such as cyano, nitro or benzimidazole, other heterocycles. Such kind of analogues gives the excellent photophysical properties. Conjugated D- $\pi$ -A materials have important electrical, optical and redox properties that make them outstanding candidates for integration into electro-optical and lightemitting devices (LEDs) [5, 6].

There have been tremendous research activity in the field of styryl dyes as they have promising applications in the high technology areas. One of the reasons for this is the relative ease of synthesis of such dyes. The styryl dyes have a number of good properties, like fluorescence and good photo stability as compared to the cyanine analogous. Styryl dyes with absorption ranging from UV to near infrared region can be synthesized by using different substituent on the chromophore [7, 8].

The 2, 5-diamino-3,6-dicynopyrazine derivatives have a small chromophoric system but have strong fluorescence even in the solid state [9]. The dicynopyrazine have very strong electron withdrawing ability, and derivative thereof can be are expected to have strong intramolecular charge transfer interaction in their self-assemble aggregates [10].

The compounds having an intramolecular charge transfer properties are one of the most important materials. Such materials are usually functionalized by electron-donating (D) and electron-accepting (A) groups through a  $\pi$ -conjugated bridge which makes it possible to reduce the gap between HOMO and LUMO orbital of the molecule for increasing the range of absorption and to study the relationship between the variation of donor-acceptor chromophores and their corresponding photophysical and electrochemical properties [11, 12].

The electron-rich benzo[a]phenazin-5-ol unit is donor moiety of donor-acceptor type of functional molecules. Phenazine derivatives are important molecules in dye-sensitized solar cells (DSSCs) [13, 14]. Phenazine  $\pi$ -conjugated skeleton derivatives have also attracted considerable interest in colorimetric and ratiometric near-infrared fluorescent cyanide chemodosimeter. With these approach, to explore the relationship between chemical structures and various properties of these compounds, we have designed and synthesized a new series of intramolecular charge transfer (ICT) compounds by incorporating the benzo[a]phenazin-5-ol moiety (electron donor) with isophoron bridge or 3-acetylcoumarin groups (electron acceptor), and studied their absorption and fluorescence spectroscopy, thermo gravimetric analysis and density functional theory calculations.

Some of these dyes showed fluorescence in the solid state. The synthesized phenazine  $\pi$ -conjugated dyes have shown red-shifted absorption properties in comparison with the phenazine  $\pi$ -conjugated based dyes reported earlier [10–12]. Density functional theory computations [B3LYP/6-31G (d)] were carried out to study the geometrical and electronic properties, and its related properties were computed using B3LYP/ 6-31G (d) on the basis of the finite field approach [13–15].

# Experimental

### **Materials and Instrumentation**

2-Hydroxy-1, 4-napthaquinone, substituted ophenylenediamine, o-aminothiophenol, and malononitrile were procured from Sigma Aldrich. 2-(3,5,5-trimethylcyclohex-2en-1-ylidene)malononitrile and 2-(1-(2-oxo-2 H-chromen-3yl)ethylidene) malononitrile were synthesized by the reported method. The reaction was monitored by TLC using 0.25 mm E-Merck silica gel 60 F<sub>254</sub> percolated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai, and are uncorrected. The FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR Spectrometer. <sup>1</sup>HNMR spectra were recorded on VXR 300 MHz instrument using TMS as an internal standard. The visible absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV-Visible spectrophotometer. Emission and excitation spectra of the compounds are measured on Varian Cary eclipse spectrofluorimeter.

### **Computational Methods**

Gaussian 09 program package was used to optimize geometry and to study the synthesized azo dyes in their azo and hydrazone tautomeric forms [16]. Ground state (S0) geometry of the dyes in gas and solvent was optimized in their C1 symmetry using DFT [17]. The Becke's three parameter exchange functional (B3) [18] combining with nonlocal correlation functional by Lee, Yang and Parr (LYP) [19] and basis set6-31G (d)was used for all atom. Same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. Time Dependent Density Functional Theory (TD- DFT) computations were used to obtain the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries at the same hybrid functional and basis set [20–22]. All the computations in solvents of different polarities were carried out using the Self-Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM) [23].

### Synthetic Strategy

#### General Method for the Synthesis and Characterization of 3

2-Hydroxy-1, 4-napthaquinone 1 (2 mmol) and substituted ophenylenediamine 2 (2 mmol) were stirred in a mixture of AcOH: EtOH (50:50) (20 ml) at 80 °C for 1–1.5 h. Completion of the reaction was monitored by TLC. After completion of the reaction, the reaction mass was poured in crushed ice and stirred for 30 min at room temperature. The reaction mass was filtered and the product was purified by column chromatography using silica gel 100–200 mesh and ethyl acetate: hexane (50:50) as eluent system.

#### General Procedure for the Synthesis of 4a

POCl<sub>3</sub> (0.015 mmol) was added to DMF (0.20 mmol) at 0 °C within 15 min and stirred for 30 min at 0 ° C. Naphtho [1,2-a]phenazin-5-ol **3** (0.01 mmol) dissolved in DMF (5 ml) was added slowly at 0–5 °C and stirred for 2–3 h at room temperature. The completion of the reaction was monitored by TLC. The reaction mass was poured in ice and stirred, neutralized with sodium bicarbonate, filtered and dried. The crude aldehyde was recrystallized from ethanol. The product was purified by column chromatography using silica gel 100–200 mesh and ethyl acetate: hexane (10:90) as eluent system. **Yield = 69 %, Melting point: 163–168 °C** FT-IR (KBr, cm<sup>-1</sup>): 3100 (–OH), 2930 (COH), 1600 (CO), 1577 (C = N), 1200 (C-O).

Mass: m/z 274 [M + 1].<sup>1</sup> H NMR (CDCl<sub>3</sub>, 300 MHz) =  $\delta$ 3.67 (t, 4 H, J = 6.9, 4.7 Hz), 3.83 (t, 4 H, J = 7.4, 5.1 Hz), 7.29 (m, 4 H), 8.60 (bs, 1 H), 8.5 (s, 1 H) ppm.

### Procedure for the Synthesis of 4b

 $POCl_3$  (0.015 mmol) was added to DMF (0.20 mmol) at 0 °C within 15 min and stirred for 30 min at 0 °C. Naphtho [1,2-

a]phenazin-5-ol **17** (0.01 mmol) dissolved in DMF (5 ml) was added slowly at 0–5 °C and stirred and heated up to 90 °C for 2–3 h. The completion of the reaction was monitored by TLC. The reaction mass was poured in ice and stirred, neutralized with sodium bicarbonate, filtered and dried. The crude aldehyde was recrystallized from ethanol. The product was purified by column chromatography using silica gel 100–200 mesh and hexane as eluent system. **Yield = 58 %, Melting point: 173–178 °C** FT-IR (cm<sup>-1</sup>) = 1701 (C = O), 1586 (C = C, aromatic). Mass = m/z = 292.08, M + 1 = 293.08 M + 2 = 294.08, (M + 1).<sup>1</sup> H NMR (CDCl3, 300 MHz) =  $\delta$  10.24 (s, 1 H) 7.66–7.80 (m, 4 H), 7.83–7.95 (m, 4 H).

### General Procedure for the Synthesis of 6a-6d

5-Hydroxybenzo[a]phenazine-6-carbaldehyde **4a** or **4b** (1.8 mmol) and 2-(3, 5, 5-trimethylcyclohex-2-en-1-ethylidene) malononitrile **5a** or 2-(1-(2-oxo-2 H-chromen-3-yl) ethylene) malononitrile **5b** (2.0 mmol) were stirred in ethanol (20 ml). Catalytic amount of piperidine was added to the mixture and refluxed for 2 h. Completion of the

Scheme 1 Synthesis of styryl dyes 6a-6d

 Table 1
 Photophysical properties of compound 6b and 6d in different solvents

Solvents	Dye 6b Absorption			Dye 6d Absorption			
	ACN	425	0.5615	23,529.4	445	0.4424	224,719.1
640		0.3206	15,625	625	0.1212	160,000	
EtOH	415	0.6963	24,096.4	440	0.4180	227,272.8	
	480	0.5307	208,333.3	630	0.1527	158,730.1	
	650	0.4647	153,846.1				
DMF	420	0.5664	238,095.2	420	0.4962	238,095.2	
	485	0.4547	206,185.6	625	0.2451	160,000	
	650	o.4647	153,846.1				
DMSO	415	0.5708	24,096.4	425	0.4284	224,719.1	
	485	0.4547	206,185.6	640	0.2070	15,625	
	650	0.4776	153,846.1				

reaction was monitored by TLC. The compound precipitated out was filtered and purified by column chromatography using silica 100–200 mesh and ethyl acetate: hexane (60:40) as eluent.



i = ethanol/acetic acid, 80  $^{0}$ C,3 h ii = POCl<sub>3</sub>/DMF,0-R.T. iii = POCl<sub>3</sub>/DMF 80  $^{0}$ C iv = ethanol/ cat. piperiden, 6 h (*E*)-2-(3-(2-(5-hydroxybenzo[a]phenazin-6-yl)vinyl)-5,5dimethylcyclohex-2-en-1-ylidene)malononitrile **6a**.

# Yield = 54 %; Melting point = 283–285 °C.

FT-IR (cm-1) = 3029 (Ar-H), 3201 (–OH), 2920 (CH3), 1610 (C = C, aromatic), 1558 (C = N), 2110 (–CN). Mass = m/z = 442.12, M + 2 = 443.6.1 H NMR (CDCl3, 300 MHz) =  $\delta$  1.4 (s, 3 H, –CH<sub>3</sub>)  $\delta$  1.7 (s, 3 H, –CH<sub>3</sub>),  $\delta$ 2.7 (d, 2 H,-CH<sub>2</sub>),  $\delta$  3.3(s,2 H,-CH2),7.3(s,1 H),  $\delta$  7.1(dd, 1 H),7.7(s,1 H)  $\delta$  7.9–8.1(m,4 H,Ar),  $\delta$  8.2–8.4(m,4 H, Ar),  $\delta$  9.4 (br,s,1 H, –OH).

(*E*)-2-(3-(5-hydroxybenzo[a]phenazin-6-yl)-1-(2-oxo-2 Hchromen-3-yl)allylidene) malononitrile **6b**.

## Yield = 64 %; Melting point = 278–281 °C. 73.

FT-IR (cm-1) = 3013 (Ar-H), 3207 (-OH), 2910 (CH3), 1605 (C = C, aromatic), 1545 (C = N), 2210 (-CN). Mass = m/z = 492.12, M + 2 = 493.6.1 H NMR (CDCl<sub>3</sub>, 300 MHz) =  $\delta$  5.4 (s, 1 H, -OH)  $\delta$  6.8 (d, 1 H, =CH),  $\delta$  7.2 (d, 1 H,=CH),  $\delta$  7.5(s,1 H, pyrano ring proton),  $\delta$  7.2–7.4 (m, 4 H, Ar-H),  $\delta$  7.5–7.8 (m,4 H, Ar-H), 8.0–8.4 (m,4 H,Ar-H).

(*E*)-2-(3-(2-(5-chlorobenzo[a]phenazin-6-yl)vinyl)-5,5dimethylcyclohex-2-en-1-ylidene)malononitrile **6c.** 

Yield = 45 %; Melting point = 278–280 °C.

FT-IR (cm-1) = 3029 (Ar-H), 3201 (−OH), 2920 (CH<sub>3</sub>), 1610 (C = C, aromatic), 1558 (C = N), 786 (Ar-Cl) 2110 (−CN). Mass = m/z = 442.12, M + 2 = 443.6.1 H NMR (CDCl<sub>3</sub>, 300 MHz) =  $\delta$  1.4 (s, 3 H, −CH<sub>3</sub>)  $\delta$  1.7 (s, 3 H, −CH<sub>3</sub>),  $\delta$  2.7 (d, 2 H,-CH<sub>2</sub>),  $\delta$  3.3(s,2 H,-CH<sub>2</sub>),7.3(s,1 H),  $\delta$  7.1(dd,1 H),7. 7(s,1 H)  $\delta$  7.9–8.1(m,4 H,Ar),  $\delta$  8.2–8.4(m,4 H, Ar).

(*E*)-2-(3-(5-chlorobenzo[a]phenazin-6-yl)-1-(2-oxo-2 H-chromen-3-yl)allylidene)malononitrile **6d.** 

### Yield = 74 %; Melting point = 278–280 °C.

FT-IR (cm-1) = 3013 (Ar-H), 3207 (–OH), 2910 (CH<sub>3</sub>), 1605 (C = C, aromatic), 1545 (C = N), 2210 (–CN). Mass = m/z = 492.12, M + 2 = 493.6.1 H NMR (CDCl<sub>3</sub>, 300 MHz) =  $\delta$  6.8 (d, 1 H, =CH),  $\delta$  7.2 (d, 1 H,=CH),  $\delta$ 7.5(s,1 H, pyrano ring proton),  $\delta$  7.2–7.4 (m, 4 H, Ar-H),  $\delta$ 7.5–7.8 (m,4 H, Ar-H), 8.0–8.4 (m,4 H,Ar-H).

Fig. 1 Photophysical properties of compounds 6a and 6c in solid state



Fig. 2 Photophysical properties of compound 6b in different solvents

# **Result and Discussion**

## Synthesis Strategy and Characterization

The synthetic plan for the preparation of (E)-2-(3-(5hydroxybenzo[a]phenazin-6-yl)-1-(2-oxo-2 H-chromen-3yl)allylidene)malononitrile and (E)-2-(3-(5chlorobenzo[a]phenazin-6-yl)-1-(2-oxo-2 H-chromen-3vl)allylidene)malononitrile 6a-6d is shown in Scheme 1. Benzo[a]phenazin-5-ol 3 was prepared by condensation of 2-hydroxy-1,4-napthaquinone (Lawson) 1 with 1,2diaminobenzene 2 in presences of glacial acetic acid at 60 °C for 60 min. 5-Hydroxybenzo[a]phenazine-6carbaldehyde 4a and 5-Chloro[a]phenazine-6carbaldehyde 4b were prepared by the Vilsmeier Haack reaction, which was confirmed by FTIR, <sup>1</sup>HNMR, mass spectral analysis and its M + 1 peak was found to be at 274.1. The compounds 4a or 4b on treatment with 5a or 5b active methylene compounds, respectively, in the DMSO/ethanol in presence of catalytic amount of piperidine at reflux temperature (70-80 °C) for 4-5 h gave (E)-2-(3-(5hydroxybenzo [a]phenazin-6-yl)-1-(2-oxo-2 H-chromen-3-yl)allylidene)malononitrile and (E)-2-(3-(5-





Fig. 3 Photophysical properties of compound 6d in different solvents

chlorobenzo[a]phenazin-6-yl)-1-(2-oxo-2 H-chromen-3-yl)allylidene) malononitrile **6a-6d**. The synthesized compound **6b** and **6d** were purified by column chromatography and confirmed by FTIR, <sup>1</sup>HNMR, and mass spectral.

### **Electronic Spectra**

The compounds **6b** and **6d** are soluble in N, Ndimethylformamide (DMF), dimethylsulphoxide (DMSO), methanol (MeOH), ethanol (EtOH), and acetonitrile (ACN). The compounds **6a** and **6c** are insoluble in all solvents. The electronic spectra of the compounds **6b** and **6d** in solvents of differing polarity values presented in (Table 1). Which illustrates the color of the compounds in different solvents, in which the respective electronic spectra for **6b** and **6d** were, recorded (Table 1, Figs. 1 and 2). Form Fig. 2, the dye **6b** showed two absorption band in all solvents. The  $\lambda_{\text{max}}$  values of the compound **6b**, absorb at 445 and 625 nm for ACN, 440 and 630 nm in EtOH, 420 and 625 nm in DMF, 425 and 640 nm in DMSO, and 624 nm for DMF. While show three absorption band shown in Fig. 3. From the Fig. 3 the dye **6d** in different solvents were as follows: 425 and 640 nm for ACN, 415,480 and 650 nm in EtOH, 420,485 and 650 nm in DMF, 415,485 and 650 nm in DMSO. The Visible and fluorescence spectra of dyes **6a** and **6c** in solid state summarize in Fig. 1. The excitation wavelength and fluorescence maxima of these dyes in solid state were observed at 460,465 nm and emission at 552, 550 nm, for dyes **6a** and **6c** respectively.

It is well known that the fluorescence of coumarins is strongly dependent on the electron-donating-withdrawing ability of the substituents at position 7 and 3. Absorption properties of the synthesized dye **6a-6d**. In which benzo phenazine  $\pi$ -conjugated skeleton and coumarin couple via C = C bond. Their photophysical properties depicted (Table 1, Figs 1, 2 and 3). Absorption maxima reveal that the more conjugated styryl derivatives **6b** and **6d** are all red-shifted when compared with the respective isophoron styryl derivatives **6a** and **6b**.

 Table 2
 Calculated electronic absorption spectral data of 6a and 6b molecule

Solvent	Excitation	CI expansion coefficient	Wave length		Oscillator strength( $f$ )	Energy			
			Calculated	Experimental					
ACN	Excited State 1								
	127 - > 128	0.70032	526.27	640 (0.3206)	0.2611	2.3559			
	Excited State 2								
	126 - > 128	0.60565	421.65	425(0.5615)	0.0334	2.9404			
	127 - > 129	0.35253							
EtOH	Excited State 1								
	127 - > 128	0.70043	526.86	650 (0.4647)	0.2628	2.3533			
	Excited State 2								
	126 - > 128	0.61233	421.87	480 (0.5307)	0.0323	2.9389			
	127 - > 129	0.34121							
	Excited State 3								
	126- > 128	-0.34518	418.08	415(0.6963)	0.1296	2.9656			
	127- > 129	0.59854							
DMF	Excited State 1								
	127- > 128	0.70083	529.48	650 (0.465)	0.2668	2.3416			
	Excited State 2								
	126- > 128	0.64895	423.19	485 (0.455)	0.0252	2.9298			
	127- > 129	0.26749							
	Excited State 3								
	126- > 128	-0.26995	418.79	420 (0.566)	0.1471	2.9606			
	127- > 129	0.63527							

The TD- DFT is particularly well suited to low energy valence excited states that can be described by combinations of single excitations. Electronic transitions determined from excited state calculations using the TD-DFT method are listed in Table 2 for the three lowest energy transitions of the molecule. These are identified with the calculated transitions at 526, 421 and 418 nm. In this case the energy transitions are in reasonable agreement with experimental results.

### **Optimized Geometries of Dyes 6a-6d**

The optimized geometry of all studied compounds calculated by B3LYP/6-31G d are depicted in Fig. 4 and important structure parameter of these molecules are shown in Fig. 4. The optimized structure of the title compounds in the ground state show the non-planer molecular structure. Since in compound **6a**, **6b**, **6c** and **6d**  $\pi$ -bridge and acceptor cyano group is sandwich between the hydroxy benzophenazine/chloro benzophenazine and 3-acetylcoumarin/isophoron subunit. In the compounds **6b** and **6d** the connection between the two adjacent subunit of the molecules relies on single bond, it lead to elevation torsion angles between the coumarin ring and  $\pi$ - bridge similarly with benzophenazine core respectively (Fig. 4).

The optimized ground-state geometries of the studied compound are classified into three categories. The compound including the relative linking positioned of coumarin/isophoron core at one of the end of  $\pi$ -bridge and hydroxy group is substituted with the chloro group as shown in Fig. 4. The bond lengths, torsion angle, and dipole moments of 6b and 6d compounds in the ground state are shown in Fig. 4. The presence of coumarin or isophoron core brings abour appreciable cahnage in the geometry of the compounds of 6a, 6b, 6c and 6d. For all these compounds, the similar inter link bond length and different dihedral angle between  $\pi$ -bridge are attentively observed as shown in the Fig. 4. In the compound 6b, benzophenazine and coumarin core torsional angle is 27<sup>0</sup> while the same in **6d**  $19^{\circ}$  which reveals that the presence of chloro-benzophenazine favors planarity with the  $\pi$ -bridge as compared to hydroxy benzophenazine. This is because carbonyl oxygen of coumarin core and hydroxyl proton of benzophenazine core come closer to each other with an interatomic distance of 2.12225 A<sup>0</sup> while in compound **6a** and **6c** chloro group induces steric hindrance. This is because



Fig. 4 Optimized geometry of the consider molecules by DFT/B3LYP/6-31G d



Fig. 5 Molecular orbital plotting (orbital squared) for the mainly participating molecular orbitals of **6b** 

carbonyl hydroxyl group of benzophenazine core gets involved in conjugation with the  $\pi$ -bridge and acceptor cyano group.

#### **Frontier Molecular Orbital and Electronic Properties**

The ordering the occupied and virtual orbitals provide a reasonable qualitative indication of the excitation properties. A sketch of map of the HOMOs and LUMOs as well as other important orbitals for all synthesized 6a-6d molecules is plotted in (Fig. 5, 6, 7 and 8). The electron density contribution of each fragment to frontier orbitals has been listed in all the



Fig. 6 Molecular orbital plotting (orbital squared) for the mainly participating molecular orbitals of 6d





Fig. 7 Molecular orbital plotting (orbital squared) for the mainly participating molecular orbitals of **6a** 

frontier molecular orbital show  $\pi$ -character. For **6b** and **6d** molecules, the HOMO are mainly constrained towards coumarin core with largest contributions form planer benzophenazine, whereas central  $\pi$ -bridge and acceptor cyano group have dominating contribution to LUMOs. From Fig. 5-8 the electron density data imply that the benzophenazine unit serves the electron donating role, and  $\pi$ -bridge and coumarin serve as electron accepting role and its electron density strength when the core molecule alter form a coumarin to isophoron ring. However for **6a** molecule, the electronic cloud



Fig. 8 Molecular orbital plotting (orbital squared) for the mainly participating molecular orbitals of 6c

distribution is delocalized on the whole conjugated skeleton in the HOMOs. While for the LUMO, the electronic cloud is mainly transferred to isophoron bridge core, we have predicted that **6a** and **6b** core have good  $\pi$ -conjugation for electron delocalization.

### Conclusion

In this work, we have developed push-pull chromophores of A- $\pi$ -D and A- $\pi$ -D- $\pi$ -A types containing benzophenazine, coumarin and electron withdrawing cyano moieties. Benzophenazine and coumarin moiety was introduced to the make the system non-planar. These synthesized fluorophores were confirmed by FT-IR, <sup>1</sup>HNMR and Mass spectral analysis.

**Acknowledgments** The author Amol S. Choudhary is thankful to University Grants Commission (UGC), New Delhi, India for providing financial support by way of Junior Research Fellowship (JRF) and Senior Research Fellowship (SRF) and the Centre of Advanced Studies (CAS), UGC for the financial support.

### References

- Fu H, Wu H, Hou X, Xiao F, Shao B (2006) N-aryl carbazole derivatives for non-doped red OLEDs. Synth Met 156:809–814
- Katsuta S, Miyagi D, Yamada H, Okujima T, Mori S, Nakayama K, et al. (2011) Synthesis, properties, and ambipolar organic fieldeffect transistor performances of symmetrically cyanated pentacene and naphthacene as air-stable acene derivatives. Org Lett 13:1454– 1457
- 3. Sarma M, Chatterjee T, Ghanta S, Das SK (2012) D- $\pi$ -a-a- $\pi$ -D prototype 2,2 ' -bipyridine dyads exhibiting large structure and environment-sensitive fluorescence: synthesis, photophysics, and computation. J. Org. Chem. 77:432–444
- Sukeguchi D, Singh SP, Reddy MR, Yoshiyama H, Afre R, Hayashi Y, et al. (2009) New diarylmethanofullerene derivatives and their properties for organic thin-film solar cells. Beilstein J Org Chem 5:7
- 5. Shimizu H, Fujimoto K, Furusyo M, Maeda H, Nanai Y, Mizuno K, et al (2007) Highly Emissive  $\pi$ -Conjugated Alkynylpyrene Oligomers: Their Synthesis and Photophysical Properties their electrical and optical characteristics, so that the oligomers and polymers have been used for such applications as organic aromatics are important. J Org Chem 72:1530–1533
- Liu C, Tang K, Zhang H, Pan H, Hua J, et al (2012) Studies of excited-state properties of multibranched triarylamine. J Phys Chem A 116:12339–12348

- Li H, Yang L, Tang R, Hou Y, Yang Y, Wang H, Han H, Qin J, Li Q, Li Z (2013) Organic dyes incorporating N-functionalized pyrrole as conjugated bridge for dye-sensitized solar cells: convenient synthesis, additional withdrawing group on the π-bridge and the suppressed aggregation. Dye Pigment. doi:10.1016/j.dyepig.2013.05. 030
- Sturzl N, Lebedkin S, Kappes MM (2009) Revisiting the laser dye styryl-13 as a reference near-infrared fluorophore: implications for the photoluminescence quantum yields of semiconducting singlewalled carbon J. Phys Chem A 113:10238–10240
- Dreuw A, Plötner J, Lorenz L, Djanhan JE, Brüning J, et al (2005) Molecular mechanism of the solid-state fluorescence behavior of the organic pigment yellow 101 and its derivatives. Angew Chem Int Ed Engl 44:7783–7786
- Sen T, Bhattacharyya S (2012) Spectroscopic investigations on the H-type aggregation of coumarin 153 dye molecules: role of Au nanoparticles and γ – cyclodextrin. J Fluoresc 22:303–310
- Satam V, Rajule R, Bendre S, Bineesh P, Kanetkar V (2009) Synthesis and application of novel styryl dyes derived from 1,4diethyl-1,2,3,4-tetrahydro-6-methoxyquinoxaline. J Heterocyclic Chem 46:221
- Gordo J, Parola AJ, Lima C, Branco PS (2011) Convenient synthesis of 3-vinyl and 3-styryl coumarins. Org Lett 13(19):5112–5115
- Zhang G, Bala H, Cheng Y, Shi D, Lv X, Yu Q, et al (2009) High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary pi-conjugated spacer. Chem Commun (Camb):2198–2200
- Zhang X, Zhang J, Xia Y (2008) Molecular design of coumarin dyes with high efficiency in dye-sensitized solar cells. J Photochem Photobiol A Chem 194:167–172
- Deshmukh MS, Sekar N (2014) A combined experimental and TD-DFT investigation of three disperse azo dyes having the nitro terephthalate skeleton. Dyes Pigments 103:25–33
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. (2010) Gaussian 09, revision C.01. Gaussian, Inc, Wallingford CT
- Treutler O, Ahlrichs R (1995) Efficient molecular numerical integration schemes. J Chem Phys 102:346–354
- Becke AD (1993) A new mixing of hartreee fock and local densityfunctional theories. J Chem Phys 98:1372–1377
- Lee C, Yang W, Parr RG (1988) Development of the colle-salvetti correlation-en- ergy formula into a functional of the electron density. Phys Rev B 37:785–789
- 20. Hehre WJ, Radom L, Schleyer P, Pople JA (1986) Ab initio molecular orbital theory. Wiley, New York
- Bauernschmitt R, Ahlrichs R (1996) Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. Chem Phys Lett 256:454–464
- Furche F, Rappaport D (2005) Density functional theory for excited states: equilibrium structure and electronic spectra. In: Olivucci M (ed) Computational photochemistry. Elsevier, Amsterdam, p. 16[Chapter 3]
- 23. Tomasi J, Mennucci B, Cammi R (2005) Quantum mechanical continuum salvation models. Chem Rev 105:2999–3094