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ORIGINAL ARTICLE

Novel Fluorescent Phenazines : Synthesis, Characterization, Photophysical Properties and DFT Calculations

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Abstract The organic compounds with donor-π-bridge-acceptor type of architecture are of great interest for application as semiconductors. The synthesized compounds are obtained from 4-morpholino naphthalene-1,2-dione and 4-(4-(diethylamino) phenyl)naphthalene-1,2-dione and mono substituted ortho-phenylene diamines by condensation reaction. The donor groups are morpholinyl and *N,N*-diethylamino phenyl moieties, whereas acceptors are substituted phenazines. The synthesized molecules were characterized by spectral analysis.. The effect of the substitution has been studied on the basis of photophysical properties of the molecules. The halochromism behaviour of the molecule shows that at low to moderate acidity they respond differently with two types of donors. DFT computations were used in conjunction with NMR analysis to determine the ratio of the positional isomers.

Keywords Phenazines · DFT · TD-DFT · Vertical excitation · NMR

Introduction

The organic molecules with donor-π-bridge-acceptor type of architecture are of great interest for the application as semiconductors in TFT (Thin Film Transistors) [1], as sensitizers or light harvesting materials in DSSC (Dye-sensitized Solar Cells) [2] and as sensors in many applications[3–6]. The ability of these molecules to produce red emission has sought application in the field of OLEDs (Organic Light Emitting Diodes) [7, 8]. The red emission complements green [9, 10] and blue [11, 12] emission in OLEDs to create white light and covers visible spectrum for OLEDs. The placement of donor and acceptor groups affects the photophysical properties of the compounds. The π-bridge facilitates the interaction of donor and acceptors. Designing the molecule with proper placement of donor and acceptor separated by a π-bridge can modulate the properties to a great extent. The typical donors employed are triarylamines [13], carbazole [14], phenothiazine [15] and aliphatic amines [16], which are considered to be strong donors. The popular acceptor fragments are cyanoacrylic acid [17], dicyanovinyl [18], oxadiazole [19], benzothiadiazole [20], phenazine/quinoxaline and their analogs [21–23]. The substitution on the acceptor fragment also alters the signalling of the molecule [24].

In present paper, the intermediates 4-morpholinonaphthalene-1,2-dione (**2**) and 4-(4-(diethylamino)phenyl)naphthalene-1,2-dione (**3**) have been synthesized from β-naphthol derivatives. These intermediates were reacted with ortho amino aromatics to obtain desired phenazines. The donor groups are morpholinyl and *N,N*-diethylamino phenyl moieties, whereas acceptors are substituted phenazine/quinoxaline derivatives. The effect of substitution on photophysical properties were studied in solvents of different polarities. The experimental photophysical properties were compared with theoretical photophysical properties computed by DFT.

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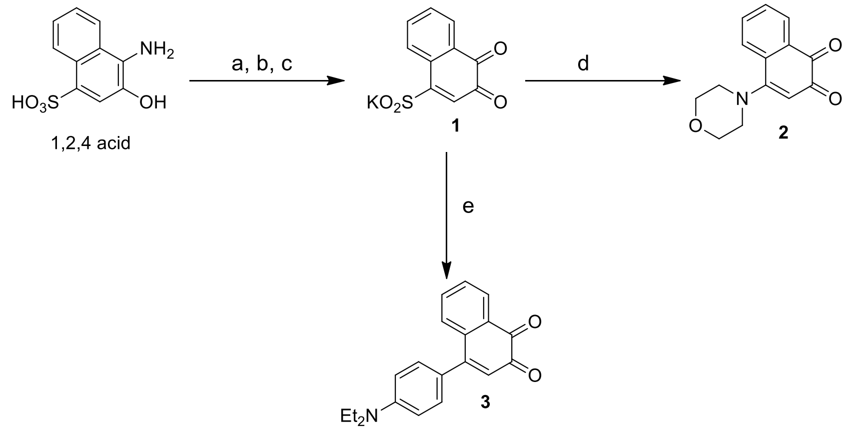
Materials and Methods

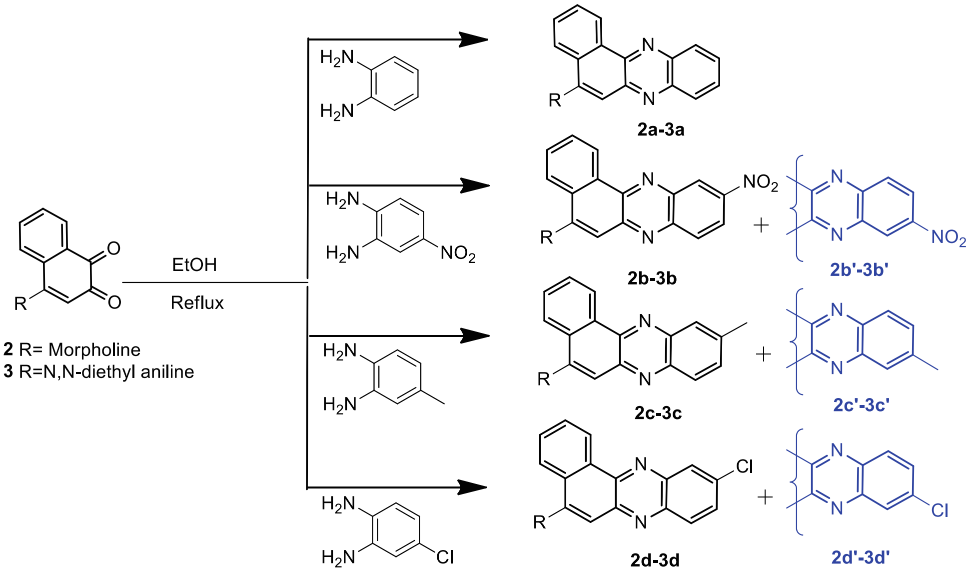
All the reagents were purchased from Sigma Aldrich and S.D. Fine Ltd., Mumbai (India) and used without further purification. Solvents used were of spectroscopic grade purchased from Rankem Ltd. Mumbai. Mass analyses were carried out with electron spray ionisation (ESI) on 410 Prostar mass spectrometer of Varian Inc. (USA). ^{1}H-NMR analyses were done using $CDCl_3$ as solvent on 500 MHz Varian Inc. The chemical shifts are expressed in δppm. Absorption spectrum was measured in standard 3.5 mL quartz cuvette with 1 cm path length using Perkin Elmer Lambda 25 spectrophotometer. Fluorescence was measured using Cary Eclipse spectrofluorometer from Varian Inc. (USA). Relative quantum yields were measured using rhodamine-6G in ethanol as standard [25].

Density Functional Theory (DFT) [26] has been used for ground state optimisations and Time Dependent-Density Functional Theory (TD-DFT) has been used for calculations of vertical excitations. Twenty lowest excitations were estimated. The functional used is B3LYP [27, 28], which is a hybrid functionals. The solvents considered were DCM, toluene DMF, acetonitrile, methanol, n-hexane and n-heptane. Solvation model used here is PCM (Polarizable Continuum Model) [29]. The Pople's basis set 6-311+G(d), was used for all atoms with added polarization function [30, 31]. Optimized structures were local minima on potential energy surface and were confirmed by vibrational analysis and show no imaginary frequencies. NMR calculated in chloroform for the protons was normalized with the calculated values of TMS (Tetramethyl silane) protons at the same level. All computations were performed with Gaussian 09 W package [32].

Fig. 1 Synthesis of phenazines



a) HNO_3, water, 10-20° C b) NH_4Cl, RT c) KCl, RT d) Morpholine, water , 0°C e) N,N-diethyl aniline, MeOH-Water, RT



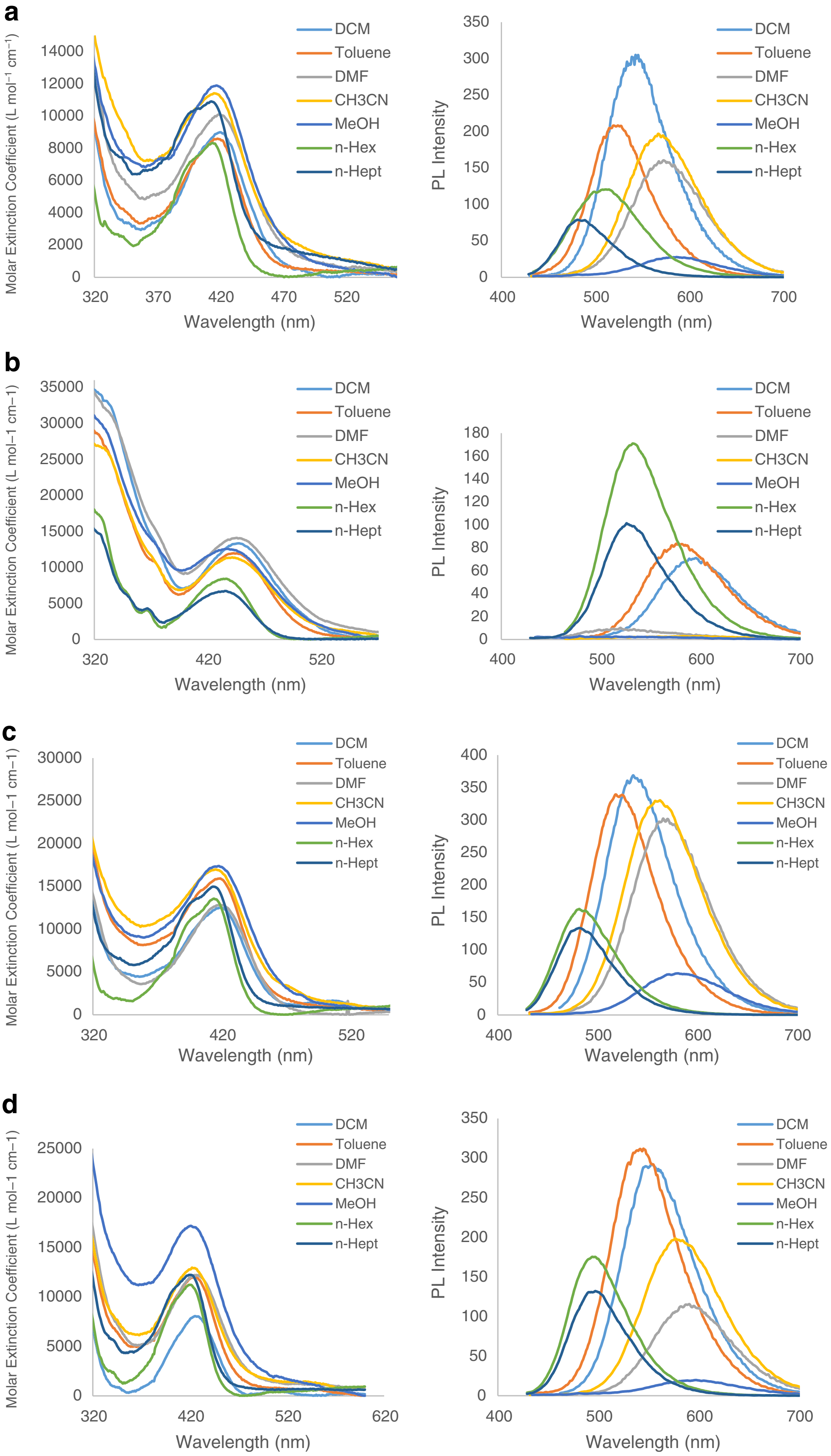


Fig. 2 UV-visible absorption and fluorescence spectra of **2a-2d** in various solvents

Results and Discussion

Synthesis and Characterization

Commercially available 1,2,4-acid was used for the synthesis of diketones. The 1,2,4-acid was converted to 1,2-diketo naphthalene 4-sulphonic acid potassium salt **1** as per reported method Fig. 1 [33].

Compound 1,2-diketo naphthalene 4-sulphonic acid potassium salt **1** was reacted with morpholine at 0 °C and with water as solvent to obtain brick red coloured compound **2** [34], which was used without further purification. The (*N,N*-diethylamino)phenyl derivative **3** was synthesized as per reported procedure [35]. The diketones **2** and **3** were condensed with substituted *ortho* phenylene diamines in ethanol at reflux temperature to obtain phenazines **2a-2d** and **3a-3d**. The molecules possessed different groups on the other side of phenazine core (considered to be an acceptor) and altered the electron withdrawing ability of the phenazine core. The synthesized molecules showed a bright yellow to brownish color.

Photophysical Study

Absorption and emission spectra were obtained in solvents of different polarities. The absorption and emission spectra are shown in Figs. 2 and 3. The absorption wavelength is independent on solvent polarity but significant effect was observed on molar extinction coefficient Table 1. Compounds showed higher molar extinction coefficients in non-polar solvents as compared to polar solvents. This may be attributed to the interaction of solvent dipoles with the molecules thus negatively affecting the charge transfer efficiency. Higher absorption intensities were observed in the solvent dichloromethane. The donor group variation between two series i.e. **2a-2d** and **3a-3d** has been clearly reflected in their absorption behaviour. The series **3a-d** compounds showed a red shift of 22 to 61 nm with respect to the corresponding **2a-d** compounds. The length of π-conjugation plays an important role for bathochromic shift for **3a-3d** as compared to **2a-2d**.

In both the type of compounds nitro substitution on the acceptor phenazine showed a red shifted absorption as compared to the –Me, −Cl, and the unsubstituted molecules. Compound **2c** was not significantly red shifted as compared to the red shift exhibited by compound **3c**. Compound **3c** showed red shifted absorption by 8 to 12 nm. In case of molecule **3d** the –Cl substitution showed a blue shifted absorption of 2 to 5 nm in all the solvents, whereas molecule **2d** showed a red shifted absorption of 6 to 9 nm. The effect of –Cl substitution is not expressed in the absorption characteristics of the molecules. The acceptor ability of phenazine core has been altered by the electron donating (−Me) as well as electron withdrawing group ($-NO_2$). The absorption of these molecules have been changed by around 80 nm with a change in the donor group and the introduction of $-NO_2$ group.

The emission characteristics of the molecules **2a-2d** and **3a-3d** are given in Table 1. The Stoke's shifts exhibited by **2a-2d** are constantly higher than the compound **3a-3d**. The compound with $-NO_2$ substitution (**2b**) showed lowest Stokes shift of 3445 cm^{-1} in acetonitrile as against the highest of 5671 cm^{-1} in dichloromethane. Stokes shift in studied solvents were summarised in Table 1. The compound **2c** with –Me substitution showed Stoke's shifts from 4652 to 6358 cm^{-1} in studied solvents. In non-polar solvents the compound with electron donating group **2c** and non-substituted compound **2a** showed a lower Stoke's shift. A reverse trend was observed for the compound with electron withdrawing group **2b.** It shows that the electron withdrawing group has enhanced the charge transfer and the polar solvent has stabilized the excited state. The electron donating group supplies electron to the acceptor (phenazine), so the molecule is less polarised and hence less affected by the polar solvents. The non-substituted compound **2a** showed the highest Stokes shifts ranging from 4705 cm^{-1} in toluene to 6471 cm^{-1} in acetonitrile among all the synthesized molecules. The compounds **2a-2d** and **3a-3d** show higher quantum yields in non-polar solvents. The quantum yields are low in polar solvents. The interaction of the polar solvents with the solute has lowered the quantum yields [36]. The compound with $-NO_2$ substitution shows lower quantum yields as the nitro group is known to quench the fluorescence [37–39].

The solvatochromic behaviour of the molecules **2a-2d** and **3a-3d** was studied with the help of Lippert [40], Weller [41] and Rettig's [41] plots. Lippert's plot is the plot of Stokes shift in cm^{-1} v/s orientation polarizability and is given in Eq. 1. Lippert function is constituted of polarity function $f(\varepsilon)$ and polarizability function $f(\eta)$

$$\vartheta_{ss} = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3} f_1 + \vartheta_{ss}{}^0 \tag{1}$$

Where,

h	Planks constant
c	velocity of light in vacuum
ϑ_{ss}	Stokes shift in solvent
ϑ_{ss}^0	Stokes shift in vacuum
f_1	polarity function and is described in Eq. 2 below

$$f_1(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

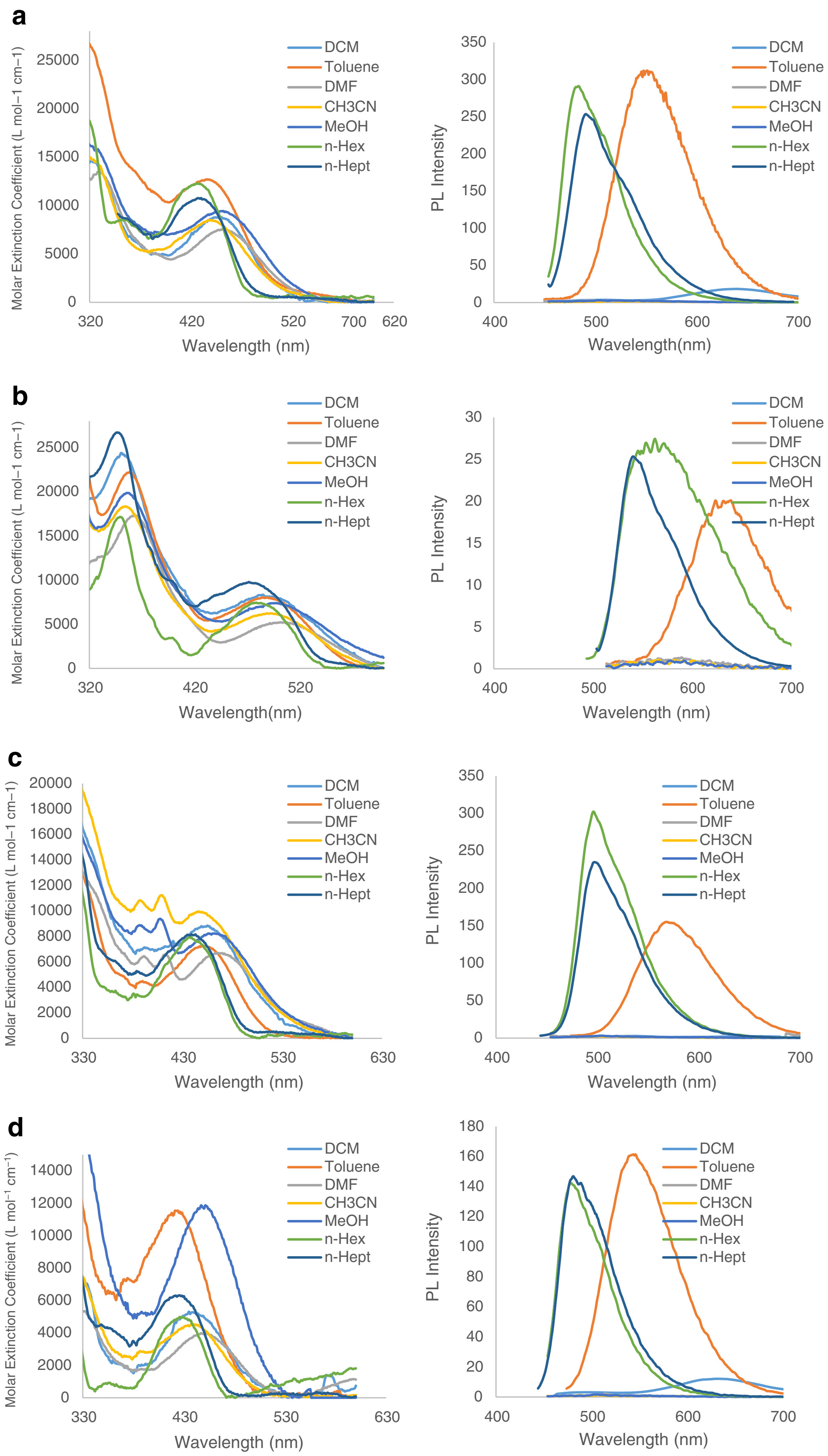


Fig. 3 UV-visible absorption and fluorescence spectra of **3a-3d** in various solvents

The Wellers equation which considers only shift in emission is given as follows,

$$\vartheta_f = \frac{2(\mu_e)^2}{hca^3} f_2 + constant \tag{3}$$

$$f_2(\varepsilon, \mathrm{n}) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\mathrm{n}^2 - 1}{4\mathrm{n}^2 + 2}, \tag{4}$$

Neglecting the ground state dipole moment with respect to that of the excited state and approximating the solute polarizability to $^{a^3}\!/_2$ the following formula is obtained as in Eq. 5,

$$\vartheta_f = \frac{2(\mu_e)^2}{hca^3} f_3 + constant \tag{5}$$

Where solvent polarity function f_3 (Rettig equation)is given as follows,

$$f_3(\varepsilon, \mathrm{n}) = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\mathrm{n}^2 - 1}{2\mathrm{n}^2 + 4} \tag{6}$$

Lippert plots for compound **2a, 2b** and **2d** are linear and showed a regression factor ≥0.800 indicating the charge transfer by local excitation (LE) occurring in these molecules. This indicates there is a good linearity and the molecules show solvtochromism in emission as the absorption is less sensitive to solvent polarity. But in the case of compound **2b**, where –NO_2 is present as a strong donor and makes molecule less sensitive to the solvent environment, the regression factor is ≤0.400. It is thus indicative that charge transfer by LE in not important in this molecule. In similar way when morpholine donor is replaced by a stronger donor *N,N*-diethylaminophenyl the molecules are not responsive to solvent polarity and the regression factors are very low for **3a-3d** series (Table 2).

Halochromism

The effect of acidity on photophysical properties of the compounds **2a-2d** (Fig. 4) and **3a-3d** (Fig. 5) were studied by addition of trifluoroacetic acid. The halochromism data of the dye **2a** is reported to show a red shift in the absorption maxima due to the protonation of nitrogen atom of the phenazine core [42–44]. The protonation of the aromatic nitrogen of phenazine enhances the charge transfer from the donor (morpholine) to acceptor (protonated Phenazine), and hence imparts a red shift in absorption. A similar trend was observed in all substituted phenazines **2a-2d**, irrespective of their substitution. The electron releasing –CH_3 group in **2c** enhances the protonation more than the acceptor –NO_2 group in **2b,** while non-substituted compound **2a** remained intermediate. The compound **2b** needed very high concentration of acid to induced red shift. The order of protonation was –CH_3> −Cl > −H > −NO_2. The red shifts induced were in the order of ~100 nm.

On the other hand the protonation of 4-(*N,N*-diethylamino)-phenyl substituted series of compounds **3a-3d** show different trend. The *N,N*-diethylamino group gets protonated first and induces a blue shift in the absorption spectrum by interrupting the electron donation by the group. Similar trend continues till the complete protonation of diethylamino group takes place, but at higher concentration of acid the phenazine nitrogen also gets protonated and gives a red shift in absorption. In this case the order of induced red shift is ~30–40 nm. This is due to the fact that in the case of morpholino substituted compounds there is no protonation of donor nitrogen, hence a better conjugation is achieved.

DFT Computations

DFT computations were performed in solution phase to understand the photophysical behaviour of the molecules Tables 3 and 4. A red shift is always observed when the substitution changes from morpholine **2a-2d** to *N,N*-diethylaminophenyl **3a-3d** and is also observed in theoretical calculations of the vertical excitations. The deviation in the experimental and computational data was found to be 1.0 % for **2c** in toluene whereas highest deviation was observed in **2b** in acetonitrile(%?). The deviation in series **3a-3d** remain mostly on negative side; however compound 3b shows a positive deviation. For series **3a-3d** the vertical excitation energy is overestimated. It was observed that for the compounds **2b** and **3b** the computed values are higher than the other derivatives in the same series. There waslittle change in the vertical excitation energies calculated with respect to the solvent polarity. Similarly the absorption values measured experimentally were too less sensitive to the solvent polarity.

NMR : Theoretical and Experimental

The comparison of calculated and experimental NMR provides an easy tool to distinguish between the closely related molecules, which could be a cumbersome task if performed otherwise. The reactions involved in the synthesis of phenazines **2b-2d** and **3b-3d** involve use of substituted asymmetric o-phenylene diamines (substitution include –NO_2, −Cl, −CH_3). The reaction products obtained are expected to have two positional isomers depending upon the position of substitution. The possible structures are shown in Fig. 1. The assignment of the proton NMR signals to the specific structure is difficult with such complicated and closely related structures. DFT has been used since a period to calculate NMR prediction of organic molecules [45–48]. The normalized calculated values give an insight into the observed NMR spectrum and based on this the assignment of major isomer has been done (Table 5).

The major isomers predicted are **2b’, 3b’, 2c, 3c, 2d** and **3d**. The –Me substitution on compounds **2c-2c’** and **3c-3c’** does not have much effect on selectivity of the product formation. The $-NO_2$ group drives the product formation at exactly reverse than the $-CH_3$, and –Cl substitution. The map of the protons used for the comparison is given in Fig. 6.

Experimental

The synthesis of compound **1** was achieved by oxidation of 4-amino-3-hydroxynaphthalene-1-sulfonic acid (1,2,4 acid) to 1,2-diquinone sulphonic acid and further converting it to ammonium and potassium salts [33]. Compound **1** was then reacted with morpholine and *N,N*-diethyl aniline in different conditions to give compound **2** and **3** respectively.

Synthesis of Phenazines

General Procedure The diketo compound (**2** or **3**) (1 mmol) was suspended in absolute ethanol (10 mL). The substituted diamines (1 mmol) were added in one portion and the mixture was heated to reflux for 2 h. The color changed to yellow (from brick red for compound **2** and bfor compound **3**). The reaction was monitored by TLC. After completion of reaction

Table 1 Photophysical properties in various solvents for compounds **2a-2d** and **3a-3d**

Solvent		2a	3a	2b	3b	2c	3c	2d	3d
Acetonitrile	λabs	418	451	441	502	420	463	427	449
	ε L mol^{-1} cm^{-1}	11400	8360	11400	6248	16960	9600	12800	4460
	λem	569	515	598	567	562	499	578	508
	Φ	0.4235	0.0065	0.0099	0.0038	0.4980	0.0065	0.4001	0.0089
	Stokes shift (cm^{-1})	6349	2755	5953	2284	6016	1558	6118	2587
Dichloromethane	λabs	422	454	446	503	420	462	427	447
	ε L mol^{-1} cm^{-1}	8996	8400	13360	8360	12480	8800	8052	5183
	λem	544	641	593	557	538	535	553	632
	Φ	0.8985	0.0799	0.1497	0.0292	0.7569	0.0125	0.9326	0.0939
	Stokes shift (cm^{-1})	5314	6426	5558	1927	5222	2953	5336	6549
N,N-dimethyl formamide	λabs	422	451	449	507	419	462	428	447
	ε L mol^{-1} cm^{-1}	10080	7440	14000	5228	12800	6572	12000	3959
	λem	569	493	572	590	569	–	591	–
	Φ	0.4443	0.0119	0.0223	0.0072	0.6805	–	0.2826	–
	Stokes shift (cm^{-1})	6122	1889	4789	2775	6292	–	6444	–
Methanol	λabs	418	452	446	507	420	464	429	450
	ε L mol^{-1} cm^{-1}	11880	9280	12400	7384	17360	8160	16800	11676
	λem	596	504	561	578	584	505	597	503
	Φ	0.0660	0.0087	0.0081	0.0030	0.5012	0.0094	0.0352	0.0034
	Stokes shift (cm^{-1})	7145	2283	4596	2423	6686	1750	6560	2342
Toluene	λabs	421	452	445	502	420	462	427	447
	ε L mol^{-1} cm^{-1}	8720	12480	11960	8012	15600	7208	12000	11352
	λem	523	548	576	640	522	568	545	546
	Φ	0.6612	0.7464	0.2248	0.0788	0.5826	0.6305	0.7660	0.4020
	Stokes shift (cm^{-1})	4633	3876	5111	4295	4652	4039	5071	4056
n-hexane	λabs	407	430	437	479	414	439	421	430
	ε L mol^{-1} cm^{-1}	8320	12160	8432	7443	13520	7920	11200	4920
	λem	513	491	534	563	483	496	494	478
	Φ	0.3576	0.4342	0.4697	0.1119	0.2337	0.6773	0.3250	0.4958
	Stokes shift (cm^{-1})	5077	2889	4157	3115	3451	2618	3510	2335
n-heptane	λabs	407	432	436	471	413	441	421	427
	ε L mol^{-1} cm^{-1}	11040	10640	6752	9736	14948	8104	12200	6264
	λem	486	491	528	541	483	498	497	481
	Φ	0.1475	0.4786	0.4672	0.0514	0.1449	0.5117	0.2191	0.4512
	Stokes shift (cm^{-1})	3994	2782	3996	2747	3509	2595	3632	2629

Table 2 Regression factor (R^2) values for various solvent polarity plots for compound **2a-2d** and **3a-3d**

	Lippert (ε, η)	Polarity (ε)	Polarizability (η)	Weller (ε, η)	Rettig (ε, η)
2a	0.8150	0.7509	0.3138	0.8702	0.8900
2b	0.3255	0.3847	0.0200	0.4845	0.0446
2c	0.8950	0.9175	0.0612	0.8952	0.8384
2d	0.8385	0.8851	0.0214	0.8485	0.7197
3a	0.0157	0.0034	0.2530	0.0217	0.0946
3b	0.4668	0.3966	0.2932	0.0003	0.2756
3c	0.4802	0.3553	0.9173	0.0156	0.4211
3d	0.0043	0.0315	0.4753	0.1075	0.0755

the separated solid was filtered and washed with cold ethanol to obtain phenazines.

Compound 2a

M.P: 160 °C; **Yield:** 83 %

^{1}H-NMR ($CDCl_3$, 500 MHz , δ ppm): δ 9.47–9.44 (m, 1H), 8.36–8.32 (m, 1H), 8.24–8.20 (m, 2H), 7.85 (dt, J=3.2, 1.6 Hz, 1H), 7.81 (ddd, J=9.4, 5.4, 2.1 Hz, 3H), 7.46 (s, 1H), 4.07–4.04 (t, 4H), 3.32 (t, 4H).

^{13}C-NMR ($CDCl_3$, 125 MHz , δ ppm): δ 153.3, 144.6, 142.4, 141.4, 141.2, 132.2, 130.4, 130.0, 129.7, 129.5, 128.9, 128.6, 128.0, 126.1, 124.3, 112.8, 67.1, 53.0.

Mass (ESI): 316.2 (M+1)

CHN Analysis : Calculated: C 76.17, H 5.43, N 13.32, O 5.07 Observed: C 76.11, H 5.39, N 13.3, O 5.01.

Compound 2b

M.P: 190 °C; **Yield:** 72 %

^{1}H-NMR ($CDCl_3$, 500 MHz , δ ppm): δ 9.42 (d, J= 8.9 Hz, 1H), 9.07 (d, J=2.2 Hz, 1H), 8.50 (dd, J=9.3, 2.3 Hz, 1H), 8.40 (d, J=9.2 Hz, 1H), 8.23–8.18 (m, 1H), 7.90–7.80 (m, 1H), 7.40 (s, 1H), 4.15 (t, 4H), 3.35 (t, 4H).

^{13}C-NMR ($CDCl_3$, 125 MHz , δ ppm): δ 152.1, 144.2, 143.7, 142.7, 141.8, 141.5, 140.6, 139.9, 139.4, 132.8, 132.1, 131.6, 130.3, 129.4, 127.4, 125.6, 123.6, 113.5, 68.3, 54.5.

Mass (ESI): 361.1 (M+1)

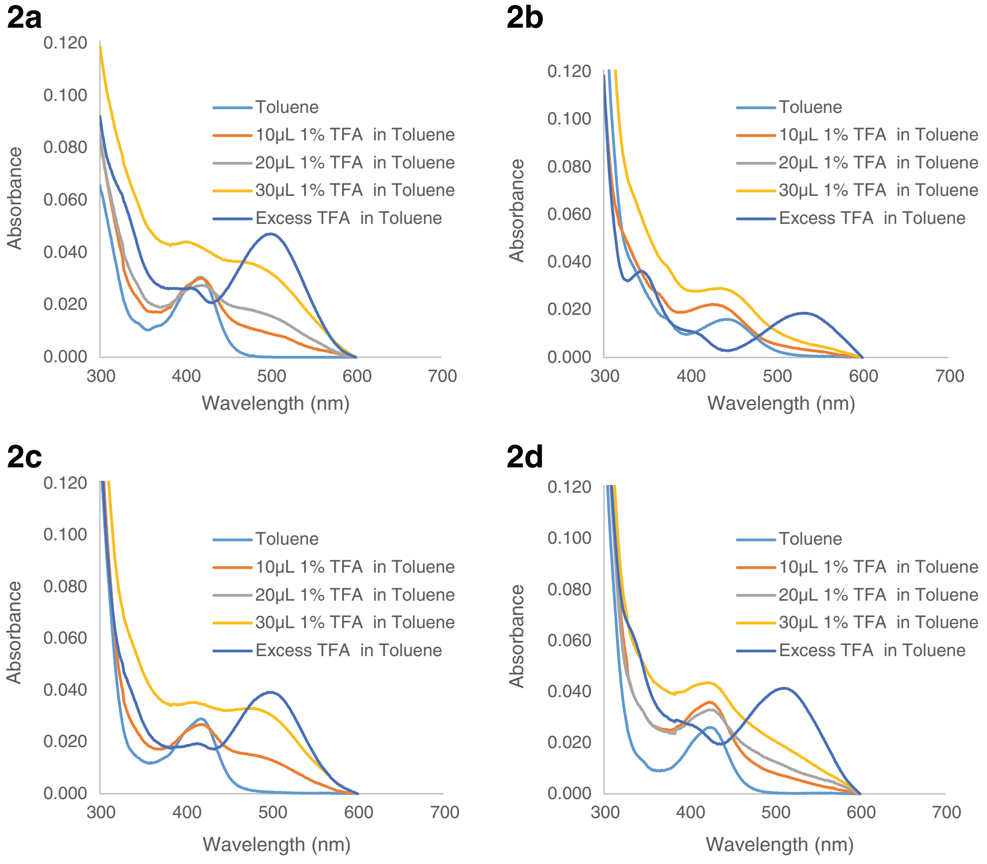


Fig. 4 Halochromism shown by compound **2a-2d** in toluene and TFA

CHN Analysis : Calculated: C 66.66, H 4.48, N 15.55, O 13.32 Observed: C 66.61, H 4.47, N 15.50, O 13.29.

Compound 2c

M.P: 157 °C; **Yield:** 68 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.42 (ddd, *J*= 6.9, 5.1, 2.0 Hz, 1H), 8.21 (td, *J*=6.8, 4.0 Hz, 1H), 8.15–8.05 (m, 1H), 7.95 (s, 1H), 7.78 (ddd, *J*=6.3, 4.8, 1.9 Hz, 2H), 7.65 (ddd, *J*=14.5, 8.7, 1.7 Hz, 1H), 7.43 (d, *J*=2.7 Hz, 1H), 4.10–4.00 (t, 4H), 3.29 (t, 4H), 2.66 (s, 3H).

^{13}C-NMR (CDCl$_3$, 125 MHz , δ ppm): δ 153.0, 152.7, 144.5, 143.9, 143.0, 141.5, 141.3, 140.6, 139.9, 139.4, 132.6, 132.2, 132.2, 131.6, 130.4, 129.4, 128.1, 127.9, 127.1, 125.9, 124.2, 124.2, 113.0, 67.1, 53.0, 22.2.

Mass (ESI): 330.2 (M+1)

CHN Analysis : Calculated: C 76.57, H 5.81, N 12.76, O 4.86 Observed: C 76.57, H 5.79, N 12.71, O 4.86.

Compound 2d

M.P:168 °C; **Yield:** 79 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.40–9.35 (m, 1H), 8.29 (d, *J*=2.1 Hz, 1H), 8.24–8.14 (m, 2H), 8.10 (d, *J*= 9.0 Hz, 1H), 7.82–7.76 (m, 2H), 7.74 (dd, *J*=9.1, 2.3 Hz, 1H), 7.38 (d, *J*=3.9 Hz, 1H), 4.04 (t, 4H), 3.30 (t, 4H).

^{13}C-NMR (CDCl$_3$, 125 MHz , δ ppm): δ 153.9, 153.5, 145.1, 144.6, 143.0, 141.8, 141.3, 141.1, 139.5, 135.7, 134.5, 131.8, 130.8, 130.5, 129.90, 129.7, 128.2, 127.2, 126.0, 124.3, 112.4, 67.0, 53.0

Mass (ESI): 350.2 (M+1)

CHN Analysis : Calculated: C 68.67, H 4.61, Cl 10.13, N 12.01, O 4.57 Observed: C 68. 62, H 4.57, Cl 10.11, N 12.00

Compound 3a

M.P: 172 °C; **Yield:** 80 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.54 (d, *J*= 8.0 Hz, 1H), 8.38 (dd, *J*=6.6, 3.2 Hz, 1H), 8.27 (dd, *J*=6.6, 3.2 Hz, 1H), 8.15 (d, *J*=7.9 Hz, 1H), 7.92 (s, 1H), 7.87–7.84 (m, 1H), 7.81 (t, *J*=7.6 Hz, 1H), 7.74 (t, *J*=7.5 Hz, 1H), 7.53 (d, *J*=8.5 Hz, 2H), 6.86 (d, *J*=5.8 Hz, 2H), 3.48 (q, *J*=7.0 Hz, 4H), 1.44–1.10 (t , *J*=7.0, 6H).

^{13}C-NMR (CDCl$_3$, 125 MHz , δ ppm): δ 145.7, 143.7, 143.1, 142.3, 141.7, 133.2, 131.6, 130.9, 129.8, 129.7, 129.4, 129.3, 129.0, 127.5, 127.3, 126.2, 125.7, 111.4, 44.4, 12.7.

Mass (ESI): 378.3 (M+1)

CHN Analysis : Calculated: C 82.73, H 6.14, N 11.13 Observed: C 82.70, H 6.09, N 11.11.

Compound 3b

M.P: 182 °C; **Yield:** 78 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.50 (d, *J*= 7.7 Hz, 1H), 9.16 (d, *J*=2.3 Hz, 1H), 8.55 (dd, *J*=9.2, 2.5 Hz, 1H), 8.46 (d, *J*=9.3 Hz, 1H), 8.17 (d, *J*=7.5 Hz,

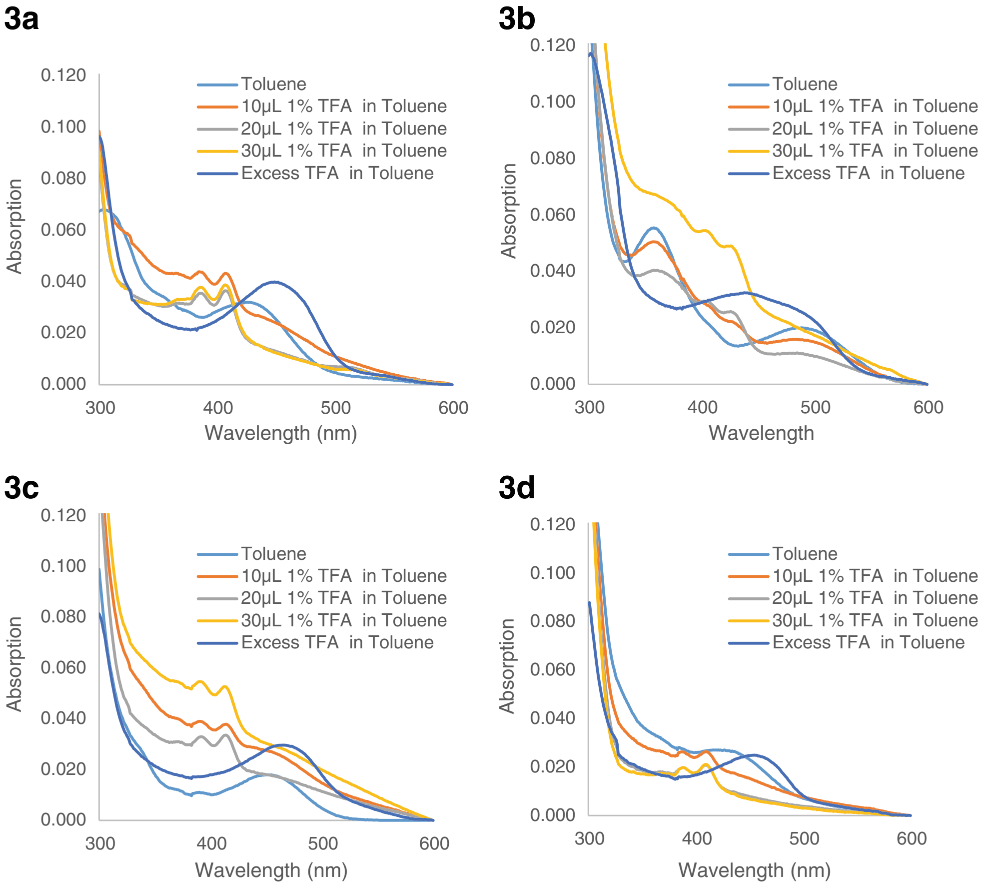


Fig. 5 Halochromism shown by compound **3a-3d** in toluene and TFA

Table 3 Photophysical properties of compounds **2a-2d** in various solvents

	Phase /solvent	Energy (Hartree)	Dipole moment (Debye)	λmax (nm)		
				Experimental	Theoretical	%D
2a	ACN	−1011.7332	1.66	418	453	8.4
	DCM	−1011.7318	1.60	422	450	6.7
	DMF	−1011.7333	1.67	422	453	7.4
	MeOH	−1011.7332	1.66	418	453	8.4
	TOL	−1011.7276	1.44	421	443	5.3
2b	ACN	−1216.2955	6.99	441	466	5.7
	DCM	−1216.2936	6.81	446	462	3.6
	DMF	−1216.2956	7.00	449	467	4.0
	MeOH	−1216.2955	6.99	446	466	4.5
	TOL	−1216.2880	6.23	445	449	0.9
2c	ACN	−1051.0393	1.02	420	431	2.6
	DCM	−1051.0376	0.95	420	429	2.2
	DMF	−1051.0393	1.02	419	432	3.1
	MeOH	−1051.0393	1.02	420	431	2.6
	TOL	−1051.0330	0.80	420	424	1.0
2d	ACN	−1471.3742	4.60	427	445	4.3
	DCM	−1471.3726	4.39	428	443	3.6
	DMF	−1471.3742	4.60	428	446	4.3
	MeOH	−1471.3741	4.59	428	444	3.8
	TOL	−1471.3683	3.84	427	436	2.2

ACN Acetonitrile, *DCM* Dichloromethane, *DMF N,N*-dimethyl formamide, *MeOH* Methanol, *TOL* Toluene

Table 4 Photophysical properties of compounds **3a-3d** in various solvents

	Phase /solvent	Energy (Hartree)	Dipole moment (Debye)	λmax (nm)		
				Experimental	Theoretical	%D
3a	ACN	−1168.4593	1.2358	451	420	−7.4
	DCM	−1168.4581	1.0829	449	418	−7.4
	DMF	−1168.4593	1.2370	450	421	−6.9
	MeOH	−1168.4593	1.2325	450	420	−7.2
	TOL	−1168.4549	0.953	450	416	−8.1
3b	ACN	−1372.9570	8.7900	506	510	1.0
	DCM	−1372.9555	8.5746	501	506	1.2
	DMF	−1372.9570	8.7926	503	510	1.7
	MeOH	−1372.9569	8.7839	502	510	1.9
	TOL	−1372.9512	7.9551	501	492	−2.2
3c	ACN	−1207.7491	1.1388	463	413	−12.0
	DCM	−1207.7478	1.0286	458	413	−10.8
	DMF	−1207.7491	1.1406	469	414	−13.2
	MeOH	−1207.7490	1.1348	464	413	−12.2
	TOL	−1207.7445	0.8037	457	410	−11.2
3d	ACN	−1628.0629	3.8054	446	425	−5.0
	DCM	−1628.0618	3.6948	445	423	−5.3
	DMF	−1628.0629	3.8076	446	425	−5.0
	MeOH	−1628.0629	3.8010	446	424	−5.3
	TOL	−1628.0587	3.4033	446	419	−6.5

ACN Acetonitrile, *DCM* Dichloromethane, *DMF N,N*-dimethyl formamide, *MeOH* Methanol, *TOL* Toluene

Table 5 Calculated and experimental δ ppm values for selected protons in compounds **2b-2d, 2b'-2d', 3b-3d** and **3b'-3d'**

Positional isomer 1		Positional isomer 2			
Proton number (δ calculated/δ experimental)	Integration	Proton number (δ calculated/δ experimental)	Integration	Ratio	Major isomer
2b		**2b'**			**2b'**
H23(9.558/9.201)	0.15	H22(9.453/9.074)	0.78	0.19	
2c		**2c'**			**2c**
H41,42,43(2.930/2.662)	3.00	H42,43,44(2.891/2.657)	2.22	1.35	
2d		**2d'**			**2d**
H7(8.095/7.745)	0.64	H7 (8.090/7.702)'	0.35	1.82	
H12(8.088/7.727)	0.63	H12(8.076/7.696)	0.32	1.96	
3b		**3b'**			**3b'**
H23(9.656/9.261)	0.22	H22(9.529/9.157)	1.00	0.22	
3c		**3c'**			**3c**
H53,54,55(3.027/2.696)	3.00	H53,54,55(3.006/2.682)	2.83	1.06	
3d		**3d'**			**3d**
H8(9.993/9.472)	1.00	H8(9.984/9.426)	0.32	3.12	

1H), 7.89 (s, 1H), 7.85–7.75 (m, 2H), 7.52 (d, *J*=8.6 Hz, 2H), 6.86 (d, *J*=8.2 Hz, 2H), 3.48 (q, *J*=7.0 Hz, 4H), 1.28 (t, *J*= 7.0 Hz, 6H).

^{13}C-NMR (CDCl$_3$, 125 MHz , δ ppm): δ 147.5, 145.3, 144.3, 143.3, 141.4, 133.8, 131.2, 130.9, 130.9, 130.6, 130.4, 128.0, 127.6, 126.3, 125.6, 125.5, 122.0, 111.3, , 44.4, 12.7.

Mass (ESI): 423.3(M+1)

CHN Analysis : Calculated: C 73.92, H 5.25, N 13.26 O, 7.57 Observed: C 73.90, H 5.24, N 13.22, O 7.55.

Compound 3c

M.P:164 °C; **Yield:** 63 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.52 (dd, *J*=7.5, 5.1 Hz, 1H), 8.27 (d, *J*=8.7 Hz, 1H), 8.15 (dd, *J*=16.8, 8.5 Hz, 2H), 8.03 (s, 1H), 7.91 (s, 1H), 7.81 (t, *J*=7.6 Hz, 1H), 7.77–7.64 (m, 2H), 7.53 (d, *J*=7.3 Hz, 2H), 3.49 (q, *J*=7.0 Hz, 4H), 2.69 (d, *J*=7.1 Hz, 3H), 1.28 (t, *J*=7.0 Hz, 6H).

^{13}C-NMR (CDCl$_3$, 125 MHz , δ ppm): δ 142.7, 141.7, 131.7, 131.6, 131.0, 129.2, 128.5, 128.2, 127.5, 127.1, 125.6, 44.4, 22.1, 12.4.

Mass (ESI): 392.3 (M+1)

CHN Analysis : Calculated: C 82.83 H 6.44 N 10.73 Observed: C 82.80, H 6.41, N 10.70.

Compound 3d

M.P: 178 °C; **Yield:** 72 %

^{1}H-NMR (CDCl$_3$, 500 MHz , δ ppm): δ 9.47 (d, *J*= 8.0 Hz, 1H), 8.37–8.22 (m, 2H), 8.17 (dd, *J*=21.5, 8.5 Hz,

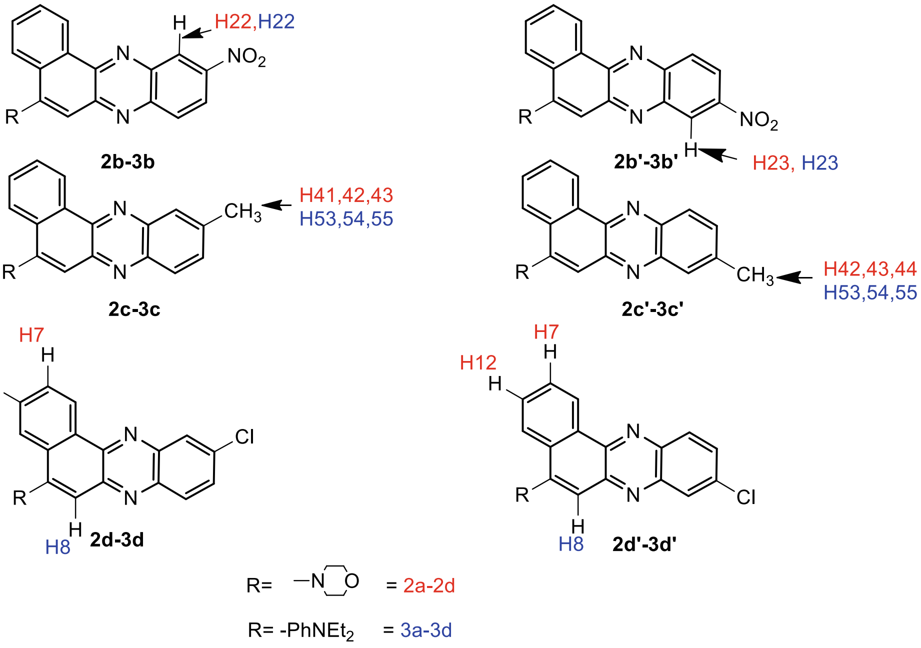


Fig. 6 Protons considered for estimation of the positional isomers

2H), 7.87 (s, 2H), 7.84–7.78 (m, 1H), 7.75 (dd, J=12.4, 8.4 Hz, 3H), 7.51 (d, J=7.2 Hz, 2H), 6.96–6.81 (m, 3H), 3.48 (dd, J=13.9, 6.9 Hz, 4H), 1.28 (t, J=7.0 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 125 MHz , δ ppm): δ 147.4, 145.2, 144.2, 143.3, 141.5, 140.8, 134.5, 131.4, 128.9, 127.6, 126.7, 125.1, 122.7, 121.3, 111.7, 43.3, 11.9.

Mass (ESI): 412.3 (M+1)

CHN Analysis : Calculated : C 75.81 H 5.38 Cl 8.61 N 10.20 Observed : C 75.55, H 5.32, Cl 8.60, N 10.15.

Conclusion

The phenazine molecules with different donor and acceptor units were synthesized and their photophysical properties were studied. The molecules with either donor i.e. morpholino or *N,N*-(diethylamino)phenyl, do not show solvatochromism. The two series with different donors behave differently in acidic environment. Compounds **2a-2d** showed red shifted absorption and with increase in the absorption intensity of red shifted band with increasing acidity. The *N,N*-diethylamino(phenyl) substituted **3a-3d** compounds show a blue shift in the absorption spectrum, it is due to the protonation of $–NEt_2$ nitrogen. Which hinders the group to take part in conjugation. But excess of acid can protonate phenazine nitrogen to impart a red shift to these molecules also. Interestingly the series **2a, 2c** and **2d** show linear solvent polarity parameter plots of their photophysical property while the molecule **2b** remains an exception. The combination of either a stronger donor-acceptor as in **3a-3d** and in compound **2b** remains less responsive to the solvent environment. The fluorescence of the molecules **2a, 2b** and **2c** show response to solvent polarity. Theoretical and practical NMR in combination was useful in obtaining the composition of positional isomers.

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