



Novel pyrazino-phenanthroline based rigid donor- π -acceptor compounds: A detail study of optical properties, acidochromism, solvatochromism and structure-property relationship



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ABSTRACT

Donor- π -acceptor- π -auxiliary acceptor type compounds have been designed and synthesized to study their rigidity and structural effects on optical properties. Structural variation is achieved by changing the central π -conjugated core with naphthalene, acenaphthene and phenanthrene based donor- π -acceptor compounds containing *N,N*-diethyl aniline or morpholine as donor and pyrazine ring fused with phenanthroline as acceptor. A detailed study of positive and negative acidochromism is performed. Intramolecular charge transfer, solvatochromism and highly polar excited state of these compounds are elucidated by Lippert-Mataga, Mac-Rae and Reichardt correlations. Multilinear regression analysis using Kamlet-Taft and Catalan parameters is also performed to support the observed solvatochromism in absorption and emission spectra from non-polar to polar solvents. All the spectroscopic results were correlated theoretically by Density Functional Theory (DFT) computations.

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1. Introduction

Rigid polyaromatic planar heterocyclic compounds with donor- π -acceptor architecture have attracted much attention in recent years due to their special electro-optical properties originating from their low band gap [1,2]. Due to their facile synthesis, versatility, strong electron-withdrawing ability and easy functionalization different pyrazine derivatives such as 2,3-diphenylquinoxaline [3–6], thienopyrazine [7–9], pyridopyrazine [10,11] have been successfully implemented in field effect transistors [12–14], photovoltaic devices [15,16] and light-emitting diodes (LEDs) [17–20]. At the same time, several researchers have developed pyrazine or quinoxaline based organic sensitizers for their high performance in dye sensitized solar cells (DSSC) [21–25]. Different pyrazine mediated π -extended long chain fused azacene derivatives have been reported [26,27] and applied in bulk heterojunction organic solar cells [28,29], n-type organic semiconductors [30–33] and as charge transfer species [34–38].

Dipyrido[3,2-a:2',3'-c]phenazine (dppz) ligand is a combination of 1,10 phenanthroline and quinoxaline system. The diimine site of

dppz allows coordination with various transition metal ions to yield stable metal-organic complexes and introduction of functional groups in the dppz core can fine tune the HOMO-LUMO gaps of resultant compounds [39–42]. As the pyrazine core in dppz ligand acts as an electron acceptor, its intramolecular charge transfer (ICT) character was tested by attaching different electron donating group on the side arms at different positions keeping two more nitrogen free as the metal chelating site [43,44]. Novel fused pyrazino-phenanthroline systems with ICT and solvent sensitive emission behavior were studied also [45].

A very good structure-property relationship, variation in band gap and strengthening of ICT character was found after fusing thiophene or benzene rings and/or putting additional donating groups on main pyrazine core at different locations [36,46–48]. The environment sensitive fluorescent dyes e.g. solvatochromic dyes, found their applications for monitoring protein, DNA and biomembranes. These dyes show strong changes in their dipole moments upon electronic excitation and thus show red shift in their emission maximum upon an increase in polarity of the solvent environment [49–53]. Few phenazine based solvatochromic dyes are also reported where pyrazine core acts as electron acceptor [54–56]. Recently from our group phenazine fused benzocoumarins were reported where negative and positive solvatochromisms

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were observed [57,58].

On protonation of the central electron withdrawing nitrogen of different pyridine type heterocyclic compounds enhancement in electron withdrawing ability and stabilization of LUMO were observed causing a dramatic red-shift in absorption [59–62]. Few nitrogen containing heterocycles were also studied for their acidochromic properties where extraordinary red shift in absorption λ_{max} was observed on addition of TFA [63–66].

We synthesized four novel benzo[*h*]dipyrido[3,2-*a*:2',3'-*c'*]phenazine derivatives where 5,6-diaminophenanthroline was used to obtain more extended conjugation with two more free nitrogen atoms as metal chelating sites and as supporting electron acceptor. To get the desired amine substituted phenazine derivatives we used potassium 3,4-dioxo-3,4-dihydronaphthalene-1-sulfonate instead of naphthalene-1,2-dione which was synthesized by following the reported procedure [67] where the sulfonate salt acts as better leaving group than hydrogen in a Michael type addition. We synthesized two more derivatives by substituting 5-bromoacenaphthylene-1, 2-dione and 3-bromophenanthrene-9, 10-dione with morpholine to study the structural effects on the electrochemical and photophysical properties. The respective 5-bromoacenaphthylene-1, 2-dione and 3-bromophenanthrene-9, 10-dione intermediates were synthesized by following the reported procedure [68,69]. As the donor-acceptor interaction in such molecules is mainly dependent on the strength of the donor or acceptor, conjugation length and nature of the conjugating unit, we incorporated almost same donating group i.e. morpholine and varied the conjugation length except in the case of compound **4** where *N,N*-diethyl aniline was used as donating group. The structures of all the four newly synthesized donor-acceptor compounds are represented in Fig. 1.

2. Experimental section

2.1. Materials and equipments

All the required chemicals were obtained from commercial sources and used as received without any further purification. The solvents used for synthesis and analytical measurements were obtained from S. D. Fine Chemicals (India), dried by following standard procedures and distilled prior to use. All the reactions were monitored by TLC (thin layer chromatography) with detection by UV light. 100–200 Mesh silica was used in column chromatography as the stationary phase for purification. ^1H and ^{13}C NMR spectral data were recorded on a 500 MHz instrument using TMS as an internal standard. Mass spectra were recorded on Finnigen mass spectrometer and HRMS analysis was done using a QTOF LC/MS

spectrometer. The absorption and emission spectra were recorded at room temperature using a 10 mm cuvette with a 2.5 nm slit width. Emission quantum yields were obtained by using coumarin-6 ($\Phi = 0.94$ in chloroform) as reference. Cyclic voltammetry experiments were performed using glassy carbon (2 mm diameter) as working electrode, platinum wire as counter electrode, and standard calomel electrode as reference electrode with 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBu_4NPF_6) as supporting electrolyte in DCM solvent.

2.2. Computational methods

The ground state (S_0) geometry of all compounds was optimized using Density Functional Theory (DFT) [70] by using the Gaussian 09 package and the popular hybrid functional B3LYP. The B3LYP combines Becke's three parameter exchange functional (B3) [71] with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [72]. The basis set used for all atoms was 6-31G (d) in both DFT and time-dependent density functional theory (TD-DFT) method. The low-lying first singlet excited states (S_1) of the dyes were relaxed to obtain their minimum energy geometries using the TD-DFT. The vertical excitation energies and oscillator strengths were obtained for the lowest 10 singlet-singlet transitions at the optimized ground state equilibrium geometries by using TD-DFT at the same hybrid functional and basis set [73]. Emissions were obtained by calculating difference between the energies of the optimized geometries at first singlet excited state and ground state. Frequency computations were also carried out on the optimized geometry of the low-lying vibronically relaxed first excited state of conformers. The computations in various solvent media were carried out using the self-consistent reaction field (SCRF) under the polarizable continuum model (PCM) [74]. Optimized ground structures were utilized to obtain the electronic absorption spectra, including maximum absorption and emission wavelengths, oscillator strengths, and main configuration assignment by using TD-DFT with the PCM model.

2.3. Synthesis

2.3.1. synthesis of 4-(4-(diethylamino)phenyl)naphthalene-1,2-dione (**2**)

The diketo compound (2.8 g, 10.13 mmol) was dissolved in methanol: water (3:1) (30 mL) and then *N,N* diethyl aniline (2.1 mL, 13.173 mmol) was added in the reaction mixture slowly and stirred for 24 h at room temperature. On completion the reaction mixture was concentrated by evaporating methanol. The dark blue colored solid separated out was filtered and dried well to get pure product

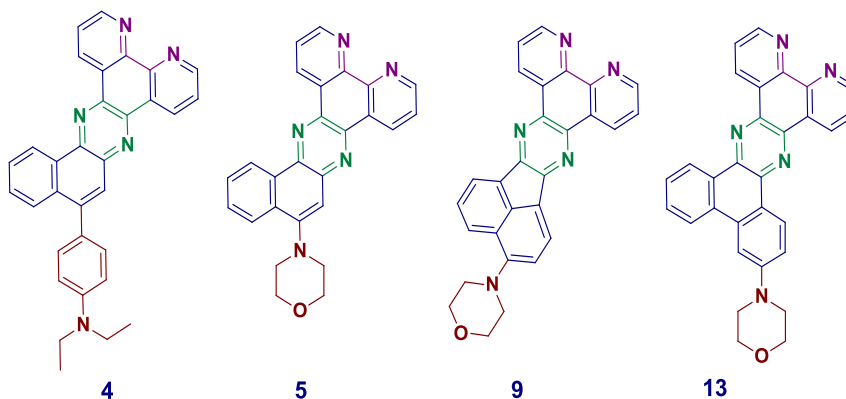


Fig. 1. Structure of the synthesized compounds.

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