

Fluorescent aromatic symmetrical azines: Synthesis and appraisal of their photophysical and electrochemical properties

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ABSTRACT

There is an immense push for the development of innovative, convenient and high-performance organic electronics. In this study, we present the synthesis of two azines and the exploration of their photophysical, surface morphological, electrochemical and electroluminescence properties for application in organic electronic devices. A diphenol substituted azine, 2,2'-[hydrazine-1,2-diylidenedimethylidene]diphenol was synthesized by refluxing ethanolic solution of hydrazine hydrate with ethyl 2-oxo-2H-chromene-3-carboxylate. It was then converted into an azine spacer incorporated new tetrazo dye, bis-[2-(iminomethyl)-4-(phenyl diazenyl)phenol] by coupling with benzenediazonium chloride. The structures of the symmetrical azines were confirmed by FT-IR, NMR and mass spectroscopic techniques. Both the azines in thin film states exhibited deep yellow photoluminescence on UV excitation at 570 nm. The HOMO and LUMO energy levels assessed by cyclic voltammetry measurements, conformed to the electrochemical band gap energies of 4.41–4.55 eV. The p-type conductivity of the azines were confirmed by hot probe technique. The transport properties of both the azines were investigated by fabricating a bi-layer device. The successful construction of diodes with azines suggest that they could play a significant role as organic materials in the construction of electronic devices.

1. Introduction

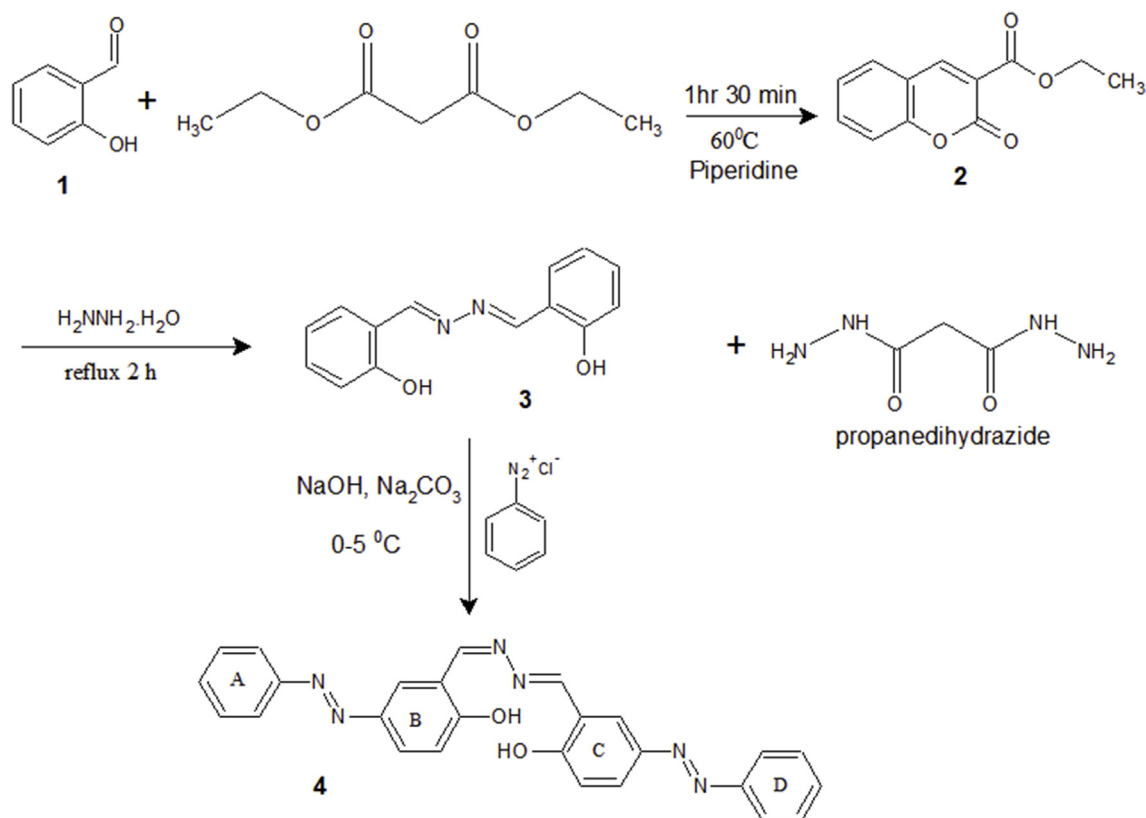
There is a growing need for replacing traditional inorganic silicon with alternate cost-effective materials that could offer comparatively simpler and commercially feasible technologies in niche fields of flexible organic electronics, electronic displays, transistors, detectors, memory devices and organic photovoltaic devices [1]. The remarkable properties of organic semiconductor materials like low-cost, lightweight, solution processability and compatibility with flexible substrates have unwrapped immense opportunities for innovative, convenient and high-performance electronic devices like solar cells, light-emitting diodes, transistors, and lasers too. In that context, all organic semiconducting materials, whether polymers, small molecules, or more complex structures that depend on conjugated π -electron frameworks for their conduction behavior are noteworthy [2]. Design and development of luminescent conjugated organic small molecules are of pronounced interest commercially, attributed to their broad range of applications in the development of light emitting diode and fluorescence sensing devices [3]. Investigations on organic planar backbones incorporating two conjugated double bonds with delocalized π -electron

system that manifests itself with various molecular properties like intramolecular charge transfer and elongated conjugated double bonds is one among the key dynamic research areas in heterocyclic chemistry [4].

Azines are N–N-linked diimines that are 2,3-diaza substituted analogs of 1,3-butadienes [5]. Azines display versatile chemical properties and are synthons for the preparation of several heterocycles [6,7]. Easy synthetic procedures with good quantitative yield of the preferred product, which can be easily purified are the two key benefits of symmetrical azines. The stereochemically significant nitrogen donor ligands in organometallic complexes of azines form an important class of pharmacologically active lead molecules [8–11]. Azine derivatives have been extensively studied for their material applications as dyes [12], liquid crystalline (especially twisted nematic) molecules [13], non-linear optical fluorophores [14,15] etc. The photoluminescence properties of 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene and polymers based on symmetrical azines incorporating 1-phenyl-1,2,3,4-tetrahydroquinoline groups in the solid state were investigated as optoelectronic materials [16]. Besides, azines are found to demonstrate both non solvent and concentration induced aggregates and are good

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Scheme 1. Synthetic pathway for azine derivatives.

prototypes that display aggregation induced emission (AIE) [17].

Azobenzenes are another class of compounds that find admirable opportunities as dynamic molecular devices or switches since the presence of a light or heat source readily permits reversible *cis-trans* transformation of their N=N double bonds. This isomerization prompts a major geometric change [18]. Besides, chemical structures carrying two (tetrazo) or more azobenzene units are of prime attention mainly attributed to their multiphotochromic behavior, that might be beneficial for molecular-level information processing and storage, and the cooperation of various photoisomerisable entities that can generally amplify the geometrical alterations associated with the *E-Z* transformation, thereby generating new light-induced functions [19].

To the best of our knowledge, there are only a few literature evidences available on the synthesis and exploration of photophysical properties of fluorescent azo dyes carrying azine (>C=N-N=C<) spacers [17]. Besides, there are no reports on the synthesis of tetrazo azine dyes and their characteristic features for application in organic electronics. In this regard, we present the synthesis of two fluorescent azines: 2,2'-[hydrazine-1,2-diylidenedimethylylidene]diphenol and introduction of extended conjugation on either side of the N–N-linked diimine linkage to prepare its tetrazo azine dye derivative, bis-[2-(iminomethyl)-4-(phenyl diazenyl)phenol]. An attempt to probe into their photophysical, surface morphological, electrochemical and electroluminescence properties, have also been carried out.

2. Materials and methods

The chemicals utilized for the study were procured from commercial sources like Sigma–Aldrich and Spectrochem Ltd. and were used as received. Thin layer chromatography to check the reaction progress was carried out using pre-coated aluminium sheets with aluchrosep silica gel 60/UV254, followed by visualization of spots in a UV chamber. IR spectra were recorded in Shimadzu FTIR 8400 S spectrometer. Agilent 6510 series mass spectrometer was used to record the mass spectra.

NMR spectra were taken in a Bruker 400 MHz instrument using DMSO-*d*₆ as the solvent. Melting points were determined by open capillary method and are uncorrected. The photophysical properties were studied using 1800 shimadzu UV–visible spectrophotometer and Varioskan Flash spectrofluorometer. Surface morphology analysis of thin solid films were performed using Carl Zeiss EVO 18 analytical scanning microscope (SEM) and INNOVA SPM atomic force microscope (AFM). The cyclic voltammetry (CV) measurements were performed with a conventional three-electrode cell system using CHI608E electrochemical analyzer at a scanning rate of 0.1 v/s or 100 mv/s at room temperature with tetrabutylammonium hexafluoro phosphate as the supporting electrolyte. Ag/AgCl and glassy carbon were used as reference and working electrodes respectively. The solutions taken in the cell were purged with ultra-high-pure nitrogen for 10–15 min before every experiment. All measurements were calibrated using ferrocenium/ferrocene (Fc⁺/Fc) redox system as internal standard. Current–voltage characteristics of the bilayer devices were recorded with a 4200 SCS semiconductor parameter analyzer.

3. Results and discussion

3.1. Synthesis and characterization

2-Hydroxybenzaldehyde was allowed to undergo sonication reaction with diethyl malonate in presence of catalytic quantity of piperidine to give the coumarin ester, ethyl 2-oxo-2*H*-chromene-3-carboxylate (2). During nucleophilic attack, the pyran-2-one ring of the ester can either undergo ring-opening at the lactone acyl moiety, or nucleophilic conjugate addition to the C=C bond [20]. Thus, there are two nucleophilic centers in the ester (2) apart from the carbonyl group in the coumarin side chain. Hence the ethanolic solution of ester was further allowed to reflux with excess of hydrazine hydrate to yield a symmetrical azine 2,2'-[hydrazine-1,2-diylidenedimethylylidene]diphenol (3) with propanedihydrazide as a by-product. Further, alkaline

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