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Synthesis and Characterization of New D-π-D Type Schiff Base Ligands

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Abstract—Two Schiff bases of D-p-D type (L_1 and L_2) have been successfully synthesized by the reaction of 3,3'-dimethylnapthide and 3,3',5,5'-tetramethylbenzidine with 4-(dimethylamino)cinnamic aldehyde. The ligands L_1 and L_2 have been characterized by IR, UV-visible, ^{1}H NMR and fluorescence spectra, as well as, TGA–DSC–DTG, elemental analyses and mass spectra.

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The past few decades have witnessed an explosion in the field of organic-based conjugated materials. The structural moiety provides a rigidly planar benzene and naphthalene unit within the molecular backbone. Substituent derivations at the naphthalene can modify properties such as solubility, emission wavelengths, processing ability and also mediate potential interchain interactions in polymer films [1–5].

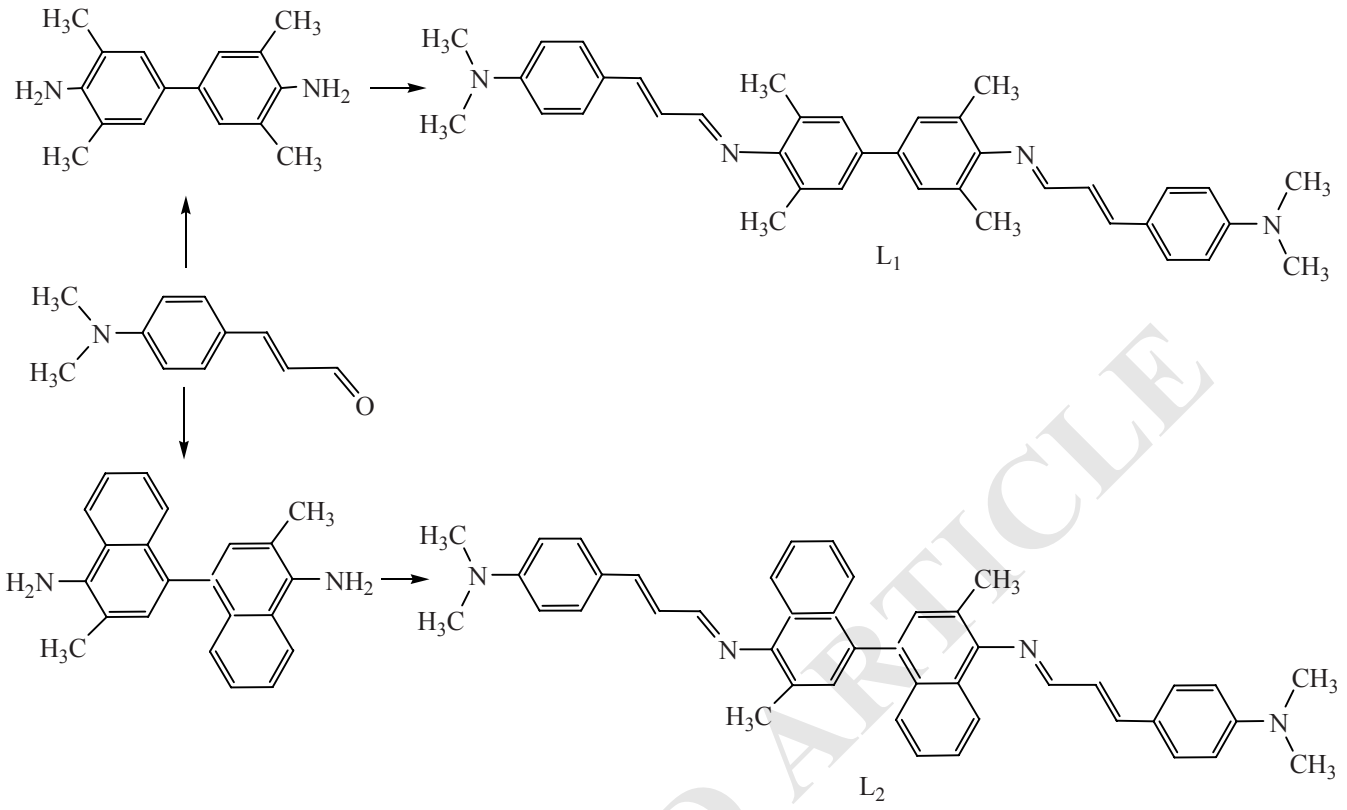
As is known, Schiff bases are reagents which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology. Moreover, Schiff base compounds have been regarded as excellent fluorescent materials because of their ability to achieve high thermal stability as well as high photoluminescent efficiency. Conjugated Schiff base systems that contain electronically coupled photo- and/or redox-active sites across an unsaturated organic bridge are of considerable current interest [6–11].

Many complicated factors can affect the two-photon excitation properties of organic materials. So it is important to investigate the structure and the two-photon excitation effect relationships of organic materials. However, most of these compounds employ C=C bonds as the conjugation bridge, the compounds with C=N structure such as Schiff bases are less studied to our knowledge [12–13].

In our recent research we have focused on the preparation of a new family of conjugated Schiff bases of D-π-D type, in which naphthalene units are liked together by imine. In this paper, we describe the synthesis and characterization of new Schiff ligands. The ligands structures were determined by elemental analysis, IR, UV-visible and ^{1}H NMR spectroscopy, TGA–DSC–DTG and LC–MS spectrometry. The fluorescence properties of the ligands were examined.

The new Schiff base ligands were synthesized by the reaction of 3,3'-dimethylnapthidine (3,3'-DFT) and 3,3',5,5'-tetramethylbenzidine (TMB) with 4-(dimethyl amino)cinnamic aldehyde (DMZ) in a good yield. The IR spectra of the L_1 and L_2 ligands shows characteristic Schiff base stretching bands at 1601 and 1598 cm^{-1} . These intense bands are assigned to the –C=N– stretching frequency of both ligands and are typical for the azomethine moiety of most Schiff base compounds. The absorption band of the C=O in the 4-(dimethylamino)cinnamaldehyde disappeared in the infrared spectrum of the ligand, which indicate that the condensation has occurred. The alkyl and aryl bands of the ligands are observed at 2854–2911, 1365–1469 and 1149–1151 cm^{-1} respectively.

Elemental analyses of Schiff base ligands show good agreement with the proposed structures. The ^{1}H NMR spectrum of the L_1 and L_2 ligands in $CDCl_3$ confirmed the proposed structure showing one D_2O-exchangeble proton at 7.8 and 8.1 ppm for the HC=N group. The assignments of the protons are highly complicated in the region 2.2–2.6 and 6.2–7.4 ppm,



where the signals are due to the protons of the alkyl and aromatic group.

Thermal behavior of the L_1 and L_2 ligands was determined in nitrogen atmosphere (20 ml min^{-1}) with a heating rate of 10°C min^{-1} in the temperature range 20–600°C. Thermal decomposition of DMZ, 3,3'-DFT, TMB and L_1, L_2 ligand was studied by thermogravimetric analysis: differential scanning calorimetry. The thermograms of the L_1 show decomposition within a mass loss of 79.10 % in the temperature range 365.0–425.0°C and the residue was 11.40% of the total weight. It was observed only one exothermic peak at 330.44°C belonging to L_2 while two exothermic peak at 144.45 and 219.5 belong to DMZ and tree exothermic peak at 200, 250, and 388°C belong to 3,3'-DFT, DMZ and 3,3'-DFT decomposing above 150, 250°C. The obtained L_2 ligand exhibited a higher decomposition temperature (above 330°C) and weight loss (32%) as compared to DMZ, 3,3'-DFT [14–17].

The ligands are stable at room temperature but hygroscopic. The ligands are soluble in common polar organic solvents, such as ethanol, methanol and chloroform but partially soluble in non-polar organic solvents such as benzene and hexane. The UV-vis spectral data for the L_1 ligand shows low-energy band at approximately 180–290 nm and high energy band at approximately 340–440 nm, while L_2 ligand shows high-energy band at approximately 220–300 nm and low energy band at approximately 320–440 nm, due to n–π* and π–π* transitions of the azomethine group in the ligands [18, 19]. The peaks recorded in the spectrum are broadened and slightly red-shifted.

In the mass spectra, the molecular ion peaks of the L_1 appeared at *m/z* 555.60 $[M]^+$ in the LC/MS–APCI spectra. The most intense peaks at *m/z* 469, 316 and 262 correspond to the fragments $[C_{34}H_{33}N_2]^+$, $[C_{22}H_{23}N_2]^+$, $[C_{18}H_{18}N_2]^+$. The molecular ion peaks *m/z* 627.50 $[M]^+$ of the L_2 ligand are present in the LC-MS spectra and support the proposed structures. The most intense peaks at *m/z* 470.51, 332.55 correspond to the fragments $[C_{33}H_{31}N_3]^+$, $[C_{24}H_{18}N_2]^+$ respectively. Mass spectral data confirmed the proposed structure of Schiff base ligands.

The solvents used in the fluorescence studies were spectrophotometric grade and were checked by fluorescence spectroscopy to make sure that they contain no fluorescence impurities before use. As a result, several experimental optimum fluorescence

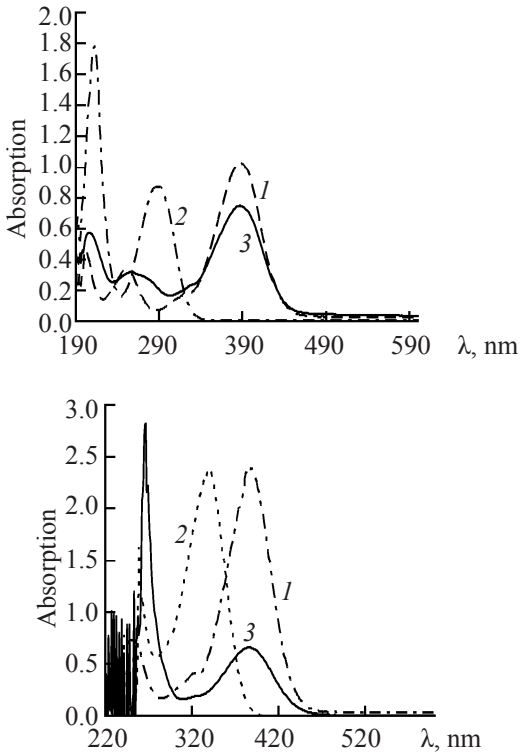


Fig. 1. UV spectra of the ligands L_1 and L_2 in ethanol at room temperature. (*1*) dimethylaminocymmamic aldehyde; (*2*) 3,3',5,5'-tetramethylbenzidine; and (*3*) ligands L_1 and L_2.

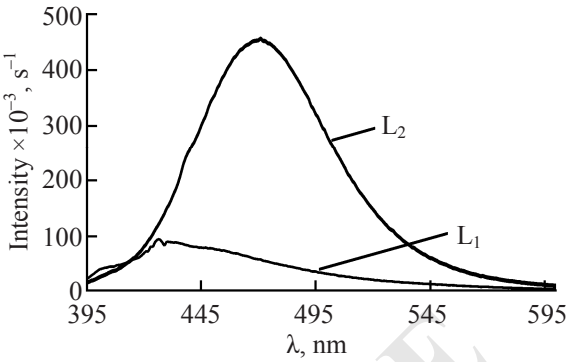


Fig. 2. The fluorescence emission spectra of ligand L_1 and L_2 at room temperature (1×10^{-5} M in ethanol).

emissions of the L_1 and L_2 were obtained in ethanol, methanol and chloroform at room temperature. The emission band maxima of L_2 were at 470 nm in chloroform, at 465 nm in methanol, and at 476 nm in ethanol. The emission band maxima of the L_1 were at 440 nm in chloroform, at 445 nm in methanol, and at 457 nm in ethanol. We measured the lifetime of the L_1, L_2 in ethanol and selected excited-state lifetimes 6.4 ns and 9.2 ns respectively. It was found that the optimum interval of concentration was between 1×10^{-4} M and 1×10^{-5} M [20, 21].

EXPERIMENTAL

All chemicals were of the highest grade available. IR spectra were recorded from KBr disks on a Mattson 1000 IR spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC-200 MHz spectrometer ($CDCl_3$). Absorption spectra were recorded with an Agilent 8453 UV-visible spectrophotometer. The elemental analyses and mass spectra (LC-MS) were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Fluorescence spectra were measured on a PTI time master C71 fluorescence spectrophotometer. Melting points were obtained with a BÜCHI melting point B-540 apparatus in open capillaries. TGA–DSC–DTG curves were obtained with a TA SDT Q 600 thermal analyzer apparatus using flowing nitrogen over a temperature range 20–600°C at 100 ml min^{-1} at a heating rate of 10°C min^{-1}.

The starting compounds, 3,3'-dimethylnapthidine, 3,3',5,5'-tetramethylbenzidine and 4-(dimethylamino) cinnamaldehyde were prepared according the reported procedures [22–24].

(*E*)-*N*-((*E*)-3-[4-(dimethylamino)phenyl]allylidene)-4(4-(((*E*)-(*E*)-3-[4-(dimethylamino)phenyl]allylidene)-amino-2,6-dimethylphenyl)-2,6-dimethylphenyl-1-amine (L_1). A solution of 3,3',5,5'-tetramethylbenzidine (0.11 g, 0.570 mmol) in 20 ml of dry ethanol was added dropwise to a solution of 4-(dimethylamino)cinnamaldehyde (0.1 g, 0.570 mmol) in 10 ml dry ethanol and the mixture was stirred under argon for 12 h at 90°C. The solvent was evaporated to 1/2 of the initial volume and petroleum ether was added at room temperature. A yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered off and then recrystallized from 2:1 *n*-hexane/ethyl acetate. Yield 48 %, mp 147–148°C. IR spectrum (ν, cm^{-1}): 3050 ν(Ar, w), 2911–2853 ν(CH_3–, m), 1601 ν(HC=N, s). ^{1}H NMR spectrum (δ, ppm): 7.8 d (H, HC=N) (disappeared with D_2O), 6.6–7.4 m (12 H, Ar–H), 3.0 s (12 H, N–CH_3), 2.2 s (12 H, CH_3). LC–MS (APCI), *m/z*: 555.60 (*M* + 1), ($C_{38}H_{42}N_4$ requires 554.75). Calculated, %: C 82.2; H 7.63; N 10.10. Found, %: C, 81.60; H, 7.55; N, 9.83.

(*E*)-*N*-((*E*)-3-(4-(dimethylamino)phenyl)allylidene)-4-(4-((*E*)-((*E*))-3-(4-(dimethylamino)phenyl)allylidene)-amino)-3-methylnaphthalen-1-yl)-2-methylnaphthalen-

1-amine (L_2). A solution of 3,3'-Dimethylnapthide (0.090 g, 0.285 mmol) in 20 ml of dry ethanol was added dropwise to a solution of 4-(Dimethylamino) cinn-amaldehyde (0.1 g, 0.570 mmol) in 10 ml dry ethanol and the mixture was stirred under argon for 15 h at 90°C. The solvent was evaporated to 1/2 of the initial volume and petroleum ether was added at room temperature. A yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered off and then recrystallized from 1:1 *n*-hexane/ethyl acetate. Yield: 54 %, m.p. 265–267°C. IR spectrum (ν, cm^{-1}): 3050 ν(Ar, w), 2918–2854 ν(CH_3–, m), 1598 ν(HC=N, s). ^1H NMR spectrum (δ, ppm): 8.1 d (H, HC=N)(disappeared with D_2O), 6.2–7.0 m (18 H, Ar–H), 3.4 s (12 H, N–CH_3), 2.6 s (6 H, CH_3). LC–MS (APCI), *m/z*: 627.50 (*M* + 1). ($C_{44}H_{42}N_4$ requires 626.83). Calculated, %: C, 84.31; H, 6.75; N, 8.94. Found, %: C, 84.02; H, 6.67; N, 8.91.

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