#### Polyhedron 29 (2010) 3089-3096

Contents lists available at ScienceDirect

# Polyhedron



# Novel photoluminescent hemi-disclike liquid crystalline Zn(II) complexes of $[N_2O_2]$ donor 4-alkoxy substituted salicyldimine Schiff base with aromatic spacer

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#### ARTICLE INFO

Article history: Received 14 July 2010 Accepted 12 August 2010 Available online 20 August 2010

Keywords: Zinc Schiff base Metallomesogen DFT Fluorescence

#### ABSTRACT

A series of novel hemi-disclike four coordinated distorted square planar Zn(II) Schiff base complexes containing 4-substituted alkoxy chains on the side aromatic ring [Zn  $(4-C_nH_{2n+1}O)_2$  salophen], n = 14, 16, 18 and salophen = N,N'-4-methyl phenylene bis (salicylideneiminato), have been prepared and their mesogenic, photophysical properties were investigated. The phase behavior of these compounds were characterized by differential scanning calorimetry, polarized optical microscopy and variable temperature PXRD study. The ligands are non-mesogenic but the complexes exhibited an unprecedented 2D-hexagonal columnar mesophase (Col<sub>h</sub>) in the temperature 175–185 °C range. In the mesophase (Col<sub>h</sub>), the molecules self assemble in a columnar stack in antiparallel fashion. All  $\lambda_{max}$  of the UV-Vis absorption and photoluminescence band occurred at ca. 291–425 and 504–524 nm, respectively. The ligands are non-emissive, but on coordination with Zn(II), the complexes show intense green emission at room temperature in dichloromethane solution (~505 nm,  $\Phi = 20\%$ ) as well as in solid (~522 nm,  $\Phi = 9\%$ ) at 360 nm excitation. The DFT calculations were performed using DMoI3 program at BLYP/DNP level to obtain the stable electronic structure of the complex. A small LUMO-HOMO band gap (~2.1 eV), presumably suggests a rather strong electronic correlation among the molecules along the column.

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## 1. Introduction

Metallomesogen derived from Schiff-base ligands feature amongst the earliest and most widely studied class of complexes [1]. Compounds showing both luminescence and liquid crystallinity are one of the most promising area for the applications in OLEDs, information storage, sensors, and enhanced contrast displays [2]. Major research on blue luminescent materials has been carried out mainly for the metals such as Al, Be, Cu, and Zn [3]. Photoluminescent metallomesogens have been documented with lanthanide metals, Pd, Pt, Ag and Au, Cu [4–8]. Zinc analogs are tardy though many non-mesogenic zinc complexes are known to display interesting optical properties for LED and sensory device applications [9-12]. Pyrazole based zinc complexes with non-conventional tetrahedral geometry displaying both supramolecular mesomorphic order and luminescence has been reported recently [13]. The Schiff base complexes of first row transition metal with 5-substituted long alkoxy chains forming linear rod like (1D) structure showing smectic mesophases has been extensively studied [2,13-16]. In contrast, 4-substituted salen framework based Schiff base ligands are very sparse [17]. Accessibility, ease of derivatization has rendered such ligands as versatile synthons for wider use in supramolecular chemistry, nanotechnology and design of novel (bio-inspired) materials [17]. Quite surprisingly such ligands with aromatic spacers are not known till date [18]. Recently Daniela Pucci et al. reported some blue light emitting nonlinear 4-substituted Zn(II) complexes with central aliphatic spacer showing SmC mesophase [19]. Choice of metal ion, nature and position of the substituent on side aromatic ring as well as spacers are known to greatly influence the mesogenic behavior [20]. Zinc complexes based on salen type framework with high thermal and redox stability are attractive as low cost accessible building blocks for newer light-emitting materials [19]. Emission performance of such systems are dependent on the nature of central bridging diamine core [19]. Though few complexes of VO(IV/V), Ni(II), and Cu(II) with 4-substituted long alkoxy chains (n = 8-18) of aromatic rings of salen-type Schiff base ligands with ethylene diamine or propylene diamine as rigid cores are on record there is no report on the related zinc(II) complexes with aromatic core as central linking group [21-23]. Zinc(II) complexes of suitably substituted 2,2',-bipyridyl ligands have been shown to exhibit hexagonal columnar mesomorphism regardless their rigid central core and tetrahedral coordination geometry [24,25]. In the present study, a series of new tetradentate [N<sub>2</sub>O<sub>2</sub>] donor Schiff base with a methyl





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<sup>0277-5387/\$ -</sup> see front matter @ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2010.08.017



Scheme 1. (i) C<sub>n</sub>H<sub>2n+1</sub> Br, KHCO<sub>3</sub>, KI, dry acetone, Δ, 40 h, (ii) glacial AcOH, absolute EtOH Δ, 4 h and (iii) Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, MeOH, TEA Δ, 1 h.

substituted aromatic rigid spacer and 4-substituted long alkoxy group at the side aromatic rings have been synthesized and their Zn(II) complexes exhibiting green luminescence were accessed. Though the ligands are non-mesogenic, the complexes showed 2D-hexagonal columnar mesophases (Col<sub>h</sub>) hitherto unreported for such 4-substituted compounds [2,9,11,14–23].

#### 2. Experimental

#### 2.1. General details

All solvents were purified and dried using standard procedures. The materials were procured from Tokyo Kasei and Lancaster Chemicals. Silica (60-120 mesh) from Spectrochem was used for chromatographic separation. Silica gel G (E-Merck, India) was used for TLC. The C, H and N analyses were carried out using PE2400 elemental analyzer. The <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer in CDCl<sub>3</sub> (chemical shift in  $\delta$ ) solution with TMS as internal standard. UV-Vis absorption spectra of the compounds in CH<sub>2</sub>Cl<sub>2</sub> were recorded on a Shimadzu UV-160PC spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu RF-5301PC spectrophotometer. The fluorescence quantum yield in dichloromethane were determined by dilution method using 9,10-diphenyl anthracene as standard. Infrared spectra were recorded on a Perkin-Elmer L 120-000A spectrometer on KBr disc. The optical textures of the different phase of the compounds were studied using a polarizing microscope (Nikon optiphot-2-pol) attached with Instec hot and cold stage HCS302, with STC200 temperature controller of 0.1 °C accuracy. The thermal behavior of the compounds were studied using a Perkin-Elmer differential scanning calorimeter (DSC) Pyris-1 spectrometer with a heating or cooling rate of 5 °C/min. Variable temperature powder X-ray diffraction (PXRD) of the samples were recorded on a Bruker D8 Discover instrument using Cu K $\alpha$  radiation. Quantum chemical calculation on Zn-18mpd was carried out using density functional theory (DFT) as implemented in DMol3 package.

## 2.2. Synthesis and analysis

The Schiff base ligands, were synthesized by condensation of 4alkoxysubstituted aldehyde with the 4-methyl-1,2-phenylene diamine with slight modification of the literature procedure [26]. The synthetic strategy for the ligands [(L = N,N'-bis-(4-(4'-n-alkoxy)-salicylidene) 4-Me-1,2-phenylenediamine), hereafter abbreviated as n-mpd, where n indicates the number of carbon atoms in alkyl chains, n = 14,16,18 and mpd = 4-methyl-1,2-phenylene diamine] and the mononuclear Zn(II) complexes (Zn-nmpd) are presented in Scheme 1.

#### 2.2.1. Synthesis of n-alkoxysalicyldehyde (n = 14, 16, 18)

Alkoxysalicyldehyde derivatives were prepared following the general method reported in literature [26]. 2,4-Dihydroxybenzaldehyde (10 mmol, 1.38 g), KHCO<sub>3</sub> (10 mmol, 1 g), KI (catalytic amount) and 1-bromotetradecane (10 mL, 2.5 g) or 1-bromohexadecane (10 mL, 2.8 g) or 1-bromooctaadecane (10 mL, 3 g) were mixed in 250 mL of dry acetone. The mixture was heated under reflux for 24 h, and then filtered, while hot, to remove any insoluble solids. Dilute HCl was added to neutralize the warm solution, which was then extracted with chloroform (100 mL). The combined chloroform extract was concentrated to give a purple solid. The solid was purified by column chromatography using a mixture of chloroform and hexane (v/v, 1/1) as eluent. Evaporation of the solvents afforded a white solid product.

### 2.2.2. Synthesis of N,N-bis-(4-(4'-n-octadecyloxy)-salicylidene)-4-Me-1,2-phenylenediamine (18-mpd)

An ethanolic solution of 2-hydroxy-(4-octadecyloxy)-salicylaldehyde (0.33 g, 1 mmol) was added to an ethanolic solution of 4-Me-1,2-phenylenediamine (0.06 g, 1 mmol). The solution mixture was refluxed with a few drops of acetic acid as catalyst for 3 h to yield the yellow Schiff base N,N'-bis-(4-(4'-n-alkoxy)-salicylidene)-4-Me-1,2-phenylenediamine. The compound was collected by filtration and recrystallised from absolute ethanol to obtain a pure compound. Yield: 0.279 g (75%); m.p., 126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.07 (s, 1H, H<sup>9</sup>), 8.77 (s, 1H, H<sup>4</sup>), 7.74 (d, *J* = 8.54 Hz, H<sup>5</sup>), 7.24 (d, 2H, H<sup>7</sup>), 7.14 (t, *J* = 8.43 Hz, 2H, H<sup>1</sup>), 7.13  $(dd, I = 2.41 Hz, I = 9.0, 2H, H^{6}), 6.61 (d, I = 2.44 Hz, 2H, H^{3}), 6.49$ (dd, J = 2.44 Hz, J = 8.29 Hz, 2H, H<sup>2</sup>), 3.97 (t, J = 6.8 Hz, 2H, -OCH<sub>2</sub>), 2.1 (s, 1H, H<sup>8</sup>), 0.89 (t, J = 6.8 Hz, 6H, CH<sub>3</sub>), 0.86 (m, -CH<sub>2</sub>) of methylene proton in side chain). <sup>13</sup>C NMR (75.45 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 134.03 (-C<sub>1</sub>), 118.14 (-C<sub>5</sub>), 141.7 (-C<sub>11</sub>), 135.82 (- $C_{10}$ ), 128.03 (- $C_6$ ), 120.93 (- $C_7$ ), 140.34 (- $C_{12}$ ), 162.52 (-NCH), 113.00 (-C<sub>13</sub>), 164.12 (-C<sub>14</sub>), 108.13 (-C<sub>3</sub>), 162.79 (-C<sub>15</sub>), 115.64 (-C<sub>2</sub>). IR (v<sub>max.cm<sup>-1</sup></sub>, KBr): 3500 (v<sub>OH</sub>), 2925 (v<sub>as(C-H)</sub>, CH<sub>3</sub>),

2921 ( $\nu_{as(C-H)}$ , CH<sub>2</sub>), 2873 ( $\nu_{s(C-H)}$ , CH<sub>3</sub>), 2850 ( $\nu_{as(C-H)}$ , CH<sub>2</sub>), 1629 ( $\nu_{C=N}$ ), 1298 ( $\nu_{C-O}$ ).

### 2.2.3. Synthesis of N,N'-bis-(4-(4'-n-hexadecyloxy)-salicylidene)-4-Me-1,2-phenylenediamine (16-mpd)

Yield: 0.21 g (73%); m.p., 128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 13.01 (s, 1H, H<sup>9</sup>), 8.72 (s, 1H, H<sup>4</sup>), 7.77 (d, *J* = 8.54 Hz, H<sup>5</sup>), 7.24 (d, 2H, H<sup>7</sup>), 7.15 (dd, *J* = 2.41 Hz, *J* = 9.0, 2H, H<sup>6</sup>), 7.14 (t, *J* = 8.43, 2H, H<sup>1</sup>), 6.49 (dd, *J* = 2.14 Hz, *J* = 8.29 Hz, 2H, H<sup>2</sup>), 6.45 (d, *J* = 2.13 Hz, 2H, H<sup>3</sup>), 3.91 (t, *J* = 6.8 Hz, 2H,  $-\text{OCH}_2$ ), 2.5 (s, 1H, H<sup>8</sup>), 0.98 (t, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 0.82 (m,  $-\text{CH}_2$  of methylene proton in side chain). IR ( $\nu_{\text{max,cm}^{-1}}$ , KBr): 3434 ( $\nu_{\text{OH}}$ ), 2916 ( $\nu_{\text{as(C-H)}}$ , CH<sub>3</sub>), 2918 ( $\nu_{\text{as(C-H)}}$ , CH<sub>2</sub>), 2844 ( $\nu_{\text{s(C-H)}}$ , CH<sub>3</sub>), 2845 ( $\nu_{\text{as(C-H)}}$ , CH<sub>2</sub>), 1622 ( $\nu_{\text{C=N}}$ ), 1289 ( $\nu_{\text{C-O}}$ ).

#### 2.2.4. Synthesis of N,N'-bis-(4-(4'-n-tetradecyloxy)-salicylidene)-4-Me-1,2-phenylenediamine (14-mpd)

Yield: 0.19 g (74%) m.p., 130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 13.12 (s, 1H, H<sup>9</sup>), 8.77 (s, 1H, H<sup>4</sup>), 7.74 (d, *J* = 8.54 Hz, H<sup>5</sup>), 7.24 (d, 2H, H<sup>7</sup>), 7.23 (dd, *J* = 2.81 Hz, *J* = 9.0, 2H, H<sup>6</sup>), 7.15 (t, *J* = 8.43, 2H, H<sup>1</sup>), 6.66 (d, *J* = 2.44 Hz, 2H, H<sup>3</sup>), 6.43 (dd, *J* = 2.44 Hz, *J* = 8.29 Hz, 2H, H<sup>2</sup>), 3.97 (t, *J* = 6.8 Hz, 2H,  $-\text{OCH}_2$ ), 2.5 (s, 1H, H<sup>8</sup>). 0.99 (t, *J* = 6.3 Hz, 6H, CH<sub>3</sub>), 0.88 (m,  $-\text{CH}_2$  of methylene proton in side chain). IR ( $v_{\text{max,cm}^{-1}}$ , KBr): 3433 ( $v_{\text{OH}}$ ), 2918 ( $v_{\text{as(C-H)}}$ , CH<sub>3</sub>), 2919 ( $v_{\text{as(C-H)}}$ , CH<sub>2</sub>), 2849 ( $v_{\text{s(C-H)}}$ , CH<sub>3</sub>), 2850 ( $v_{\text{as(C-H)}}$ , CH<sub>2</sub>), 1626( $v_{\text{C=N}}$ ), 1287( $v_{\text{C-O}}$ ).

# 2.2.5. Synthesis of mononuclear zinc(II) complexes (Zn-nmpd n = 14,16,18)

2.2.5.1. General procedure. The ligand 18-mpd (0.075 g,0.1 mmol) or 16-mpd (0.062 g,0.1 mmol) or 14-mpd (0.060 g,0.01 mmol) was dissolved in minimum volume of absolute ethanol. To this, an equimolar amount of zinc acetate Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.02 g, 0.1 mmol) in methanol was then added slowly and stirred for 2 h at room temperature. A yellow solid formed immediately was filtered, washed with diethyl ether and recrystallised from chloroform–ethanol (1:1).

2.2.5.2. Zn-18mpd. Yield = 0.0.07 g (75%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ , 8.21 (s, 1H, H<sup>4</sup>), 7.70 (d, *J* = 8.51 Hz, H<sup>5</sup>), 7.20 (d, 2H, H<sup>7</sup>), 7.12 (t, *J* = 8.34, 2H, H<sup>1</sup>), 7.01 (dd, *J* = 2.35 Hz, *J* = 8.59, 2H, H<sup>6</sup>), 6.56 (d, *J* = 2.44 Hz, 2H, H<sup>3</sup>), 6.39 (dd, *J* = 2.34 Hz, *J* = 8.19 Hz, 2H, H<sup>2</sup>), 3.97 (t, *J* = 6.8 Hz, 2H, -OCH<sub>2</sub>), 2.1 (s, 1H, H<sup>8</sup>), 0.89 (t, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 0.86 (m, -CH<sub>2</sub> of methylene proton in side chain). IR ( $\nu_{max,cm^{-1}}$ , KBr): 2920 ( $\nu_{as(C-H)}$ , CH<sub>3</sub>), 2850 ( $\nu_{as(C-H)}$ , CH<sub>2</sub>), 1612 ( $\nu_{C=N}$ ).

2.2.5.3. *Zn*-16mpd. Yield = 0.03 g (70%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ , 8.04 (s, 1H, H<sup>4</sup>), 7.70 (d, *J* = 8.51 Hz, H<sup>5</sup>), 7.25 (d, 2H, H<sup>7</sup>), 7.10 (t, *J* = 8.34 Hz, 2H, H<sup>1</sup>), 7.09 (dd, *J* = 2.35 Hz, *J* = 8.59, 2H, H<sup>6</sup>), 6.54 (d, *J* = 2.44 Hz, 2H, H<sup>3</sup>), 6.32 (dd, *J* = 2.34 Hz, *J* = 8.19 Hz, 2H, H<sup>2</sup>), 3.97 (t, *J* = 6.8 Hz, 2H, -OCH<sub>2</sub>), 2.1 (s, 1H, H<sup>8</sup>) 0.89 (t, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 0.84 (m, -CH<sub>2</sub> of methylene proton in side chain). IR ( $v_{max,cm^{-1}}$ , KBr): 2919 ( $v_{as(C-H)}$ , CH<sub>3</sub>), 2849 ( $v_{as(C-H)}$ , CH<sub>2</sub>), 1583 ( $v_{C=N}$ ).

2.2.5.4. *Zn*-14*mpd*. Yield = 0.06 g (75%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ , 8.21 (s, 1H, H<sup>4</sup>), 7.70 (d, *J* = 8.51 Hz, H<sup>5</sup>), 7.21 (d, 2H, H<sup>7</sup>), 7.16 (t, *J* = 8.34 Hz, 2H, H<sup>1</sup>),7.01 (dd, *J* = 2.35 Hz, *J* = 8.54, 2H, H<sup>6</sup>), 6.56 (d, *J* = 2.44 Hz, 2H, H<sup>3</sup>), 6.39 (dd, *J* = 2.34 Hz, *J* = 8.19 Hz, 2H, H<sup>2</sup>), 3.97 (t, *J* = 6.8 Hz, 2H, -OCH<sub>2</sub>), 2.1 (s, 1H, H<sup>8</sup>), 0.99 (t, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 0.89 (m, -CH<sub>2</sub> of methylene proton in side chain). IR ( $\nu_{max,cm^{-1}}$ , KBr): 2919 ( $\nu_{as(C-H)}$ , CH<sub>3</sub>), 2851 ( $\nu_{as(C-H)}$ , CH<sub>2</sub>), 1589( $\nu_{C=N}$ ).

#### 3. Results and discussion

### 3.1. Spectral investigation

The characterizations of the compounds were made by elemental analyses, FT-IR, <sup>1</sup>H NMR, and mass spectrometry. The analytical data of the compounds Table 1, are in good agreement with the proposed formulae of the compounds. The shift of  $v_{CN}$  vibrational stretching frequency at ca. 1625 cm<sup>-1</sup> to lower wave number ( $\Delta v$  $\sim$ 30 cm<sup>-1</sup>) and absence of v<sub>OH</sub> mode upon chelation, clearly suggested the coordination of azomethine N and phenolate oxygen to the metal. The  $v_{C=N}$  stretching frequency is rather independent of the length of alkoxy side chain in both ligands and their complexes. A comparison of the <sup>1</sup>H NMR spectral data of the ligands with those of the Zn(II) complexes showed the absence of the phenolic -OH and a significant shift (8.324-8.197 ppm) in the peak positions of the -N=CH in the spectrum of the metal complex, suggesting binding through the phenolate anion and the azomethine nitrogen atom of the ligand to the metal ion [27]. The FAB-mass spectra Table 1, of the Zn(II) complexes are concordant with their formula weights. These features compare well with a related structurally analogous fluorescent but non-mesogenic 4-methoxy substituted-salophen-zinc complex (Fig. 1) [9], and a dodecyloxybis-(salicylaldiminato)zinc(II) complexes stacked in 3D aggregation with no reported mesogenicity [11].

## 3.2. Photophysical properties

The electronic absorption spectra (Fig. 2), of *n*-mpd (n = 14, 16, 18) recorded in dichloromethane ( $10^{-4}$  M), consisted of two peaks at 291 and 333 nm and a very-low intensity band at ~364 nm. The band at ~291 and ~333 nm are attributed to a  $\pi$ - $\pi^*$  transition localized on the aromatic rings, whereas the band at ~364 nm is due to the n- $\pi^*$  excitation of the lone pair on the imine nitrogen atom to the  $\pi^*$  orbital on the C=N fragment [19]. The Zn(II) complexes showed two intense bands at ~313 and ~375 nm resulting from the metal-perturbed ligand-centered transitions, which have the same origin as the two principal bands of the ligand spectrum [19]. Further, on complexation the bands at ~364 nm of the ligands are red shifted to ~425 nm, which appeared as a shoulder in the spectra. This has originated from the donation of lone pair

 Table 1

 Mass spectrometric and elemental analysis data of Zn-nmpd.<sup>a</sup>

Complex	$FAB^+$	%С	%H	%N
Zn-18mpd	928 (929)	73.2 (73.5)	9.4 (9.6)	3.1 (3.0)
Zn-16mpd	872 (873)	72.1 (72.7)	9.5 (9.3)	3.3 (3.2)
Zn-14mpd	815 (816)	70.4 (70.9)	8.5 (8.8)	3.2 (3.4)

<sup>a</sup> Calculated values are in brackets.



Fig. 1. Zinc salophen complex with 4-methoxy substituent.



Fig. 2. UV-Vis absorption spectra of 18-mpd and Zn-18mpd in CH<sub>2</sub>Cl<sub>2</sub>.

electrons to the metal further attesting the coordination of azomethine [28,29].

The study of luminescent Zn(II) complexes is not only of fundamental interest, but also significant for different applications (optical amplifiers, optical waveguides, OLEDs, etc.) [19]. Photoluminescence study of the Zn(II) complexes are carried out at room temperature in dichloromethane solution and also in the solid state (Fig. 3). The ligands are non-emissive while the corresponding Zn(II) complexes emit intense green light (Fig. 4) at ~505–522 nm with high emission quantum yield of ~20% (solution), and 9% (solid) when excited at 360 nm, Table 2. For Zn(II) complexes, no emission originating from metal-centered MLCT/LMCT excited states is expected due to redox insensitive stable Zn<sup>2+</sup>(d<sup>10</sup>) configuration [19,30–32]. The intense emission observed at room temperature in the complex stems from the intraligand



Fig. 3. Photoluminescence spectrum of Zn-18mpd in solid (1) and in solution (2).



Fig. 4. Fluorescent image of Zn-18mpd in solid state.

Table 2				
UV-Vis and photoluminescence	data of ligands	(n-mpd)and 2	Zn-nmpd	complexes.

Compounds	$\pi \rightarrow \pi^*$ ( $\varepsilon$ , l mol <sup>-1</sup> cm <sup>-1</sup> )	$n \rightarrow \pi^*$ ( $\varepsilon$ , l mol <sup>-1</sup> cm <sup>-1</sup> )	PL <sup>a</sup> (Solution)	PL <sup>a</sup> (Solid)
18-mpd	292 (11300) 331 (14200)	366 (9900)	-	
Zn-18mpd	314 (11200) 377 (14100)	425 (8100)	504	520
16-mpd	291 (11400) 333 (14400)	364 (9100)	-	
Zn-16mpd	316 (11400) 379 (14400)	426 (8200)	507	522
14-mpd	293 (11200) 332 (14600)	366 (9300)	-	
Zn-14mpd	314 (11300) 376 (11500)	425 (8400)	509	524

<sup>a</sup> Photoluminescence data of Zn-nmpd.



Fig. 5. Overlap of UV-Vis and fluoroscence spectra of Zn-18mpd.

 $(\pi-\pi^*)$  fluorescence, and the role of the central  $Zn^{2*}$  ion is to provide stability to the ligand [30–32]. The solid state emission spectra of the complexes were recorded by placing a uniform powder sheet between two quartz plates. The emission band at ~504 nm in solution is red shifted by ~20 nm in all the complexes. This shift is due to the intermolecular aromatic interaction which is weaker in solution than that in the solid [3,19,13]. Moreover in the solid state, a larger electronic delocalization leads to a lowering of energy of the electronic states. On the basis of overlap of the fluorescence emission (508 nm) with the lowest energy UV–Vis absorption band (425 nm), (Fig. 5) the lowest excited singlet state energy is experimentally calculated to be ~260 kJ mol<sup>-1</sup>.

# 3.3. Thermal microscopy and differential scanning calorimetric studies: mesomorphic behavior

The ligands *N* ,*N*-bis-(4-(4'-*n*-alkoxy)-salicylidene)-4-Me-1,2phenylenediamine are non-mesogenic. Polarized optical microscopy studies of the complexes with alkoxy chain lengths, n = 14, 16, 18 exhibited monotropic mesomorphic behavior in the temperature range 175–185 °C. Upon cooling the sample from isotropic phase, a sphereulitic growth appeared, which coalesce to a focal conic fan texture (Fig. 6) with large homeotropic regions, suggesting a hexagonal columnar mesophase (Col<sub>h</sub>). A similar observation has been reported earlier for platinum metal complexes [33]. Large homeotropic regions are caused by the bulky alkoxy groups in the molecules. Pertinent here is to mention that all other previously reported metallomesogens with 4-substituted alkoxy-salen type



Fig. 6. Optical micrograph of the fan like textures of Zn-16mpd at 169 °C (cooling cycle).

Schiff base showed either smectic, lamellar (Col<sub>1</sub>) or rectangular (Col<sub>r</sub>) columnar mesophase [21–23]. DSC thermograms of the complexes Zn-18mpd and Zn-16mpd (Fig. 7), exhibited solid-solid, solid-liquid transitions in heating and isotropic liquid to mesophase and then to solid in the cooling cycle, however, the Zn-14mpd complex exhibited an additional solid-solid (Cr1-Cr2) phase transitions in the heating cycle Table 3. This solid-solid transition could not be detected in thermal microscopy. All the complexes are highly viscous imposing severe restriction in the molecular mobility. However, on pressing the sample with a needle on glass cover slips, fluidity could be observed. The DSC trace for the complex Zn-16mpd at 182.9 °C ( $\Delta H = 6.7 \text{ kJ mol}^{-1}$ ) is due to I–Col<sub>h</sub>



Fig. 7. DSC thermogram of Zn-16mpd.

Table 3	
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Compounds	T ( °C) <sup>a</sup>	Transition <sup>b</sup>	$\Delta H$ (kJ mol <sup>-1</sup> )
Zn-18mpd	101.6	Cr-Cr1	14.9
	182.9	Cr1-I	16.4
	175.8	I-Col <sub>h</sub>	3.2
	161.1	Col <sub>h</sub> -Cr1	2.1
Zn-16mpd	123.3	Cr-Cr1	17.5
	192.2	Cr1-I	19.2
	182.9	I-Col <sub>h</sub>	6.7
	175.7	Col <sub>h</sub> -Cr1	5.4
Zn-14mpd	101.6	Cr-Cr1	7.7
	120.0	Cr1-Cr2	17.2
	197.3	Cr2–I	18.0
	184.4	I-Col <sub>h</sub>	2.2
	182.3	Col <sub>h</sub> -Cr2	3.8

Transition temperature obtained from onset peak.

<sup>b</sup> Cr: crystal; Col<sub>h</sub>: hexagonal columnar.

phase transition. The clearing temperatures of the complexes which usually correspond to the breakdown of the packing and columnar stacking showed a marginal increase (5-10 °C increment) with decrease in alkoxy chain length. The isotropic to columnar (I-Col<sub>h</sub>) phase transition temperatures also exhibited a similar dependence on alkoxy chain length. Self-assembly into columnar phases and strong electronic interaction within the columns, render them as potential charge carrier system [22]. The  $\pi$ - $\pi$  orbital overlap of the rigid aromatic spacer further augment such charge transport along the columns holding promises for application in the area of molecular electronics, optoelectronics, photoconductivity etc. [1,34].

#### 3.4. X-ray diffraction studies

Powder X-ray diffraction (PXRD) pattern (Fig. 8) of Zn-18mpd at 175 °C was recorded on a Bruker D8 Discover instrument using Cu K $\alpha$  radiation. In the low-angle region, four sharp peaks Table 4, one very strong and three weak reflections are seen whose d-spacings are in the ratio of  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ . Identifying the first peak with the Miller index [10], the ratios confirm a two-dimensional hexagonal lattice [35]. In the wide angle region three diffuse reflections are



Fig. 8. X-ray diffraction pattern of Zn-18mpd at 175 °C.

Table	4		
PXRD	data	of Zn-1	8mpd

Т

$d_{\rm obs}$ (Å) <sup>a</sup>	Ι	hk <sup>b</sup>	$d_{\text{calc}}(\text{\AA})^{\text{c}}$	Parameters <sup>d</sup>
Zn-18mpd				
22.14	vs	10	22.12	a = 25.5 Å
12.69	w	11	12.67	$S = 566 \text{ Å}^2$
10.98	w	20	10.84	$V_{\rm m}$ = 1722 Å <sup>3</sup>
8.19	w	21	8.21	h = 3.04
7.4	br	h'		N = 1
4.9	br	h <sub>Ch</sub>		
3.7	S	h <sub>o</sub>		

d<sub>obs</sub> is experimentally and theoretically measured diffraction spacings at 175 °C.

[hk] are indexation of the reflections.

 $^{c}$   $d_{calc}$  is experimentally and theoretically measured diffraction spacings at 175 °C.

<sup>d</sup> The mesophase parameters are deduced from the following mathematical expressions for the columnar phase  $\langle d_{10} \rangle = 1/N_{hk} \left[ \sum_{hk} d_{hk} (h^2 + k^2 + hk)^{1/2} \right]$  where  $N_{\rm hk}$  is the number of hk reflections and  $a = 2 < d_{10} > /\sqrt{3}$  (for Col<sub>h</sub>). Molecular volume  $V_{\rm m}$  is calculated using the formula:  $V_{\rm m} = M/\lambda \rho N_{\rm A}$  where M is the molecular weight of the compound,  $N_A$  is the Avogadro number,  $\rho$  is the volume mass ( $\approx 1 \text{ g cm}^{-3}$ ), and  $\lambda$ (T) is a temperature correction coefficient at the temperature of the experiment (T).  $\lambda = V_{CH_2} (T^0) / V_{CH_2} (T), T^0 = 25 \circ C. V_{CH_2} (T) = 26.5616 + 0.02023.$  The intracolumnar repeating distance h is calculated directly from the estimated molecular volume V<sub>m</sub> according to the equation:  $h = NV_m/S$ , in which N is the number of molecules (here N is chosen equal to 1), and S is the lattice area (columnar cross-section). For a hexagonal lattice:  $S = a^2 \sqrt{3}/2$ .



Fig. 9. Organization of single molecule in a unit cell.

seen. The broad one centered at 4.9 Å corresponds to the liquid like order of the aliphatic chains. The relatively sharper one at about 3.7 Å, well separated from the broad one is due to the stacking of the molecular cores on top of one another [35]. The presence of another weak and somewhat broad halo at 7.4 Å ( $\sim$ h' = 2h<sub>0</sub>) suggest a staggered dimeric interactions of the molecules along the column [36]. The intracolumnar repeating periodicity (*h*) along the columnar axis, the columnar cross section (*S*) and the molecular volume (*V*<sub>m</sub>) are related analytically through the relation hS = NV<sub>m</sub> where *N* is the number of molecules within the fraction of the column.

pound in the Col<sub>h</sub> mesophase to be close to 1 g cm<sup>-3</sup>, it turns out that the columnar cross-sections ( $S = 566 \text{ Å}^2$ ) are made of a single molecule (Fig. 9). A comparison of the radii (22.1 Å) of half disc molecule in its extended form as obtained from DFT calculation and the lattice constant (25.5 Å) clearly reflect substantial interdigitation of the antiparallel molten chains in the columnar stack (Fig. 10), as postulated by Swager et al. and others for related materials [37–42]. This back to back arrangement leads to a discoid-like shell around the rigid aromatic core of the complex molecule. Moreover the observed stacking distance  $h_0$  (3.7 Å) being larger than the intracolumnar repeating distance, h (3.04 Å), suggest strong undulations of the columnar cores about the columnar axis [43–45]. These results indicate a lateral expansion of the randomly



Fig. 10. Face-to-face arrangement of two adjacent molecules of Zn-18mpd in a column.



Fig. 11. Undulations of molecules within a column.



Fig. 12. DFT optimized structures of (a) 18mpd and (b) Zn-18mpd.

piled tilted disc within the column (Fig. 11). The tetrahedral methyl substituent in the phenylene spacer is presumed to force the neighboring molecules above and below the plane by an angle in order to be well stacked in the column.

#### 3.5. Theoretical study of 18-mpd and Zn-18mpd

As efforts to obtain single crystal of the complexes failed, guantum chemical calculation is performed to investigate the electronic structure of the ligand, 18-mpd and its Zn(II) complex (Fig. 12), using density functional theory (DFT). Full geometry optimization of the complex without symmetry constrain has been carried out using DMoL3 program package at BLYP/DNP level [46]. BLYP is the most widely used exchange-correlation functional suggested exchange potential by Becke [47] with gradient corrected correlation provided by Lee et al. [48]. DNP is the double numerical with polarization basis set (all core electrons included), whose size though comparable to 6-31G\*\* basis set of Hehre et al. [49] is believed to be much more accurate. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) diagram of the complex is presented in (Fig. 13). The electron density of the HOMO is localized mainly on the aromatic rings. The HOMO and LUMO energies of the complex calculated to be -4.61 and -2.51 eV, respectively,  $\Delta E = 2.1$  eV matched well with those reported for similar Schiff base complexes of zinc [3]. The HOMO (-4.55 eV)-LUMO (2.63 eV) gap for the ligand was found to be 1.92 eV. The length and bent angle of the molecule in its extended form are found to be ~44 Å and 98°, respectively, from DFT calculation. Some of the selective geometric parameters of optimized Zn(II) complex, evaluated by DFT calculation at BLYP/DNP level are shown in Table 5. The average Zn–O1 and Zn–N1 bond lengths of the complex are 1.96 and 2.08 Å, respectively, implying the pres-



Fig. 13. LUMO and HOMO orbital diagram of Zn-18mpd obtained from DFT calculation.

Table 5							
Selected	bond	lengths	and	bond	angles	of	Zn-
18mnd							

Structure parameter	Zn-18mpd <sup>a</sup>
Zn-O(1)	2.084
Zn-O(2)	2.081
Zn-N(1)	1.966
Zn-N(2)	1.966
O(1)-Zn-O(2)	98.6
N(1)-Zn-N(2)	80.9
N(1)-Zn-O(2)	92.3
O(1) - Zn - N(1)	162.6
O(1) - Zn - N(2)	162.5
N(2)-Zn-O(2)	92.4

 $^{\rm a}$  Bond lengths are reported in Å and bond angles in  $^{\circ}\!.$ 

ence of regular  $\sigma$  and dative bonding, respectively. The bond angles 96.6° and 80.9° for O1–Zn–O2 and N1–Zn–N2, respectively, around the zinc atom deviate substantially from the tetrahedral values indicating a distorted planar four coordinate geometry. A short central bridge, methyl substituted aromatic core in the present complexes presumably prevented the formation of a tetrahedral environment around zinc(II), leading to a distorted planar geometry [19] Flexible spacers such as alkyl chain,  $(CH_2)_n$  between two imine nitrogen donor atoms in such Schiff base complexes, however, are known to facilitate a distorted tetrahedral geometry usually preferred by zinc [19].

#### 4. Conclusion

A series of new hemi-disclike mononuclear zinc(II) complexes of tetradentate [N<sub>2</sub>O<sub>2</sub>] donor Schiff base bearing long alkoxy substituent of variable chain length in 4-position of the side aromatic ring and a central methyl substituted aromatic spacer group have been successfully synthesized. All the ligands are non-mesogenic, however, the complexes exhibited unprecedented monotropic hexagonal columnar mesophase in the temperature range 175-185 °C. The columnar mesophases (Col<sub>h</sub>) are presumed to have been built from the stacking of flat and rigid phenylenediamine spacer. The complexes exhibited intense green fluorescence both in solid and solution state. Based on spectral and DFT study, four coordinated distorted square planar geometry have been conjectured. The strategy adopted herein can be effectively employed to access newer green emitting metallomesogens with tunable molecular construction motifs leading to smart multifunctional materials.

#### Acknowledgments

The authors are thankful to SAIF, NEHU and CDRI, Lucknow for analytical and spectral data. GD acknowledges financial support from DST and UGC, Govt. of India. Thanks are also due to Dr. R.C. Deka, Tezpur University for computational facility.

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