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Novel Green Light Emitting Nondiscoid Liquid Crystalline Zinc(II) Schiff-Base Complexes

Chira R. Bhattacharjee,*[a] Gobinda Das,[a] Paritosh Mondal,[a] Subbarao Krishna Prasad,[b] and D. S. Shankar Rao[b]

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A new series of nondisc-like Zn^{II} Schiff base complexes of the type [Zn $(4\text{-}C_nH_{2n+1}O)_2$ salophen], n = 14, 16, 18, salophen = N,N'-phenylenebis(salicylideneiminato), have been prepared and their mesogenic, photophysical properties investigated. The mesomorphic behaviour of these compounds was studied by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction (XRD) techniques. The ligands are found to be nonmesogenic, but their complexes exhibited a columnar mesomorphism. The XRD-study revealed that the molecules are self-organized into columnar mesophase of the primitive rectangular (Col_r) and/or monoclinic oblique type. At room temperature with 360 nm excitation, all the complexes showed green emission in dichloromethane solution (ca. 507 nm, Φ = 22 %) as well as in the solid state (ca. 516 nm, Φ = 9 %). The DFT calculations were performed using the DMol3 program at BLYP/DNP level to obtain the stable electronic structure of the complex.

Introduction

The synthesis of salen-based zinc(II) complexes has been a recurring theme of current research owing to their versatile physical properties such as thermal stability as well as luminescence, which are very useful for applications in electroptic devices.[1] The combination of luminescent molecules and soft materials to generate new electronic devices is a fast growing field of research.[2] The design of luminescent and photoresponsive liquid crystals is particularly attractive owing to their potential applications in OLEDs, information storage, sensors, and enhanced contrast displays.[3] Luminescent mesogens have been well documented with metals such as the lanthanide group,[4] Pd,[5] Pt,[3,6] Au,[7] and Ag.[8] Unlike other first-row transition metals only very few examples of mesomorphic zinc(II) derivatives were reported until now.[9] Zinc(II) complexes are widely applied in OLED technology for their electron-transporting ability, light-emitting efficiency, high thermal and redox stability, and tunable electronic properties.[1a,9] Pyrazole-based zinc complexes displaying both supramolecular mesomorphic structure and luminescence have been reported recently.[9d] Metallomesogens based on 4-substituted salen-type framework Schiff base ligands have been inadequately addressed. Some blue light emitting nonlinear 4-substituted Zn^{II} complexes with a central aliphatic core showing SmC mesophase have recently been reported.[1a] Very recently we have reported the synthesis of a series of novel photoluminescent liquid crystalline Zn^{II}-salen complexes with a methyl-substituted phenylenediamine spacer and alkoxy tail of carbon chain lengths of 14, 16, and 18 atoms which showed hexagonal columnar mesomorphism.[9e] Interestingly, similar zinc complexes with carbon chain lengths of 8, 10, and 12 atoms are on record with no reported mesogenicity.[10]

The choice of the metal ion, nature and position of the substituents of aromatic substituents as well as of spacers are known to greatly influence the mesogenic behavior. For some compounds even a minor changes within the mesogenic core can lead to major differences in molecular organization and in turn liquid-crystalline behavior.[11] The present work mainly focuses on hitherto unreported photoluminescent zinc(II) complexes with a phenylenediamine spacer. Quite surprisingly only by creating a minor modification (absence of methyl group) at the central aromatic spacer, the molecules were found to exhibit a rare nonconventional though not unprecedented[12] columnar primitive rectangular (P_{222}) to monoclinic oblique P_{112} lattice phase crossover, the latter being stable down to room temperature.

Results and Discussion

Synthesis and Chracterisation

Synthesis of the complexes were carried out following a procedure (Scheme 1) similar to that reported for related zinc complexes.[9e] The ligands ({L = N,N'-bis[4′-(n-alkoxy)salicylidene]-1,2-phenylenediamine}, hereafter abbreviated as n-opd, where n indicates the number of carbon

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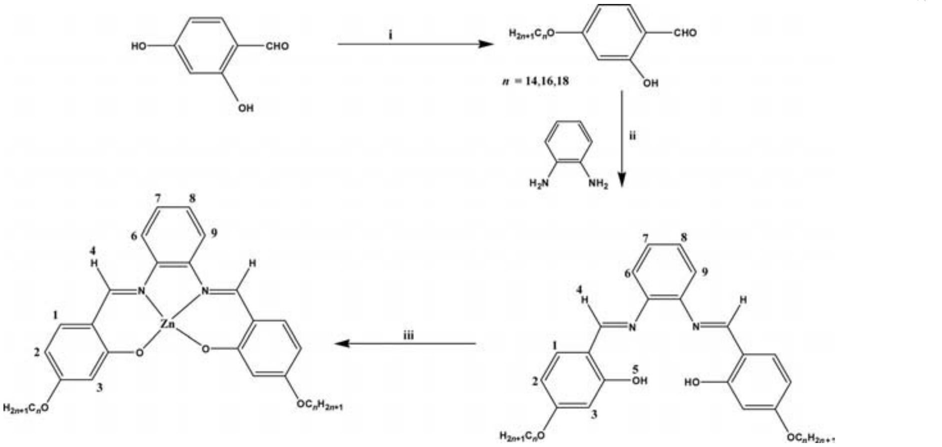
[a] Department of chemistry, Assam University,
Silchar 788011, Assam, India
E-mail: crbhattacharjee@rediffmail.com
[b] Centre for Soft Matter Research,
Jalahalli, Bangalore 560013, India



Scheme 1. i. $C_nH_{2n+1}Br$, $KHCO_3$, KI, dry acetone, Δ, 40 h, and ii. glacial AcOH, absolute EtOH Δ, 4 h iii. $Zn(OAc)_2·2H_2O$, MeOH, TEA. Δ, 1 h.

atoms in alkoxy chains, n = 14, 16, 18 and opd = 1,2-phenylenediamine) and the mononuclear zinc(II) complexes (Zn-nopd). Chemical structures were ascertained by ^1H NMR, FAB mass, IR, UV/Vis, and elemental analysis. The IR spectra of the ligands (n-opd) exhibit a broad band at ca. 3432 cm^{-1} attributed to the phenolic OH group. The C=N stretching vibrations of the ligands are located in the region of 1634–1625 cm^{-1}. Upon complexation the shift of the ν_{CN} vibrational stretching frequency at ca. 1625 cm^{-1} to lower wave number ($\Delta\nu \approx 30\ cm^{-1}$) and the absence of the ν_{OH} mode clearly suggest the coordination of the azomethine N and phenolate oxygen to the metal. The ^1H NMR spectra of the metal complex show no signal for a phenolic OH proton and an upfield shift in the peak positions of the –N=CH signal. This finding is in line with bonds between the phenolate anions and the azomethine nitrogen atoms of the ligand and the metal ion.[13]

Photophysical Properties

The absorption spectra (Figure 1) of the compounds were recorded from CH_2Cl_2 solutions (10^{-4} M) at room temperature (Table 1). The ligands n-opd show two absorption bands centered at 290 and 331 nm, attributed to π-π* transition localized on the aromatic rings and a shoulder at ca. 363 nm due to π-π* transition of the C=N fragment. Upon complexation these bands are red-shifted to 315 nm, 376 nm and 425 nm. Photoluminescence study of the zinc(II) complexes were made at room temperature in CH_2Cl_2 solution and also in the solid state (Figure 2). The complexes exhibit green luminescence at ca. 507–516 nm with

Table 1. UV/Vis and photoluminescence data of ligands (n-opd) and Zn-nopd complexes.

	π→π* (ε, L mol^{-1} cm^{-1})	π→π* (ε, L mol^{-1} cm^{-1})	PL[a] (solution)	PL[a] (solid)
18opd	290 (11300) 331 (14200)	363 (9800)	–	
Zn-18opd	315 (11200) 376 (14100)	425 (8100)	507	516
16opd	291 (11400) 333 (14400)	364 (9100)	–	
Zn-16opd	316 (11400) 374 (14400)	424 (8200)	506	515
14opd	289 (11200) 331 (14600)	364 (9300)	–	
Zn-14opd	314 (11300) 373 (11500)	425 (8400)	509	518

[a] Photoluminescence data of Zn-nopd.

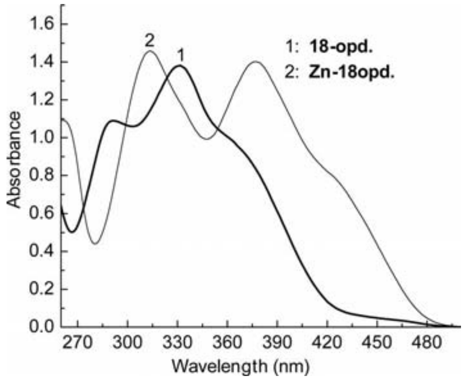


Figure 1. Absorption spectra of 18-opd and Zn-18opd in dichloromethane.

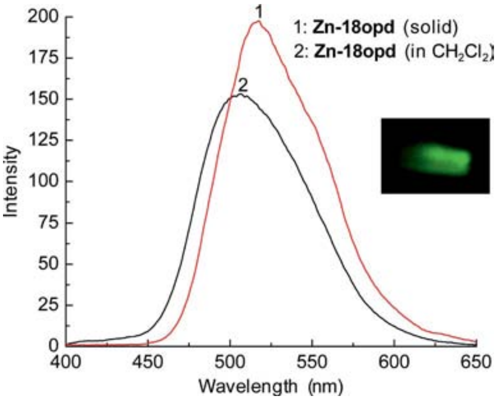


Figure 2. Emission spectra of Zn-18opd in solid state (1) and solution (2).

high emission quantum yield of about 22% (solution), and ca. 9% (solid) under UV irradiation (360 nm). The fluorescence emission originates from a π,π* ligand-centered transition. The role of the central atom is to provide stability to the ligand.[1a,14–16] The emission wavelength in the solid state is red-shifted by ca. 10 nm compared to the solution. Such a shift is due to the high degree of intermolecular aromatic interaction and a larger electronic delocalization in the solid state which leads to a lowering of energy of the electronic states.[1a,9d,17] The lowest-excited singlet-state energy was experimentally calculated to be ca. 260 kJ mol^{-1} on the basis of overlap of the fluorescence emission (508 nm) with the lowest energy UV/Vis absorption band (425 nm); see Figure 3.

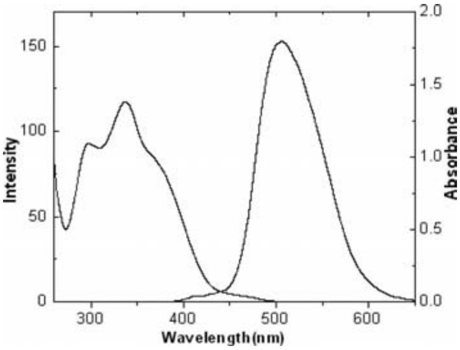


Figure 3. Overlap of UV/Vis and fluorescence spectra of Zn-18opd.

Mesomorphism

The mesomorphic behavior was studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The free ligands with two alkoxy arms, n = 14, 16, 18 and a central aromatic core were found to be nonmesogenic. The probable reason for the lack of mesogenicity may be due to greater conformational flexibility of the ligands. However, on complexation this flexibility is reduced and columnar mesomorphism is induced. In POM, the compound Zn-18opd melts directly to the isotropic liquid. On slow cooling, a fan-like texture (Figure 4) was observed at 176 °C which remained stable until ambient temperature. When mechanically sheared, a textural change (Figure 5) was noticed. The DSC traces (Table 1) of Zn-18opd revealed a single peak in heating due apparently to crystal-isotropic and at 176 °C in cooling cycle (Figure 6) for isotropic-columnar transition. A very weak transition observed at 52.1 °C (ΔH = 0.98 kJ mol^{-1}) was attributed to another mesophase transition (Table 2). The clearing temperature decreases with increasing carbon length of side chains. The isotropic to columnar (I-Col) phase transition temperatures also exhibited a similar dependence on alkoxy

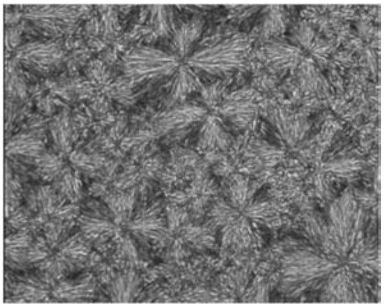


Figure 4. Optical micrograph of Zn-18opd at 176 °C.

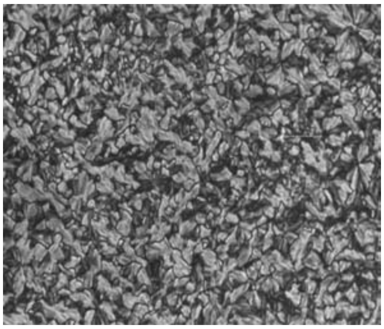


Figure 5. Optical micrograph of Zn-18opd on mechanical shearing.

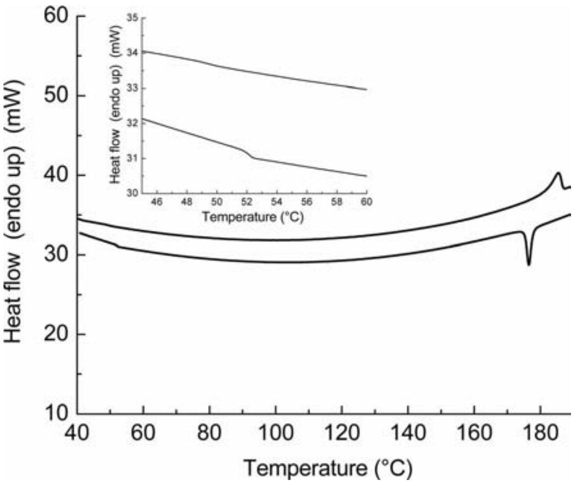


Figure 6. DSC thermogram of Zn-18opd.

Table 2. DSC data of the Zn-nopd complexes.

	T [°C][a]	Transition[b]	ΔH [kJ mol^{-1}]
Zn-18opd	187.4	Cr-I	13.5
	176.8	I-Col$_r$	11.8
	52.1	Col$_r$-Col$_o$	0.98
Zn-16opd	190.9	Cr-I	12.7
	178.3	I-Col$_r$	11.6
	54.1	Col$_r$-Col$_o$	0.95
Zn-14opd	194.7	Cr-I	14.6
	181.5	I-Col$_r$	14.0
	56.1	Col$_r$-Col$_o$	0.96

[a] Temperature data as onset peak. [b] Cr: crystal, Col$_r$: columnar rectangular, Col$_o$: columnar oblique.

chain length. A somewhat irregular trend in the enthalpies of columnar-isotropic phase transition as a function chain length is not readily discernible at this point.

XRD Study

To elucidate the symmetry of the mesophase, powder-XRD investigation was carried out at 165 and 50 °C. At both temperatures, the diffractograms (see Figures 7 and 8) exhibit several peaks in the low-angle region. In the wide-angle region, two intensity maxima are observed, one ($2\theta_{max} \approx 20°$) very broad and diffuse compared to the other ($2\theta_{max} \approx 25°$). Qualitatively these features are compatible with columnar phase structures. The 20° diffuse reflection corresponding to a spacing of ca. 0.36 nm can be attributed to the average distance between the liquid-like (molten) aliphatic side chains. The relatively sharper one seen at higher 2θ values and well separated from the broad one is due to the stacking of the molecular cores one on top of another. As this is a diffuse peak it suggests that the stacking of the discs within each column is correlated over short distances only. This correlation length was determined by fitting the data to a Lorentzian expression yielding a value of 5.6 nm. Since this is a liquid-like correlation, Scherrer's formula was not employed. Considering the spacing of 0.36 nm corresponding to this reflection, also obtained from the fit, we see that about 16 molecules are correlated within the column, a large value indeed. At 50 °C, this number increases slightly to 18 molecules as revealed from the low-angle data (Table 3). At 165 °C the lattice parameters are a = 3.28 nm and b = 1.6 nm. On the other hand, at 50 °C, three different fundamental reflections of equal intensity were observed corresponding to the (20), (11) and $(1\bar{1})$ reflections which could be better fitted to a monoclinic oblique lattice P_{112}, with a = 3.12 nm, b = 1.71 nm and γ = 91°.[9c] Since the lattice constant (a) in both cases is larger than the radius of the half disc, the two half disc molecules organise themselves in an anti-parallel fashion, head-to-head, to form a discoid shell (Figure 9). A similar type of observation was reported earlier.[5a] At 165 °C, the spacings could be indexed to a primitive rectangular lattice P_{222}, considering the column axis to be the c axis, and ab forming the lattice plane (Figure 10, a). These axes are oriented alternately along two different directions perpendicular to the columnar axis (herringbone packing of elliptical columns).[18] In the Col_o phase, the columnar axis is perpendicular to the normal of the lattice plane (Figure 10, b), and the projection of the hard cores onto the lattice plane gives rise to a 2D lattice parallelogram which corresponds to the arrangement of the columns, and the elementary cell is monoclinic.[9c] It is interesting to note that the presence of a methyl

Table 3. XRD data of Zn-18opd at 165 °C and 50 °C.

	T = 165 °C d [nm]	(hk)	T = 50 °C d [nm]	(hk)
1	3.28	(10)	3.12	(10)
2	1.64	(20)	1.57	(20)
3	1.58	(01)	1.46	$(1\bar{1})$
4	1.43	(11)	1.37	(11)
5	1.14	(21)	1.17	$(2\bar{1})$
6	1.09	(30)	1.04	(30)
7	0.91	(31)	0.91	$(3\bar{1})$
8	0.88		0.85	(31)
9	0.82	(40)	0.78	(40)
10	0.45	–	0.45	–
11	0.36	–	0.36	–
a = 3.28 nm, b = 1.60 nm, c = 0.36 nm			a = 3.12 nm, b = 1.71 nm, c = 0.36 nm, γ = 91°	

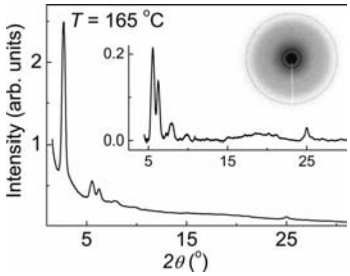


Figure 7. X-ray diffraction pattern of Zn-18opd at 165 °C.

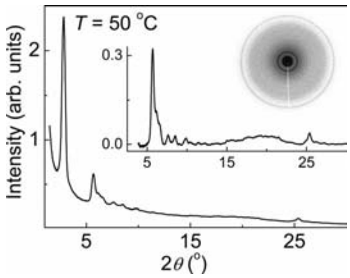


Figure 8. X-ray diffraction pattern of Zn-18opd at 50 °C.

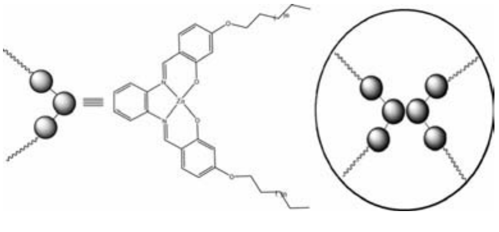


Figure 9. Antiparallel dimeric arrangement of molecules.

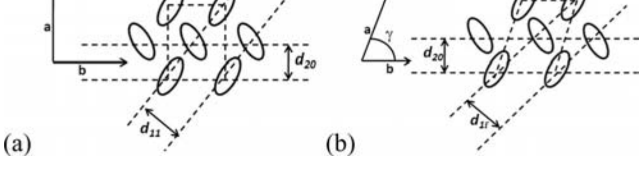


Figure 10. Plane views of the 2D lattices in (a) primitive rectangular and (b) monoclinic oblique.

group on the central aromatic ring in an analogous complex alters the type of mesophase drastically, resulting in a hexagonal (Col_h) lattice.[9e] Though this structural change increases the area only slightly (≈ 8 %). The molecular volume and various lattice parameters were calculated by using standard formulae.

Mesophase parameters, for rectangular primitive lattice molecular volume V_m is calculated using the formula: $V_m = M/\lambda\rho N_A$ where M is the molecular weight of the compound, N_A is the Avogadro number, ρ is the volume mass (≈ 1 g cm^{-3}), and $\lambda(T)$ is a temperature correction coefficient at the temperature of the experiment (T). $\lambda = V_{CH2}(T^0)/V_{CH2}(T)$, $T^0 = 25$ °C. $V_{CH2}(T) = 26.5616 + 0.02023 \cdot T$, h is the intermolecular repeating distance deduced directly from the measured molecular volume and the lattice area according to $h = V_m/S$. For the Col_r phase, the lattice parameters a and b are deduced from the mathematical expression: $a = 2d_{20}$ and $1/dhk = \sqrt{h^2/a^2 + k^2/b^2}$, where a, b are the parameters of the Col_r phase, S is the lattice area, S_{col} is the columnar cross-section ($S = ab$, $S_{col} = S/2$). $V_m = 181.34$ nm^3, $S = 52.48$ nm^2, $S_{col} = S/2 = 26.24$ nm^2, $h = 181.34/52.48 = 3.4$. For columnar oblique lattice, the unit cell volume was calculated from $V_{cell} = ab(\sin\gamma)h_{eff}$. Effective height ($h_{eff}$) of the molecule can be calculated as, $h_{eff} = 0.45/\mathrm{Sin}\,90^0$, 0.45 nm is the average distance between the molecules as obtained from the position of the diffuse wide angle scattering in the X-ray diffraction pattern. $V_{cell} = 24.00$ nm^3, $V_m = M/\lambda\rho N_A = 163.21$ nm^3, $S = ab\sin\gamma = 53.35$ nm^2.

DFT Study

From DFT calculation (Table 4), the length in fully extended form and bent angle of the molecule are found to be ca. 44 Å and 98°, respectively. Some selective geometric parameters of the optimized Zn^{II} complex were evaluated by DFT at BLYP/DNP level.[19] 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 ($\Delta E = 2.1$ eV), respectively. Based on spectral and DFT study, four-coordinated distorted square-planar geometry has been conjectured (Figure 11). With a short spacer like phenylenediamine, a square-planar geometry appears to be more plausible while a tetrahedral geometry is favoured for a long flexible spacer like $–(CH_2)_n–$.[1a,9e]

Table 4. Selected bond lengths and bond angles of Zn-18opd.

	Zn-18opd
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

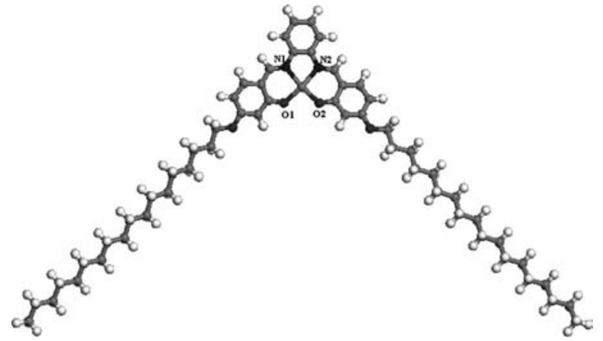


Figure 11. Optimised structure of Zn-opd.

Conclusions

A new series of novel nondiscoid mononuclear zinc(II) complexes of a tetradentate [N_2O_2] donor Schiff base containing long alkoxy substituents in 4-position of the terminal aromatic ring and a central aromatic spacer group have been successfully synthesized. The ligands are nonmesogenic but their complexes exhibit columnar mesomorphism (Col_r and Col_o) and is stable down to room temperature. Variable-temperature XRD study showed that at 165 °C the molecules are organised in a rectangular primitive lattice, whereas at 50 °C, they are self-assembled in a monoclinic oblique lattice. All the complexes are found to exhibit intense fluorescence.

Experimental Section

General: Alkoxysalicyldehyde derivatives were prepared according to the following procedure. 2,4-Dihydroxybenzaldehyde (10 mL, 1.38 g), $KHCO_3$ (10 mL, 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 aqueous 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. An ethanolic solution of 2-hydroxy-4-(*n*-alkoxy)salicylaldehyde (1 mmol) was added to an ethanolic solution of 1,2-phenylenediamine (0.5 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-(*n*-alkoxy)salicylidene]-1,2-phenylenediamine. The compound was collected by filtration and recrystallised from absolute ethanol to obtain a pure compound. The ligand 18-opd (0.075 g, 0.1 mmol) or 16-opd (0.062 g, 0.1 mmol) or 14-opd (0.060 g, 0.01 mmol) was dissolved in minimum volume of absolute ethanol. To this, an equimolar amount of zinc acetate $Zn(OAc)_2 \cdot 2H_2O$ (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 recrystallized from chloroform/ethanol (1:1). The C, H, N analyses were carried out by using a PE2400 elemental analyzer. The ^{1}H-NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer in $CDCl_3$ (chemical shift in δ) solution with TMS as internal standard. UV–vis absorption spectra of the compounds in CH_2Cl_2

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 recorded on a Perkin–Elmer L 120–000A spectrometer on KBr disc. The optical textures of the different phase of the compounds were studied by 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 behaviour 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. The XRD studies were carried out using an image plate detector (Mac Science, Japan) equipped with double mirror focusing optics, with the sample contained in a Lindmann capillary tube. Quantum chemical calculation on Zn-18opd was carried out using density functional theory (DFT) as implemented in DMol3 package.

Synthesis of *n*-Alkoxysalicyldehyde ($n = 14, 16, 18$): Alkoxysalicyldehyde derivatives were prepared following the general method reported in the literature.[9e] 2,4-Dihydroxybenzaldehyde (10 mL, 1.38 g), $KHCO_3$ (10 mL, 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.

Synthesis of the Ligands: Synthesis of *N*,*N*′-bis[4-(*n*-octadecyloxy)-salicylidene]-1,2-phenylenediamine (18-opd). An ethanolic solution of 2-hydroxy-(4-octadecyloxy)salicylaldehyde (0.39 g, 1 mmol) was added to an ethanolic solution of 1,2-phenylenediamine (0.06 g, 0.5 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-(*n*-alkoxy)salicylidene]-1,2-phenylenediamine. The compound was collected by filtration and recrystallised from absolute ethanol to obtain a pure compound; yield 0.28 g, 75%. FAB mass (*m*/*z*, fragment): *m*/*z* calcd. 852.7; found 858 $[M + H^+]$. $C_{56}H_{88}N_2O_4$ (852.7): calcd. C 78.8, H 10.3, N 3.2; found C 78.1, H 10.2, N 3.1. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 13.01$ (s, 1 H, H^5), 8.77 (s, 1 H, H^4), 7.74 (d, $J = 8.5$ Hz, H^9), 7.20 (d, 2 H, H^6), 7.12 (t, $J = 8.4$ Hz, 2 H, H^1), 7.13 (dd, $J = 2.3$, $J = 9.1$ Hz, 2 H, H^8), 6.61 (d, $J = 2.4$ Hz, 2 H, H^3), 6.49 (dd, $J = 2.4$, $J = 8.29$ Hz, 2 H, H^2), 3.97 (t, $J = 6.8$ Hz, 2 H, $-OCH_2$), 0.91 (t, $J = 6.8$ Hz, 6 H, CH_3), 0.87 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 3510$ (νOH), 2922 [ν_{as}(C–H),CH_3], 2920 [ν_{as}(C–H), CH_2], 2871 [ν_s(C–H),CH_3], 2849 [ν_{as}(C–H), CH_2], 1627 (νC=N), 1295 (νC–O) cm^{-1}.

***N*,*N*′-Bis[4-(4′-*n*-hexadecyloxy)salicylidene]-1,2-phenylenediamine (16-opd):** FAB mass (*m*/*z*, fragment): *m*/*z*: calcd. 796.6; found 797 $[M + H^+]$. $C_{52}H_{80}N_2O_4$ (796.7): calcd. C 78.3, H 10.1, N 3.5; found C 78.1, H 10.2, N 3.1. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 13.01$ (s, 1 H, H^5), 8.74 (s, 1 H, H^4), 7.72 (d, $J = 8.5$ Hz, H^9), 7.21 (d, 2 H, H^6), 7.16 (t, $J = 8.4$ Hz, 2 H, H^1), 7.15 (dd, $J = 2.3$, $J = 9.2$ Hz, 2 H, H^8), 6.61 (d, $J = 2.4$ Hz, 2 H, H^3), 6.48 (dd, $J = 2.4$, $J = 8.2$ Hz, 2 H, H^2), 3.96 (t, $J = 6.7$ Hz, 2 H, $-OCH_2$), 0.94 (t, $J = 6.7$ Hz, 6 H, CH_3), 0.87 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 3510$ (νOH), 2922 [ν_{as}(C–H),CH_3], 2920 [ν_{as}(C–H), CH_2], 2871 [νs(C–H),CH_3], 2849 [ν_{as}(C–H), CH_2], 1627 (νC=N), 1295 (νC–O) cm^{-1}.

***N*,*N*′-Bis[4-(4′-*n*-tetradecyloxy)salicylidene]-1,2-phenylenediamine (14-opd):** Yield 0.19 g, 74%. FAB mass (*m*/*z*, fragment): *m*/*z* calcd. 740.5; found 741 $[M + H^+]$. $C_{48}H_{72}N_2O_4$ (740.5): calcd. C 77.7, H 9.7, N 3.7; found C 77.1, H 9.2, N 3.4. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 13.03$ (s, 1 H, H^5), 8.74 (s, 1 H, H^4), 7.73 (d, $J = 8.4$ Hz, H^9), 7.19 (d, 2 H, H^6), 7.11 (t, $J = 8.4$ Hz, 2 H, H^1), 7.10 (dd, $J = 2.31$, $J = 9.0$ Hz, 2 H, H^8), 6.59 (d, $J = 2.4$ Hz, 2 H, H^3), 6.48 (dd, $J = 2.44$, $J = 8.2$ Hz, 2 H, H^2), 3.96 (t, $J = 6.7$ Hz, 2 H, $-OCH_2$), 0.91 (t, $J = 6.8$ Hz, 6 H, CH_3), 0.87 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 3511$ (νOH), 2921 [ν_{as}(C–H),CH_3], 2920 [ν_{as}(C–H), CH_2], 2873 [ν_s(C–H),CH_3], 2839 [ν_{as}(C–H), CH_2], 1637 (νC=N), 1294 (νC–O) cm^{-1}.

Synthesis of Mononuclear Zinc(II) Complexes (Zn-nopd, $n = 14, 16, 18$)

General Procedure: The ligand 18-opd (0.09 g, 0.1 mmol) or 16-opd (0.07 g, 0.1 mmol) or 14-opd(0.060 g, 0.01 mmol) was dissolved in minimum volume of absolute ethanol. To this, an equimolar amount of zinc acetate $Zn(OAc)_2\cdot 2H_2O$ (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 recrystallized from chloroform/ethanol (1:1).

Zn-18opd: Yield 0.08 g (75%). FAB mass (*m*/*z*, fragment): *m*/*z*: calcd. 914.6; found 915 $[M + H^+]$. $C_{56}H_{86}N_2O_4Zn$ (914.6): calcd. C 73.3, H 9.4, N 3.0; found C 73.1, H 9.2, N 3.1. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (s, 1 H, H^4), 7.72 (d, $J = 8.5$ Hz, H^9), 7.21 (d, 2 H, H^6), 7.10 (t, $J = 8.4$ Hz, 2 H, H^1), 7.16 (dd, $J = 2.3$, $J = 9.1$ Hz, 2 H, H^8), 6.61 (d, $J = 2.4$ Hz, 2 H, H^3), 6.49 (dd, $J = 2.4$, $J = 8.2$ Hz, 2 H, H^2), 3.95 (t, $J = 6.8$ Hz, 2 H, $-OCH_2$), 0.91 (t, $J = 6.8$ Hz, 6 H, CH_3), 0.87 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 2922$ [ν_{as}(C–H),CH_3], 2920 [ν_{as}(C–H), CH_2], 2870 [ν_s(C–H),CH_3], 2848 [ν_{as}(C–H), CH_2], 1611 (νC=N) cm^{-1}.

Zn-16opd: Yield 0.07 g, 70%. FAB mass (*m*/*z*, fragment): *m*/*z*: calcd. 858.5; found 859 $[M + H^+]$. $C_{52}H_{78}N_2O_4Zn$ (858.5): calcd. C 72.5, H 9.1, N 3.2; found C 72.4, H 9.0, N 3.0. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (s, 1 H, H^4), 7.72 (d, $J = 8.5$ Hz, H^9), 7.21 (d, 2 H, H^6), 7.11 (t, $J = 8.4$ Hz, 2 H, H^1), 7.16 (dd, $J = 2.33$, $J = 9.1$ Hz, 2 H, H^8), 6.61 (d, $J = 2.4$ Hz, 2 H, H^3), 6.49 (dd, $J = 2.44$, $J = 8.28$ Hz, 2 H, H^2), 3.92 (t, $J = 6.8$ Hz, 2 H, $-OCH_2$), 0.91 (t, $J = 6.8$ Hz, 6 H, CH_3), 0.87 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 2922$ [ν_{as}(C–H),CH_3], 2920 [ν_{as}(C–H), CH_2], 2870 [ν_s(C–H),CH_3], 2848 [ν_{as}(C–H), CH_2], 1613 (νC=N) cm^{-1}.

Zn-14opd: Yield 0.05 g, 74%. FAB mass (*m*/*z*, fragment): *m*/*z*: calcd. 802.5; found 803 $[M + H^+]$. $C_{48}H_{70}N_2O_4Zn$ (802.5): calcd. C 71.6, H 8.7, N 3.4; found C 71.2, H 8.4, N 3.1. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.23$ (s, 1 H, H^4), 7.77 (d, $J = 8.5$ Hz, H^9), 7.25 (d, 2 H, H^6), 7.17 (t, $J = 8.4$ Hz, 2 H, H^1), 7.18 (dd, $J = 2.33$, $J = 9.1$ Hz, 2 H, H^8), 6.64 (d, $J = 2.45$ Hz, 2 H, H^3), 6.42 (dd, $J = 2.4$, $J = 8.2$ Hz, 2 H, H^2), 3.93 (t, $J = 6.5$ Hz, 2 H, $-OCH_2$), 0.90 (t, $J = 6.8$ Hz, 6 H, CH_3), 0.88 (m, $-CH_2$ of methylene proton in side chain) ppm. IR (KBr): $\tilde{\nu}_{max} = 2921$ [ν_{as}(C–H),CH_3], 2922 [ν_{as}(C–H), CH_2], 2870 [ν_s(C–H), CH_3], 2846 [ν_{as}(C–H), CH_2], 1616 (νC=N) cm^{-1}.

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