DOI: 10.1002/ejic.201100679

Photoluminescent Hemidisc-Shaped Liquid Crystalline Nickel(II) Schiff-Base Complexes

Chira R. Bhattacharjee,*[a] Gobinda Das,[a] and Paritosh Mondal[a]

Keywords: Nickel / Metallomesogens / Liquid crystals / Luminescence / Photoluminescence / Density functional calculations

A series of new photoluminescent hemidisc-shaped Ni^{II} Schiff-base complexes has been synthesized. The ligands and their complexes were characterized by FTIR and ^1H and ^{13}C NMR spectroscopy, FAB-MS and elemental analysis. The mesomorphic behaviour of the ligands and their complexes was probed by polarizing optical microscopy and differential scanning calorimetry. The molecular organization in the mesophase was determined by X-ray diffraction techniques. The ligands are nonmesogenic but their complexes exhibited thermally stable rectangular columnar (Col_r) mesophases at about 227 °C. The complexes are blue-light emitters in solution (ca. 434 nm, $\Phi = 19\,\%$) and in the solid state (ca. 469 nm, $\Phi = 7\,\%$) at $\lambda_{ex} = 350$ nm. A DFT study was carried out using DMol3 at the BLYP/DNP level to obtain a stable, optimized structure, which revealed a distorted square-planar geometry for the nickel complexes.

Introduction

Research in the field of metallomesogens has drawn attention in recent years.[1] Mesomorphic behaviour can be induced in nonmesogenic ligands upon coordination to metal ions. Such metallomesogens combine the unique properties of liquid-crystalline anisotropic fluids with the electronic and optical properties of metal complexes. The behaviour of mesogenic molecules depends primarily on molecular shape, which is determined by the anisotropy of the rigid part of the molecule. Molecular shape is the dominant factor that determines the organization of molecules into a liquid crystalline phase. Mesomorphic behaviour can be tuned by the choice of metal ions and position of substituents on aromatic rings. Even minor changes within the mesogenic core can sometimes lead to major differences in molecular organization and liquid crystalline properties.[2] Salen-based metallomesogens are one of the major thrust areas of liquid crystals.[3] Salen-type ligands enhance the performance of metals in a variety of catalytic transformations.[4] Such ligands have been used for the design of switchable nonlinear optical materials.[5] Because of their unusual geometries, large birefringence, polarizability and paramagnetism, which lead to unique functional behaviour, metallomesogens that incorporate transition metal ions are the focus of current research.[6] In particular, materials that exhibit light emission or charge transport abilities are of immense significance due to their potential applications in areas such as displays, solar cells, active components for imaging and data treatment and storage.[7] Compounds that combine both luminescence and liquid crystallinity are one of the fastest growing fields for applications in light emitting devices, information storage, sensors and enhanced contrast displays.[8] Luminescent liquid crystals have the potential for use in organic light-emitting diodes (OLEDs).[1b,9] Phase behaviour is a function of molecular chain length, the substituent on the ligand, spacer groups and nature of the metal ions. Devising an appropriate strategy for the planned synthesis of such materials is a challenging task.

Co^{II}, Ni^{II}, Cu^{II} and $V^{IV}O$ salen complexes with 5-substituted terminal alkoxy or alkyl chains, which exhibit smectic mesomorphism have been well documented.[3a,3c,3l,3m] By coordinating nondiscoid ligands, a molecular shape with a reduced length-to-breadth ratio is formed, which leads to the formation of disc-like metallomesogens.[10] Such structures have a reduced tendency to form calamitic mesophases and favour the formation of columnar mesophases.[10] Compounds that exhibit columnar phases with axially-linked discs are of particular interest as potential 1D photoconductors, semiconductors, OLEDs and photovoltaic cells.[11] Metallomesogens comprising *d*-block elements have received much attention because of their potential applications as 1D magnets that can self-repair defects in their structure, align with very small magnetic fields and be used in magneto-optic data storage devices.[12] Unlike other first row transition metals, examples of liquid crystals that contain nickel(II) ions have been less addressed.[2b,3l,10,13] There has been no systematic investigation of metal–salen complexes that are substituted by two long alkoxy chains at the 4-positions of the aromatic ring. A series of mesogenic salen and salpn complexes that contain 4-substituted alkoxy chains on the peripheral aromatic rings have been report-

---

[a] Department of chemistry, Assam University,
Silchar 788011, Assam, India
E-mail: crbhattacharjee@rediffmail.com

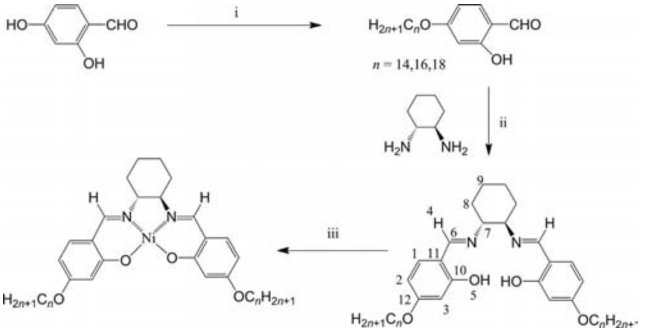
ed.[1a,3j,3k,3l] Complexes with shorter alkoxy substituents and similar spacer groups lack liquid crystalline behaviour.[14] We have recently reported a series of 4-substituted zinc(II), oxovanadium(IV) and copper(II) complexes that comprise a cyclohexane/phenylenediamine spacer, which were shown to exhibit different types of columnar phases.[15]

Here, we describe the synthesis, photophysical and mesomorphic properties of hemidisc-shaped nickel(II) complexes, which exhibit blue-light emission. Although the ligands are nonmesogenic, their complexes showed thermally stable, rectangular columnar mesomorphism (Col$_r$).

Results and Discussion

Synthesis and Characterization

Synthesis of the complexes was carried out following a procedure similar to that reported for related complexes (Scheme 1).[15a,15b] The ligands, *N*,*N′*-bis[4-(4′-*n*-alkoxy)-salicylidene]1,2-cyclohexanediamine, are abbreviated as *n*dch, where *n* indicates the number of carbon atoms in the alkoxy chains (n = 14, 16, 18), and the nickel(II) complexes are abbreviated as Ni-*n*dch. The complexes were isolated as light brown solids in good yields and were readily recrystallized from methanol/CH_2Cl_2. The compounds were characterized by ^1H and ^{13}C NMR, FTIR and UV/Vis spectroscopy and elemental analysis. The IR study showed the shift of the $\nu_{C=N}$ vibrational stretching frequency at ca. 1625 cm^{-1} to a lower wavenumber ($\Delta\nu \approx 30$ cm^{-1}) and the absence of the ν_{OH} mode of the phenolate group upon chelation, which suggested the coordination of the azomethine N and phenolate O atoms to the metal. The $\nu_{C=N}$ stretching frequency is independent of the length of the alkoxy side chain in the ligands and their complexes. The FAB-MS of the compounds matched well to their formula weights. The ^1H NMR spectra of the ligands showed two characteristic signals at 13.4–13.8 ppm, which corresponds to the OH proton, and 8.5 ppm, which corresponds to the imine proton. Moreover upon complexation, the proton signal corresponding to the OH group of the free ligand disappears and the imine proton experiences a large shielding, which further attests to the coordination of the azomethine N atom.



Scheme 1. i) $C_nH_{2n+1}Br$, $KHCO_3$, KI, dry acetone, Δ, 40 h. ii) Glacial AcOH, absolute EtOH, Δ, 4 h. iii) $Ni(OAc)_2\cdot 4H_2O$, MeOH, Et_3N, Δ, 1 h.

Photophysical Properties

The absorption spectra of the compounds were recorded in CH_2Cl_2 (10^{-4} M) at room temperature (Figure 1 and Table 1). Ligand 18dch showed two strong bands at 278 and 309 nm, which are attributed to the π–π* transitions of the aromatic ring, and a low intensity band at 389 nm corresponds to the n–π* excitation of the imine nitrogen lone pair to the π* orbital of the C=N fragment. The complexes showed two redshifted bands at 297 and 340 nm, which are attributed to the metal-perturbed ligand-centred transitions. The ligand field excited states could not be located possibly because of the high energy of the absorption. Such excited states might be involved in radiative energy dissipation. The complexes also displayed a broad band at 426 nm, which is attributed to the ligand-to-metal charge transfer (LMCT) transition (N→Ni $^{2+}$).

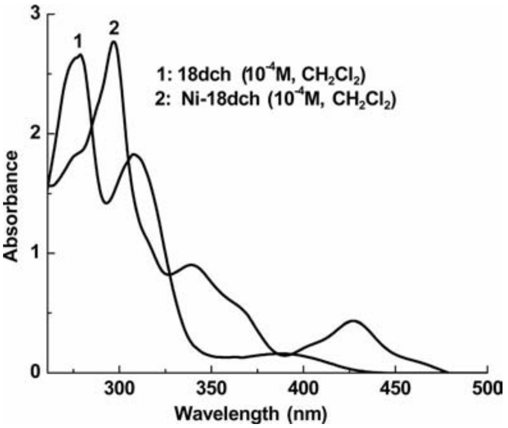


Figure 1. UV/Vis spectra of 18dch and Ni-18dch.

Table 1. UV/Vis and photoluminescence data (λ, nm; ε, l mol^{-1} cm^{-1}) for *n*dch and Ni-*n*dch.

Compd.	π→π* λ (ε)	n→π* λ (ε)	LMCT λ (ε)	PL[a] (solution) [nm]	PL[a] (solid) [nm]
18dch	278 (26000) 308 (18200)	389 (1600)	–	–	–
Ni-18dch	297 (27700) 339 (8700)	–	416 (4200)	436	469
16dch	277 (25000) 306 (18100)	388 (1400)	–	–	–
Ni-16dch	296 (27500) 341 (8800)	–	418 (4100)	434	472
14dch	277 (25000) 308 (18200)	401 (1300)	–	–	–
Ni-14dch	299 (26500) 344 (7900)	–	421 (3900)	438	476

[a] Photoluminescent emission for Ni-*n*dch.

The photoluminescence study of Ni-*n*dch was carried out at room temperature in CH_2Cl_2 solution and in the solid state (Figure 2 and Table 1). Ni-18dch emits blue light in solution and the solid state at 434 (Φ = 19%) and 469 nm (Φ = 7%), respectively, when excited at 350 nm. The emission spectra of the complexes originate from π–π* or LMCT transitions.[16a,16b] The solid state emission spectra of the complexes were recorded by placing a uniform layer of powder between two quartz plates. In the solid state, free rotation of the flexible ligand is restricted and energy dissipation through nonradiative channels is reduced, which causes enhancement of the emission wavelength. Moreover, in the solid state, larger electronic delocalization leads to a decrease in the energy of the electronic states.[1a,16c–16e]

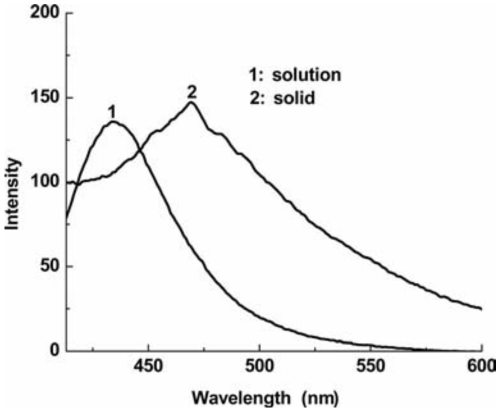


Figure 2. Emission spectra of Ni-18dch in CH_2Cl_2 (1) and in the solid state (2).

Mesomorphic Behaviour

The mesomorphic behaviour of the compounds was investigated by polarizing optical microscopy and differential scanning calorimetry (DSC). The thermal data are summarized in Table 2. The ligands did not show any mesomorphism because of their small molecular anisotropy. However, on coordination mesomorphism was induced, which reflects the conformational rigidification of the ligand. The samples became isotropic liquids at 233 °C. On cooling from the isotropic liquid, a typical broken fan-shaped texture (Figure 3) with several homeotropic regions developed at 227 °C, which is characteristic of the columnar phase, and solidification occurred at 65 °C. The DSC profile for multifarious Ni-18dch (Figure 4) shows two transitions in the heating and two in the cooling cycles. The transition at 227 °C (ΔH = 30.1 kJ mol^{-1}) is due to the I-Col mesophase transition. The enthalpy values for the I-Col phase transition are quite high, which was also noted for some related copper complexes.[15d,15e] Interestingly, the mesophase stabilities of these materials exist over wide temperature ranges. The reversibility of the thermal behaviour was established by DSC on subsequent heating and cooling runs. Notably, related hemidisc-shaped $V^{IV}O$ and Cu^{II} complexes with similar spacer groups show Col_{rp} and Col_r mesophases, respectively.[15d,15e]

Table 2. DSC data for Ni-*n*dch (second run).

Compounds	T[a] [°C]	Transition[b]	ΔH [kJ mol^{-1}]
Ni-18dch	110.8 (heating)	Cr-Col_r	50
	233.6 (heating)	Col_r-I	30.7
	227 (cooling)	I-Col_r	30.1
	65.9 (cooling)	Col_r-Cr	14.1
Ni-16dch	114.3 (heating)	Cr-Col_r	51.1
	237.5 (heating)	Col_r-I	34.5
	236.4 (cooling)	I-Col_r	34.2
	68 (cooling)	Col_r-Cr	12.9
Ni-14dch	117.7 (heating)	Cr-Col_r	53.4
	239.4 (heating)	Col_r-I	32.3
	238.7 (cooling)	I-Col_r	32.1
	64.3 (cooling)	Col_r-Cr	13.7

[a] Temperature at onset of peak. [b] Cr: crystal, Col_r: columnar rectangular.

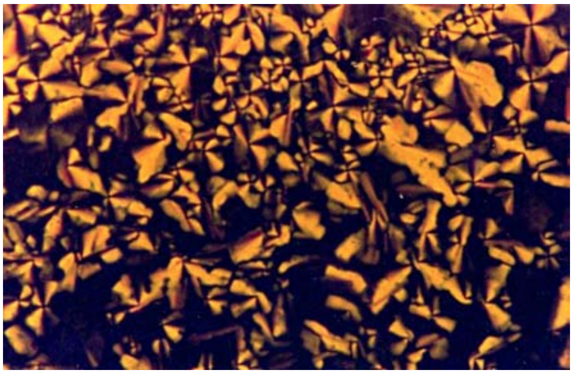


Figure 3. Optical micrograph of Ni-18dch at 227 °C.

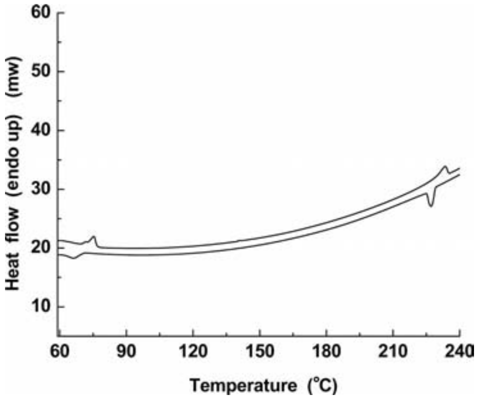


Figure 4. DSC thermogram of Ni-18dch.

XRD Study

The mesophase symmetry for Ni-18dch was examined by X-ray diffraction at 225 °C (Figure 5). In the low angle region, two fundamental, sharp reflections were indexed as (20) and (11), which are characteristic of a 2D rectangular lattice (Table 3). Three diffuse reflections were observed in the wide angle region. The broad reflection at 4.8 Å corresponds to the liquid-like nature of the molten alkyl chains. The sharper reflection at about 3.7 Å, which is well separated from the broad peak, is due to the stacking of the molecular cores on top of one another.[1b,7b] The presence of another weak and somewhat broad halo at 7.4 Å suggests the dimeric interaction of the molecules along the column (Figure 6). The absence of *hk* pairs with $h + k = 2n + 1$ unequivocally suggest *c2mm* plane group symmetry.[10,15d] The lattice constants of this rectangular phase are a =

39 and b = 16.9 Å. The lattice constant a is approximately twice the estimated radius (22 Å) of the half disc, which suggests that two half discs organize themselves in an antiparallel fashion, back-to-back, to form a discoid shell (Figure 6).[7b,10d] The molecules are stacked into columns (one molecule per columnar slice 3.7 Å thick), which self-assemble to produce a 2D-rectangular lattice (Figure 7).

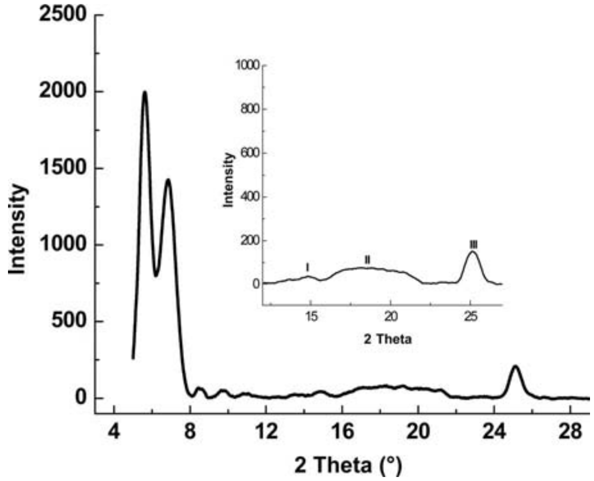


Figure 5. X-ray diffraction pattern of Ni-18dch at 225 °C.

Table 3. XRD data for Ni-18dch at 227 °C.

d_{obs}[a] [Å]	d_{calc}[a] [Å]	hk[b]	Parameters[c]
19.2	19.4	20	Col$_r$ $c2mm$
15.4	15.6	11	a = 39 Å
11.0	11.2	31	b = 16.9 Å
9.6	9.8	40	S = 659.1 Å^2
7.4	–	–	V_m = 1833 Å^3
4.8	–	–	h = 3.7
3.7	–	–	S_{col} = 329.5

[a] d_{obs} and d_{calc} are the experimentally and theoretically measured diffraction spacings at 227 °C, respectively. [b] hk is the indexation of the reflections. [c] Mesophase parameters: 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 Avogadro's number, ρ is the volume mass (ca. 1 g cm^{-3}) and λ is a temperature correction coefficient at the experimental temperature (T), $\lambda = VCH_2(T_0)/VCH_2(T)$ where T_0 = 25 °C and $VCH_2(T) = 26.5616 + 0.02023 \cdot T$. 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 $1/d_{hk} = \sqrt{h^2/a^2 + k^2/b^2}$, where a and b are the parameters of the Col$_r$ phase. S is the lattice area and S_{col} is the columnar cross-section ($S = ab$, $S_{col} = S/2$).

DFT Study

The ground state geometry of Ni-18dch in the gas phase (Figure 8) was fully optimized with restricted BLYP/DNP methods without imposing any symmetry constraint. The BLYP functional was used throughout and comprises a hybrid exchange functional as defined by Becke and the nonlocal Lee–Yang–Parr correlation functional.[17] The basis set chosen for this study was DNP, the double-numerical atomic orbitals augmented by polarization functions. All calculations were performed with the DMol3 program package. In our calculations, self-consistent field procedures were performed with a convergence criterion of 2×10^{-5} a.u. on the total energy and 10^{-6} a.u. on electron density. Selected geometric parameters of the optimized complex are shown in Table 4. From the DFT data, the molecular length was found to be 44.04 Å with average Ni–O and Ni–N bond lengths of 1.94 and 1.99 Å, respectively. The average O1–Ni–O2 and N1–Ni–N2 bond angles of 96.50 and 83.40°, respectively, around the Ni atom deviate substantially from

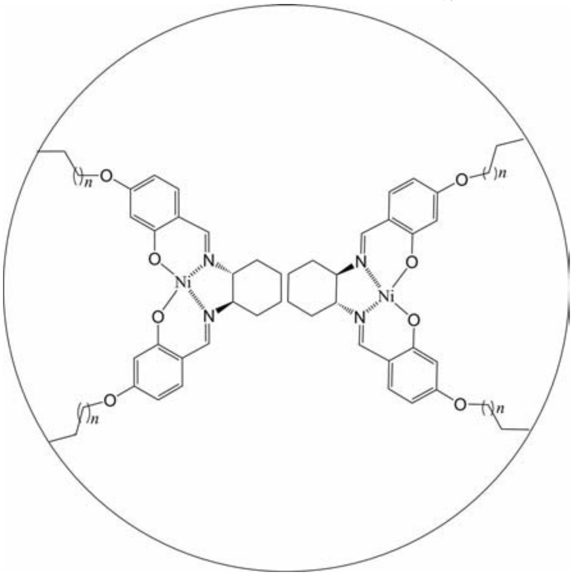


Figure 6. Antiparallel dimeric arrangement of molecules.

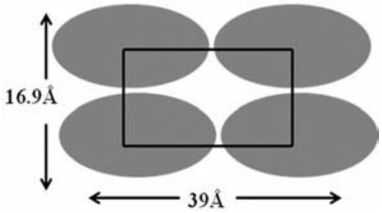


Figure 7. Proposed arrangement of the molecules in the lattice plane conforming to a rectangular lattice.

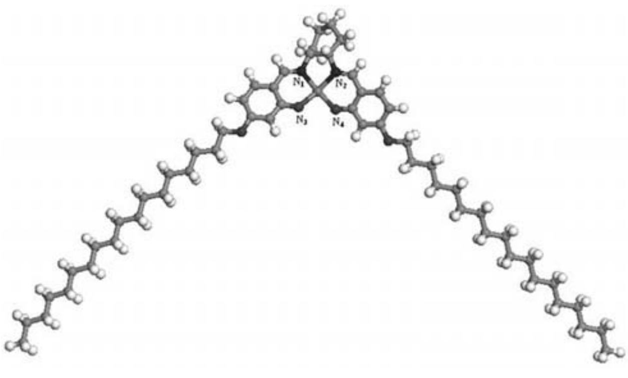


Figure 8. Optimized structure of Ni-18dch.

tetrahedral values and indicate a square-planar geometry. The 3D isosurface plots of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of Ni-18dch are shown in Figures 9 and 10, respectively. The HOMO and LUMO energies of Ni-18dch are calculated to be –3.36 and –2.03 eV, respectively. The HOMO is a π* MO, which is localized on the ligand, and the LUMO is mainly localized on a 3*d* orbital of the nickel(II) centre. The HOMO–LUMO energy gap calculated from the lowest energy UV/Vis band (425 nm) is 2.9 eV, which is substantially higher than that obtained from DFT studies (ΔE = 1.32 eV). A plausible reason for such a deviation is that the ground state of gaseous molecules was considered by the DFT method, whereas extensive intermolecular interactions were likely in the UV/Vis spectroscopic studies in solution phase.

Table 4. Selected bond lengths [Å] and angles [°] of Ni-18dch.

Bond	
Ni–O(1)	1.94
Ni–O(2)	1.93
Ni–N(1)	1.98
Ni–N(2)	1.99
O(1)–Ni–O(2)	96.5
N(1)–Ni–N(2)	83.4
N(1)–Ni–O(2)	164.5
O(1)–Ni–N(1)	92.2
O(2)–Ni–N(2)	92.8
N(2)–Ni–O(1)	158.0

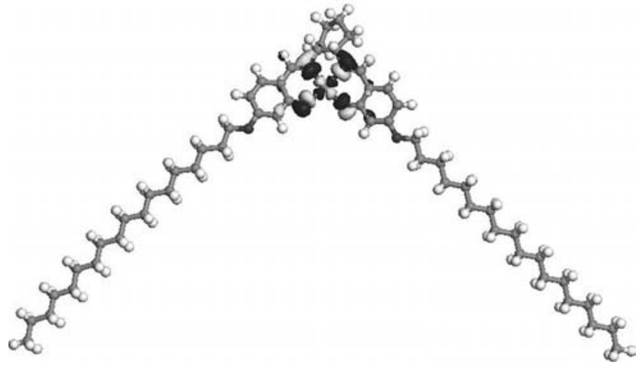


Figure 9. HOMO energy diagram of Ni-18dch.

Figure 10. LUMO energy diagram of Ni-18dch.

Conclusions

A series of hemidisc-shaped nickel(II) complexes of tetradentate [N_2O_2]-donor Schiff bases, which bear long alkoxy substituents in the 4-position of the terminal aromatic ring and a central cyclohexane spacer group, has been successfully synthesized. The ligands are nonmesogenic, but their complexes exhibited columnar $\mathrm{Col_r}$ mesomorphism. A powder XRD study of the complexes confirmed the symmetry of the mesophase to be rectangular in a 2D lattice with *c*2*mm* space group. All the complexes were found to be blue-light emitters.

Experimental Section

Physical Measurements: The C, H and N analyses were carried out with a PE2400 elemental analyzer. The ^{1}H NMR spectra were recorded with a Bruker DPX-400 MHz spectrometer in $CDCl_3$ solution with TMS as an internal standard. ^{13}C NMR spectra were recorded with a JEOL AL300 FT NMR spectrometer. UV/Vis absorption spectra of the compounds in CH_2Cl_2 were recorded with a Shimadzu UV-160PC spectrophotometer. Photoluminescence spectra were recorded with a Shimadzu RF-5301PC spectrophotometer. The fluorescence quantum yield in dichloromethane was determined by a dilution method using 9,10-diphenylanthracene as a standard. IR spectra were recorded with a Perkin–Elmer L 120–000A spectrometer as KBr discs. Mass spectra were recorded with a Jeol SX-102 spectrometer. The optical textures of the different phases of the compounds were studied using a polarizing microscope (Nikon optiphot-2-pol) equipped with a Instec hot and cold stage HCS302 with a STC200 temperature controller of 0.10 °C accuracy. The thermal behaviour of the compounds was studied with a Perkin–Elmer DSC Pyris-1 spectrometer with a heating or cooling rate of 5 °C/min. Variable-temperature powder XRD patterns were recorded with a Bruker D8 Discover instrument using Cu-K_α radiation. Quantum chemical calculations on Ni-18dch were carried out using DFT as implemented in the DMol3 package.

Materials: The materials were procured from Tokyo Kasei and Lancaster Chemicals. All solvents were purified and dried according to standard procedures. Silica (60–120 mesh) from Spectrochem was used for chromatographic separation. Silica gel G (E-Merck, India) was used for TLC.

Synthesis of *n*-Alkoxysalicyldehyde (*n* = 14, 16, 18): The alkoxysalicyldehyde derivatives were prepared according to a reported method.[13d] 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), 1-bromohexadecane (10 mL, 2.8 g) or 1-bromooctadecane (10 mL, 3 g) were mixed in dry acetone (250 mL). The mixture was heated under reflux for 24 h, and filtered while hot to remove any insoluble material. 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 with 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

***N*,*N′*-Bis[4-(4′-*n*-alkoxy)salicylidene]-*trans*-1,2-diaminocyclohexane (*n*dch), *n* = 14, 16, 18. General Procedure:** An ethanolic solution (10 mL) of 2-hydroxy-(4-octadecyloxy)salicylaldehyde (0.394 g, 1 mmol) was added to an ethanolic solution (10 mL) of *trans*-1,2-

diaminocyclohexane (0.05 g, 0.5 mmol). The mixture was heated to reflux for 3 h with a few drops of acetic acid to yield the yellow Schiff base, *N,N′*-bis[4-(4′-*n*-alkoxy)salicylidene]-*trans*-1,2-diaminocyclohexane. The compound was collected by filtration and recrystallized from absolute ethanol.

***N,N′*–Bis[4-(4′-octadecyloxy)salicylidene]-*trans*-1,2-diaminocyclohexane (18dch):** Yield 0.33 g (75%); m.p. 115 °C. FAB-MS: *m*/*z* = 859 [M + H]$^+$. $C_{56}H_{94}N_2O_4$ (858.7): calcd. C 78.2, H 10.0, N 3.2; found C 78.1, H 10.2, N 3.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.40 (s, 1 H, ph-OH), 8.04 (s, 1 H, N=CH), 7.04 (dd, J = 1.5, J = 8.2 Hz, 1 H, H^1), 6.37 (d, J = 6.1 Hz, 1 H, H^2), 6.30 (s, 1 H, H^3), 3.94 (q, J = 4 Hz, 8 H, CH_2CH_3), 3.20 (t, J = 5.6 Hz, 2 H, OCH_2), 1.80–1.95 (m, 4 H, cyclohexyl), 1.63 (m, 2 H, cyclohexyl), 1.40 (m, 2 H, cyclohexyl), 0.87 (t, J = 6.8 Hz, 6 H, CH_3), 0.84 (m, CH_2 in side chain) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$, 25 °C): δ = 130.06 (C1), 106.31 (C2), 102.11 (C3), 160.30 (C6), 70.97 (C7), 28.81 (C8), 23.01 (C9), 161.62 (C10), 115.64 (C11), 159.73 (C12) ppm. IR (KBr): $\tilde{\nu}$ = 3445 [br, ν(OH)] 1622 [s, ν(C=N)], 1143 [s, ν(C–O)] cm^{-1}.

***N,N′*–Bis[4-(4′-hexadecyloxy)salicylidene]-*trans*-1,2-diaminocyclohexane (16dch):** Yield 0.31 g (76%); m.p. 118 °C. FAB-MS: *m*/*z* = 803 [M + H]$^+$. $C_{52}H_{86}N_2O_4$ (802.6): calcd. C 77.7, H 10.7, N 3.4; found C 77.9, H 10.6, N 3.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.41 (s, 1 H, ph-OH), 8.14 (s, 1 H, N=CH), 7.02 (dd, J = 1.5, J = 8.2 Hz, 1 H, H^1), 6.33 (d, J = 6.0 Hz, 1 H, H^2), 6.31 (s, 1 H, H^3), 3.90 (q, J = 4 Hz, 8 H, CH_2CH_3), 3.22 (t, J = 5.4 Hz, 2 H, OCH_2), 1.82–1.91 (m, 4 H, cyclohexyl), 1.61 (m, 2 H, cyclohexyl), 1.41 (m, 2 H, cyclohexyl), 0.89 (t, J = 6.7 Hz, 6H, CH_3), 0.84 (m, CH_2 in side chain) ppm. IR (KBr): $\tilde{\nu}$ = 3441 [br, ν(OH)], 1627 [s, ν(C=N)], 1141 [s, ν(C–O)] cm^{-1}.

***N,N′*–Bis[4-(4′-tetradecyloxy)salicylidene]-*trans*-1,2-diaminocyclohexane (14dch):** Yield 0.26 g (77%); m.p. 121 °C. FAB-MS: *m*/*z* = 747 [M + H]$^+$. $C_{48}H_{78}N_2O_4$ (746.6): calcd. C 77.1, H 10.5, N 3.7; found C 77.1, H 10.4, N 3.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.41 (s, 1 H, ph-OH), 8.02 (s, 1 H, N=CH), 7.01 (dd, J = 1.5, J = 8.2 Hz, 1 H, H^1), 6.35 (d, J = 6.0 Hz, 1 H, H^2), 6.28 (s, 1 H, H^3), 3.88 (q, J = 4 Hz, 8 H, CH_2CH_3), 3.23 (t, J = 5.4 Hz, 2 H, OCH_2), 1.79–1.93 (m, 4 H, cyclohexyl), 1.66 (m, 2 H, cyclohexyl), 1.39 (m, 2 H, cyclohexyl), 0.91 (t, J = 6.7 Hz, 6H, CH_3), 0.88 (m, CH_2 in side chain) ppm. IR (KBr): $\tilde{\nu}$ = 3434 [br, ν(OH)], 1625 [s, ν(C=N)], 1143 [s, ν(C–O)] cm^{-1}.

Synthesis of Nickel(II) Complexes (Ni-*n*dch): General procedure: Ligand 18dch (0.85 g, 1 mmol), 16dch (0.80 g, 1 mmol) or 14dch (0.74 g, 1 mmol) was dissolved in the minimum volume of absolute ethanol. $Ni(OAc)_2{\cdot}4H_2O$ (0.02 g, 0.1 mmol) in methanol was then added slowly, and the mixture was stirred for 2 h at room temperature. The brown solid was collected by filtration, washed with diethyl ether and recrystallized from chloroform/ethanol (1:1).

Ni-18dch: Yield 0.67 g (78%). $C_{56}H_{92}N_2NiO_4$ (916.06): calcd. C 73.4, H 10.1, N 3.0; found C 73.3, H 10.2, N, 3.1. FAB-MS): *m*/*z* = 915 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1612 [ν(C=N)], 1141 [ν(C–O), phenolic] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1 H, N=CH), 6.04 (dd, J = 1.2, J = 8.1 Hz, 1 H, H^1), 6.31 (d, J = 6.1 Hz, 1 H, H^2), 6.21 (s, 1 H, H^3), 3.72 (q, J = 3.9 Hz, 8 H, CH_2CH_3), 3.10 (t, J = 5.4 Hz, 2 H, OCH_2), 1.40–1.85 (m, 4 H, cyclohexyl), 1.63 (m, 2 H, cyclohexyl), 1.40 (m, 2 H, cyclohexyl), 0.81 (t, J = 6.7 Hz, 6 H, CH_3), 0.82 (m, CH_2 in side chain) ppm.

Ni-16dch: Yield 0.61 g (75%). $C_{52}H_{78}N_2NiO_4$ (853.91): calcd. C 72.6, H 9.8, N 3.2; found C 72.4, H 9.7, N 3.1. FAB-MS: *m*/*z* = 859 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1614 [ν(C=N)], 1144 [ν(C–O), phenolic] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H, N=CH), 7.13 (dd, J = 1.4, J = 8.1 Hz, 1 H, H^1), 6.30 (d, J = 6.1 Hz, 1 H, H^2), 6.28 (s, 1 H, H^3), 3.88 (q, J = 4 Hz, 8 H, CH_2CH_3), 3.21 (t, J = 5.4 Hz, 2 H, OCH_2), 1.81–1.89 (m, 4 H, cyclohexyl), 1.61 (m, 2 H, cyclohexyl), 1.41 (m, 2 H, cyclohexyl), 0.85 (t, J = 6.7 Hz, 6 H, CH_3), 0.84 (m, CH_2 in side chain) ppm.

Ni-14dch: Yield 0.57 g (80%). $C_{48}H_{76}N_2NiO_4$ (803.85): calcd. C 71.7, H 9.5, N 3.4; found C 71.5, H 9.4, N 3.5. FAB-MS: *m*/*z* = 803 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1615 [ν(C=N)], 1145 [ν(C–O), phenolic] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (s, 1 H, N=CH), 6.91 (dd, J = 1.4, J = 8.1 Hz, 1 H, H^1), 6.34 (d, J = 6.0 Hz, 1 H, H^2), 6.25 (s, 1 H, H^3), 3.85 (q, J = 4 Hz, 8 H, CH_2CH_3), 3.22 (t, J = 5.3 Hz, 2 H, OCH_2), 1.78–1.91 (m, 4 H, cyclohexyl), 1.64 (m, 2 H, cyclohexyl), 1.37 (m, 2 H, cyclohexyl), 0.91 (t, J = 6.5 Hz, 6 H, CH_3), 0.85 (m, CH_2 in side chain) ppm.

Acknowledgments

The authors thank the Department of Science and Technology (DST), New Delhi and the University Grants Commission, New Delhi, for financial support. Prof. R. C. Deka (Tezpur University, India) is thanked for assistance with the theoretical calculations. Sophisticated Analytical Instrumentation Facility, North East Hill University, Shillong is acknowledged for spectral results.

---

[1] a) D. Pucci, I. Aiello, A. Bellusci, A. Crispini, M. Ghedini, M. La Deda, *Eur. J. Inorg. Chem.* **2009**, 4274–4281; b) V. N. Kozhevnikov, B. Donnio, D. W. Bruce, *Angew. Chem.* **2008**, *120*, 6382; *Angew. Chem. Int. Ed.* **2008**, *47*, 6286–6289; c) A. S. Mocanu, M. Amela-Cortes, Y. Molard, V. Circu, S. Cordier, *Chem. Commun.* **2011**, *47*, 2056–2058; d) C. Cordovilla, S. Coco, P. Espinet, B. Donnio, *J. Am. Chem. Soc.* **2010**, *132*, 1424–1431; e) J. L. Serrano, *Metallomesogens: Synthesis Properties, and Applications*, Wiley-VCH, Weinheim, Germany, **1996**.

[2] a) A. Glebowska, P. Przybylski, M. Winek, P. Krzyczkowaska, A. Krowczynski, Z. Szydlowska, D. Pociecha, E. Gorecka, *J. Mater. Chem.* **2009**, *19*, 1395–1398; b) J. Szydlowska, A. Krowczynski, E. Gorecka, D. Pociecha, *Inorg. Chem.* **2000**, *39*, 4879–4885.

[3] a) R. Paschke, D. Balkow, E. Sinn, *Inorg. Chem.* **2002**, *41*, 1949–1953; b) I. Aiello, M. Ghedini, F. Neve, D. Pucci, *Chem. Mater.* **1997**, *9*, 2107–2112; c) K. Nejati, Z. Rezvani, *New J. Chem.* **2003**, *27*, 1665–1669; d) A. G. Serrette, C. K. Lai, T. M. Swager, *Chem. Mater.* **1994**, *6*, 2252–2268; e) R. Paschke, H. Zaschke, A. Madicke, J. R. Chipperfield, A. B. Blake, P. G. Nelson, G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.* **1988**, *6*, 81–85; f) T. D. Shaffer, K. A. Sheth, *Mol. Cryst. Liq. Cryst.* **1989**, *172*, 27–39; g) A. G. Serrette, T. M. Swager, *Chem. Mater.* **1993**, *115*, 8879–8880; h) D. Killian, D. Knawby, M. A. Athanassopoulou, S. T. Trzaska, T. M. Swager, S. Wrobel, W. Haase, *Liq. Cryst.* **2000**, *27*, 509–521; i) K. Binnemans, K. Lodewyckx, B. Donnio, D. Guillon, *Chem. Eur. J.* **2002**, *8*, 1101–1105; j) Y. Abe, N. Nakazima, T. Tanase, S. Katano, H. Mukai, K. Ohta, *Mol. Cryst. Liq. Cryst.* **2007**, *466*, 129–147; k) Y. Abe, K. Nakabayashi, N. Matsukawa, H. Takashima, M. Iida, T. Tanase, M. Sugibayashi, H. Mukai, K. Ohta, *Inorg. Chim. Acta* **2006**, *359*, 3934–3946; l) Y. Abe, K. Nakabayashi, N. Matsukawa, M. Iida, T. Tanase, M. Sugibayashia, K. Ohta, *Inorg. Chem. Commun.* **2004**, *7*, 580–583; m) D. Pucci, I. Aiello, A. Bellusci, G. Callipari, A. Crispini, M. Ghedini, *Mol. Cryst. Liq. Cryst.* **2009**, *500*, 144–154; n) Z. Rezvani, M. A. Ghanea, K. S. Nejati, A. Baghaei, *Polyhedron* **2009**, *28*, 2913–2918.

[4] a) P. G. Cozzi, L. S. Dolci, A. Garelli, M. Montalti, L. Prodi, N. Zaccheroni, *New J. Chem.* **2003**, *27*, 692–697; b) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410–421; c) C. Gennari, U. Piarulli, *Chem. Rev.* **2003**, *103*, 3071–3100; d) R. I. Kureshy, I. Ahmad,

N. H. Khan, S. H. R. Abdi, K. Pathak, *J. Catal.* **2006**, *238*, 134–141.

[5] a) V. Aubert, V. Guerchais, E. Ishow, K. T.-Hoang, I. Ledoux, K. Nakatani, L. H. Bozec, *Angew. Chem.* **2008**, *120*, 587; *Angew. Chem. Int. Ed.* **2008**, *47*, 577–580; b) I. Sasaki, L. Vender, A. S.-Saquet, P. G. Lacroix, *Eur. J. Inorg. Chem.* **2006**, 3294–3302.

[6] a) A. M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem.* **1991**, *103*, 370; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375–402; b) N. Hoshino, *Coord. Chem. Rev.* **1998**, *174*, 77–108.

[7] a) S. R. Forrest, *Nature* **2004**, *428*, 911; b) M. Ghedini, D. Pucci, A. Crispini, A. Bellusci, M. La Deda, I. Aiello, T. Pugliese, *Inorg. Chem. Commun.* **2007**, *10*, 243–247.

[8] a) C. Pettinari, N. Masciocchi, L. Pandolfo, D. Pucci, *Chem. Eur. J.* **2010**, *16*, 1106–1123; b) E. I. Sezerb, A. M. Talarico, I. Aiello, A. Crispini, N. Godbert, D. Pucci, T. Pugliese, M. Ghedini, *Eur. J. Inorg. Chem.* **2010**, 3270–3277; c) D. Pucci, I. Aiello, A. Bellusci, A. Crispini, I. De Franco, M. Ghedini, M. La Deda, *Chem. Commun.* **2008**, 2254–2256; d) D. Pucci, G. Barberio, A. Bellusci, A. Crispini, M. La Deda, M. Ghedini, E. I. Sezerb, *Eur. J. Inorg. Chem.* **2005**, 2457–2463; e) D. Pucci, G. Barberio, A. Crispini, O. Francescangeli, M. Ghedini, M. La Deda, *Eur. J. Inorg. Chem.* **2003**, 3649–3661.

[9] a) R. Gimenez, M. Pinol, J. L. Serrano, *Chem. Mater.* **2004**, *16*, 1377–1383; b) Y. Sagara, S. Yamane, T. Mutai, K. Araki, T. Kato, *Adv. Funct. Mater.* **2009**, *19*, 1869–1875.

[10] F. Morale, R. W. Date, D. Guillon, D. W. Bruce, R. L. Finn, C. Wilson, A. J. Blake, M. Schroder, B. Donnio, *Chem. Eur. J.* **2003**, *9*, 2484–2501.

[11] a) S. Kumar, *Chem. Soc. Rev.* **2006**, *35*, 83–109; b) J. W. Goodby, V. Gortz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegnu, P. Boullanger, D. Lafont, Y. Queneau, S. Chambert, J. Fitremann, *Chem. Soc. Rev.* **2007**, *36*, 1971–2032; c) M. O'Neill, S. M. Kelly, *Adv. Mater.* **2003**, *15*, 1135–1146; d) R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos, R. L. Longo, *Chem. Commun.* **2008**, 5134–5136; e) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902–1929; f) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953–1010; g) M. Sawamura, K. Kawai, Y. Matusuo, K. Kanie, T. Kato, *Nature* **2002**, *419*, 702–705; h) I. Seguy, P. Jolinat, P. Destruel, R. Mamy, *J. Appl. Phys.* **2001**, *89*, 5442–5448; i) A. M. Van de Craats, N. Stutzmann, M. M. Nielsen, M. Watson, *Adv. Mater.* **2003**, *15*, 495–499; j) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887.

[12] a) C. K. Lai, C.-H. Chang, C.-H. Tsai, *J. Mater. Chem.* **2007**, *17*, 2319–2328; b) J. Barbera, A. M. Levelut, M. Marcos, P. Romero, J. L. Serrano, *Liq. Cryst.* **1991**, *10*, 119–126; c) J. Barbera, R. Gimenez, N. Gimeno, M. Marcos, M. D. C. Pina, J. L. Serrano, *Liq. Cryst.* **2003**, *30*, 651–661.

[13] a) I. Aiello, M. Ghedini, A. Grisolia, D. Pucci, O. Francescangeli, *Liq. Cryst.* **2005**, *32*, 763–769; b) Y. Abe, H. Akao, Y. Yoshida, H. Takashima, T. Tanase, H. Mukai, K. Ohta, *Inorg. Chim. Acta* **2006**, *359*, 3147–3155; c) S.-Y. Chou, C.-J. Chen, S.-L. Tsai, H.-S. Sheu, G.-H. Lee, C. K. Lai, *Tetrahedron* **2009**, *65*, 1130–1139; d) C. P. Roll, A. G. Martin, H. Gorls, G. Leibeling, D. Guillon, B. Donnio, W. Weigand, *J. Mater. Chem.* **2004**, *14*, 1722–1730.

[14] Y. Abe, A. Iyoda, K. Seto, A. Moriguchi, T. Tanase, H. Yokoyama, *Eur. J. Inorg. Chem.* **2008**, 2148–2157.

[15] a) C. R. Bhattacharjee, G. Das, P. Mondal, N. V. S. Rao, *Polyhedron* **2010**, *29*, 3089–3096; b) C. R. Bhattacharjee, G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Eur. J. Inorg. Chem.* **2011**, 1418–1424; c) C. R. Bhattacharjee, G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Inorg. Chem. Commun.* **2011**, *14*, 606–612; d) C. R. Bhattacharjee, G. Das, P. Mondal, *Liq. Cryst.* **2011**, *38*, 441–449; e) C. R. Bhattacharjee, G. Das, P. Mondal, S. K. Prasad, D. S. S. Rao, *Liq. Cryst.* **2011**, *38*, 615–623.

[16] a) Y. H. Xing, J. Han, G. H. Zhou, Z. Sun, X. J. Zhang, B. L. Zhang, Y. H. Zhang, H. Q. Yuan, M. F. Ge, *J. Coord. Chem.* **2008**, *61*, 715–730; b) J.-M. Lin, W.-B. Chen, X.-M. Lin, A.-H. Lin, C.-Y. Ma, W. Dong, C.-E. Tian, *Chem. Commun.* **2011**, *47*, 2402–2404; c) T. Chattopadhyay, M. Mukherjee, K. S. Banu, A. Banerjee, E. Suresh, E. Zangrando, D. Das, *J. Coord. Chem.* **2009**, *62*, 967–979; d) H.-J. Son, W.-S. Han, J.-Y. Chun, B.-K. Kang, S.-N. Kwon, J. Ko, S. J. Han, C. Lee, S. J. Klm, S. O. Kang, *Inorg. Chem.* **2008**, *47*, 5666–5676; e) E. Cavero, S. Uriel, P. Romero, J. L. Serrano, R. Giménez, *J. Am. Chem. Soc.* **2007**, *129*, 11608–11618.

[17] a) B. Delley, *J. Chem. Phys.* **1990**, *92*, 508–518; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; d) W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab initio Molecular Orbital Theory*, John Wiley & Sons, New York, **1986**.

Received: July 4, 2011