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Metallomesogens: Supramolecular Design via Alkane-rich Metal Complexes

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Abstract: Molecules that use non-covalent interactions to self-organize into supramolecular structures have the potential to generate functional materials with a broad range of applications. This review article focuses on the design and synthesis of molecules that use transition metal ions and long alkyl chains to direct the formation of ordered supramolecular phases. This unique combination of coordination bonds and alkyl interdigitation provide exceptional control over intermolecular interactions and can generate nanoscale molecular order as liquid crystalline states, Langmuir-Blodgett films on surfaces, highly ordered lyotropic phases such as metallo-micelles in water and reverse metallo-micelles in organic media. The synthetic strategy for alkane-rich ligands and the coordination- and lipid-directed self-assembly of these molecules are described.

1. INTRODUCTION

The design of synthetic molecules with self-organized behavior is one of the fastest growing areas of research today. Molecular materials that arise from the self-organizing properties of the molecules may afford supramolecular architectures (structures beyond the molecule) with chemical and physical properties that may become useful in emerging technologies and medicine [1]. Early pioneers that applied this approach of using non-covalent interactions as the synthetic vectors to direct abiological supramolecular complexity were Jean-Marie Lehn, Donald Cram, and Peter J. Stang, and ever since the literature has featured many elegant examples of self-organized chemical systems [2]. Recent examples are molecules encoded with well-defined metal-ligand coordination interactions in which the components interact with each other in edge-directed [3] or face-directed [4] fashion with symmetric complementarity are able to generate triangular [5], quadrangular [6] supramolecular systems, as well three-dimensional Platonic [7] and Archimedean [8] polyhedra, including adamantanoids [9], molecular boxes [10], prisms [11], and tetrahedrons [12]. Similarly, molecules encoded with well-defined hydrogen bonding [13-16] and π - π stacking interactions [17] are able to generate predictable supramolecular materials in the solid-state.

Another intermolecular "attractor" used to guide the self-organization of molecules is based on alkane interdigitation, which is driven primarily by the hydrophobic effect or the dielectric affinity of the molecular components. This has become a rather new paradigm among self-organized systems of rational design. This approach is able to generate materials possessing mesogenic properties, such as liquid crystalline behavior and other supramolecular arrangements that organize the molecules into mesophases that exist between the molecular and micron scales [18].

Recently, hybrid materials that combine several types of simultaneous intermolecular interactions [19,20], have emerged as a new class of materials due to the multifunctional properties that they evoke. In particular, among these materials are those that combine *metal coordination*- and *alkane*-directing interactions as the attractor vectors that guide molecular self-assembly. For example, alkane-rich molecules ligated to transition metal ions form metallo-lipid complexes that exhibit extraordinary self-assembly properties guided by coordination and alkane interdigitation interactions. Many of these materials are able to form liquid crystals in the ionic melt state and hence, they have been called metallomesogens. In 1996, metallomesogens were the subject of a book and it established them as a unique class of liquid crystals [21]. They have also been the subject of earlier reviews [22-24], which have focused on correlations of molecular structure with liquid crystalline properties. In this present review, we place a particular focus on the design and synthesis of alkane-rich metal complexes along with a general discussion of their self-organized properties, which in some cases go beyond liquid crystalline behavior and are able to form Langmuir-Blodgett films on surfaces, ordered lyotropic phases such as micelles and liposomes in water and reverse micelles in organic media. We hope that the current strategies for the synthesis of these hybrid materials inspire the reader with new ideas for further innovation into the molecular architecture of metallomesogens. This review presents illustrative current examples of alkane-containing ligands (organized into mono-, di-, tri-, tetra-, and poly-dentate order), a scheme of their synthesis, and a discussion of their coordination chemistry and self-assembly.

2. DESIGN PRINCIPLES

Incorporating long-alkane groups on metal complexes has been achieved via two routes: (1) by covalent bonding of the alkane groups at the periphery of Lewis bases (ligands) with subsequent metal complexation, and (2) using coulombic interactions between ionic metal complexes and ionic surfactants of opposite charge, (Fig. 1).

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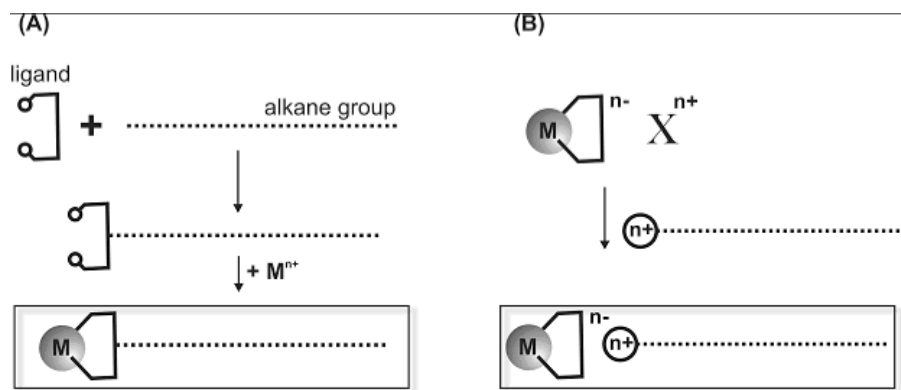


Fig. (1). Approaches to incorporate alkane groups on metal complexes: (A) covalent attachment of alkane groups at the ligand periphery, and (B) ionic coupling between surfactants and metal complexes.

Most of the reported systems to date have used the former approach (covalent attachment); however, the later approach (ionic association), albeit it has been scarcely used, has yielded some fantastic materials with enormous potential for future work [25].

Some of the variables used during the molecular design are: (1) changes in the length of the hydrocarbon groups C_xH_y , where $x > 6$, (2) hydrocarbon saturation, (3) hydrocarbon branching degree, (4) hydrocarbon position around the metal centers, (5) the ratio between the number of hydrocarbons and metal ions, (6) the nuclearity (number of metal ions) of the final complex, and (7) the oxidation state of the metal ions. All these factors significantly influence the self-organization properties of the final products. The metal-binding ligands may vary in terms of donor types (C, N, O, and S) and number of donor groups per molecule (monodentate, bidentate, tridentate, tetradentate and polydentate). The metals are typically transition metal ions of distinct oxidation states and coordination geometry, and may allow for the

formation of discrete mononuclear or multinuclear systems. The design possibilities of alkane-rich metal complexes are infinite and limited only by human imagination. Despite the enormous progress to date, metallomesogens are at the dawn of their potential and they represent one of the most promising and fertile areas in metal-organic functional materials.

3. MONODENTATE SYSTEMS

N-donors. Monodentate alkane-rich ligands with a single N pyridyl donor group were originally prepared by Bruce and coworkers [26]. These ligands use an (alkyloxy)stilbazole core from which several derivatives with additional alkane-substitutions at the 3rd and 4th position on the benzyl group have been prepared (1) [27,28]. The alkane groups were varied in length with C_nH_{n+1} ($n = 1 - 12$) and the ligands contain one or two alkane substitutions. The synthesis for these derivatives is shown in Fig. (2).

The silver (I) complexes of (alkyloxy)stilbazole derivatives have been prepared. The complexes were formed in

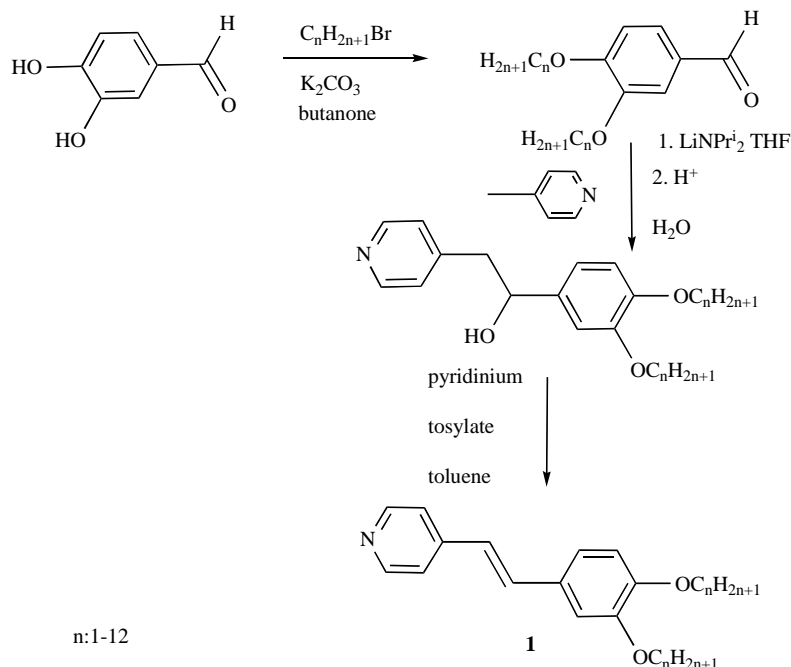
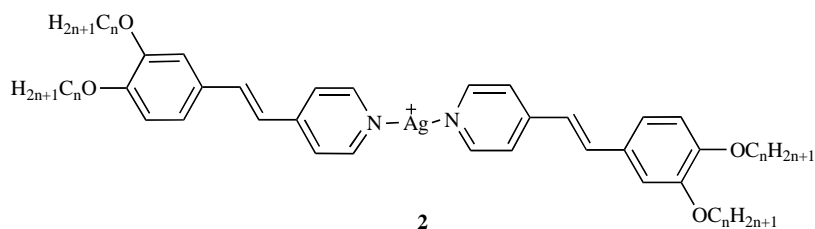
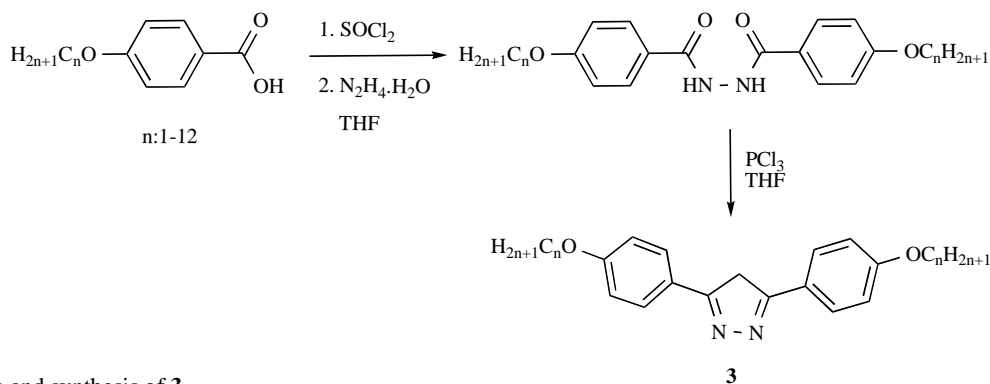


Fig. (2). Synthesis and Structure of 1.

Fig. (3). Structure of **2**.Fig. (4). Structure and synthesis of **3**.

aprotic polar solvents such as acetone and the triflate or tetrafluoroborate salts of silver(I) were used as the metal source. The reaction gives the cationic bis(alkoxy)stilbazole silver (I) complexes (**2**), (Fig. 3). Additional alkane groups were incorporated into **2** via ion-exchange reactions in dichloromethane between the triflate salts and dodecyl-sulfate ions. This approach used the secondary alkane functionalization strategy outlined in Fig. (1B) and resulted in dinuclear Ag(I) complexes associated with six alkane groups [29].

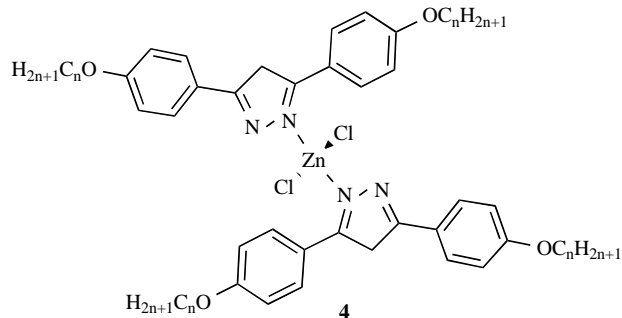
The Pd (II) and Pt (II) complexes of bis(alkoxy)stilbazole have been prepared [30,31]. They were prepared from reactions of the ligand and the dichloride salts of the metals in acetone to give the corresponding *trans*-products, $[M(\mathbf{1})_2Cl_2]$, where $M = Pd(II)$ and $Pt(II)$. Similarly, the monosubstituted Rh and Ir dicarbonyl complexes with formula $[M(\mathbf{1})(CO)_2Cl]$, where $M = Rh$ and Ir , have been reported [32,33].

The metal complexes derived from analogues of **1** exhibit extraordinary self-organized behavior in the melt ionic state. These complexes are able to form nematic, smectic, columnar or cubic supramolecular order based on changes in the length, number and position of alkane groups with respect to the metal ions [34]. Typical melting points for these complexes were between 61–90 °C, and for the complexes that include the dodecyl sulfate counterions, 110–140 °C.

Other monodentate alkane-rich ligands with N coordination are the derivatives of pyrazole ligands. Originally prepared by Serrano and coworkers [35,36], these ligands are highly versatile and exhibit the ability to form mono- and trinuclear complexes. Recent modifications in the way the alkane moieties are attached to the pyrazole rings have generated new ligand forms with interesting self-assembly properties. Fig. (4) shows the synthetic scheme of the most recent

version of this ligand (**3**) [37]. These ligands comprise alkoxy groups of $C_{10}H_{21}$ and systematically modify their position in the ligand frame.

The Zn(II) complexes of **3** have been prepared. The reaction between $ZnCl_2$ and **3** in THF at room temperature gave the mononuclear complex dichlorobis(3,5-bis(3',4',5'-trimethoxyphenyl)-1H-pyrazole)zinc(II), namely $[Zn(\mathbf{3})_2Cl_2]$ (**4**). Systematic modifications on the molecular structure, particularly varying the position and number of the decyloxy groups on the phenyl moieties, resulted in materials with distinct supramolecular order in the melt ionic state, which included smectic A and C and columnar phases between 86–115 °C, depending on the number and position of the alkoxy in the molecular structure. Interestingly, this type of Zn(II) complexes also exhibit fluorescence near the blue (365 nm) upon excitation at 263 nm [38].

Fig. (5). Structure of **4**.

Similarly, Rh(I) complexes with derivatives of **3** were prepared [39]. Using $[Rh(\mu-Cl)(CO)_2]_2$ as the metal source and the ligand in dichloromethane at room temperature, the complex with formula *cis*- $[Rh(\mathbf{3})(CO)_2Cl]$ (**5**) was isolated,

(Fig. 6). Derivatives of this complex vary in terms of number (4 – 6) of decyloxy groups. Although most derivatives exhibit low melting points (27 – 91 °C), only the complex with the highest number of alkane-substitutions exhibits self-organization behavior in the ionic melt state. It forms columnar supramolecular phases between 31 – 47 °C.

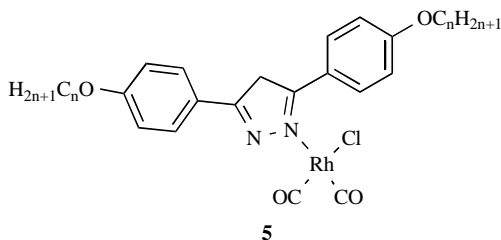


Fig. (6). Structure of 5.

Trinuclear Au(I) complexes of alkane-rich pyrazolato ligands have been prepared. Using acetone solutions of the sodium salt of the diarylpyrazolato form of the ligand and [AuCl(tht)], where tht = tetrahydrothiophene, at room temperature gave the trinuclear product (6), (Fig. 7). These metal complexes tend to stack into supramolecular columnar phases and exhibit very low melting temperatures in the range of 35 – 59 °C. Similar Au(I) macrocycles were made except with pyrazolato groups that comprised direct connections of the alkane groups [40] as well as aryl-mediated alkoxyde groups [41]. Supramolecular columnar phases were also observed to form between 56 – 87 °C.

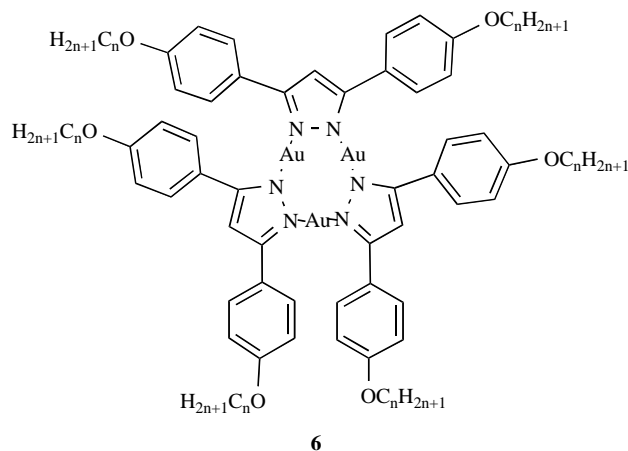


Fig. (7). Structure of 6.

The trinuclear Cu(I) complexes of a different alkane-rich pyrazolato ligands have also been prepared [42]. They use a slightly modified pyrazolato ligand with C₁₂H₂₅ and C₁₈H₃₇ groups (7), Fig. (8). The corresponding trinuclear products [Cu₃(7)₃] (8) have the ability to self-assemble into supramolecular columnar structures between 39 and 61 °C. Kishimura and coworkers demonstrated their potential in fluorescent printing technologies with write-erase features [42].

O-donors. Monodentate alkane-rich ligands with a single O carboxylate donor group (alkanoates) have been used to make a wide variety of metal complexes with self-organized properties. Among the first made was the Cu(II) stearate

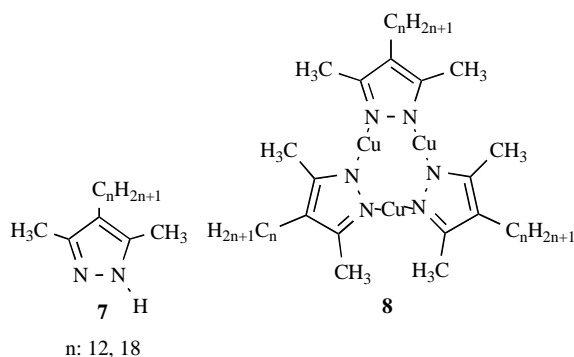


Fig. (8). Structure of 7 and 8.

complex 9, (Fig. 9), which was prepared by Grant and co-workers [43], and later systematically modified by varying alkyl chain length C_nH_{n+1} (n = 4 – 24) of the alkanooate moiety [44]. Other alkanooate complexes with similar formulae are those containing Ru(II) [45], and Cr(II), Mo(II) and W(II) [46] centers.

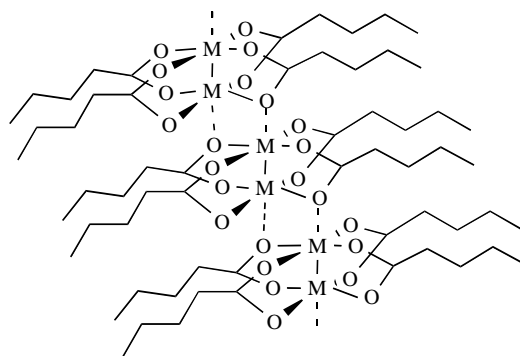


Fig. (9). Structure of 9.

The Cu(II) complex 9 was prepared from mixtures of the corresponding chloride salt of the metal with the sodium salts of the ligands in methanol. For second- and third-row transition metals, such as the Mo(II) and W(II), the hexacarbonyl Mo(CO)₆ and chloride salt W₂Cl₄(THF)₄ were used as the metal sources and reacted under refluxing diglyme and THF, respectively. All the dinuclear tetracarboxylato complexes analogous to 9 are able to self-organize into hexagonal-columnar supramolecular structures between 100 – 180 °C.

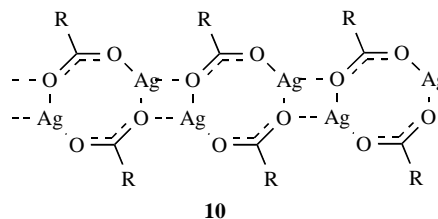


Fig. (10). Structure of 10.

A different type of alkanoates metal complex was achieved with the Ag(I) complexes (10). These complexes were prepared using the metathesis reaction of the corresponding sodium salt of the ligand and the nitrate salt of Ag(I) in absolute ethanol [47]. Alkane length variations were introduced into the molecular structure and the complexes

are able to self-organize into classical smectic supramolecular phases, except with unusual one-dimensional Ag(I) coordination networks, (Fig. 10). Typical melting temperatures were between 100 – 220 °C, with significant decomposition on the higher melting systems.

Lanthanide (III) complexes with alkaneate ligands, including 4-alkoxybenzoates, have been prepared [48-50]. For example, La (III) and Ho(III) complexes with metal to ligand ratios of 1:3 were prepared using the metathesis reaction between the corresponding metal nitrate salts and the ligand in ethanol. In addition, complexes in which mixtures of lanthanide ions such as La(III), Eu(III), Ne(III), Te(III), Ho(III), and Y(III) make up the composition of the products were prepared and characterized [51]. Typical transition melting temperatures of lanthanide (III) alkaneates were near 100 °C, and formed, depending on hydrocarbon length, lamellar bilayer structures as well as smectic A liquid crystalline phases.

Alkane-rich carboxylate donors with more complex formula are derivatives of 11. Each alkaneate comprises three hydrocarbon groups of varying length C_nH_{n+1} ($n = 4 - 24$). The synthesis of 11 is shown in Fig. (11).

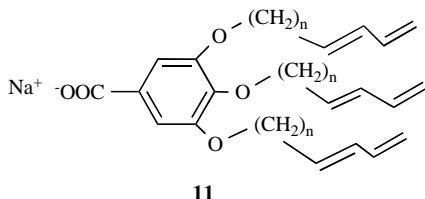


Fig. (11). Structure of 11.

Transition metal complexes of 11 using Co(II), Ni(II), Cd(II), Eu(III), and Ce(III) [52] as well as Cu(II) and Mn(II) [53] have been prepared using acetone/methanol mixtures (10:1) and the corresponding nitrate salts of the metal ions. The products exhibit a 1:2 metal to ligand ratio. Interestingly, when these materials are hydrated by 5 – 15% wt, they adopt a hexagonal organization at room temperature. These alkaneate ligands were also functionalized with divinylbenzene groups, which allowed the researchers to apply photoinitiators agents and light (1800 mW/cm²) to cross-polymerize the hexagonal supramolecular phases, (Fig. 12) [54].

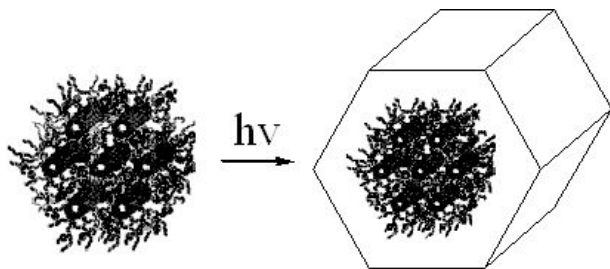


Fig. (12). Self-assembly and photopolymerization of $[M(11)_2]$ systems.

The monodentate alkane-rich ligands with an effective single O phenolate donor group for lanthanide ions were prepared by Galyametdinov and co-workers [55,56]. In par-

ticular, the Schiff base ligand 4-(alkoxy)-*N*-alkyl-2-hydroxybenzaldehyde (12) was prepared according to Fig. (13).

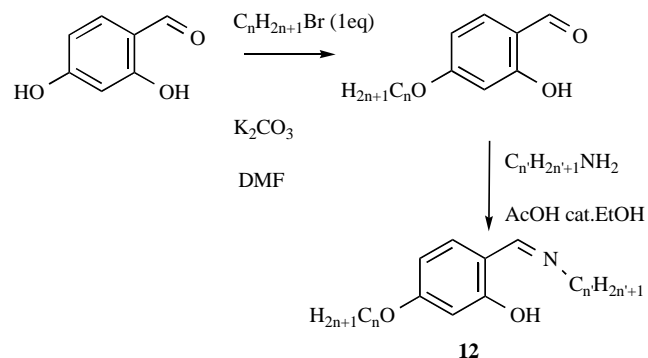


Fig. (13). Structure and synthesis of 12.

Ligand derivatives of 12 form asymmetrical complexes with lanthanide (III) ions. For example, the complexes $[Ln(12)_3(NO_3)_3]$, where Ln = Nd(III), Tb(III), and Dy(III), have been prepared, (Fig. 14) [57]. In addition, the nitrate ions in these complexes have been substituted with β -diketonato [58], β 2-thenoyltrifluoroacetate, and benzoyltrifluoroacetate groups [59]. For the β 2-thenoyltrifluoroacetate derivative (13), this was prepared from mixtures between the tris-Ln(III) acetonate system and 12 in toluene at 50°C. Similar reactions gave the other acetonato derivatives. Interestingly, these complexes self-organize into liquid crystalline smectic A phases near room temperature (60 °C).

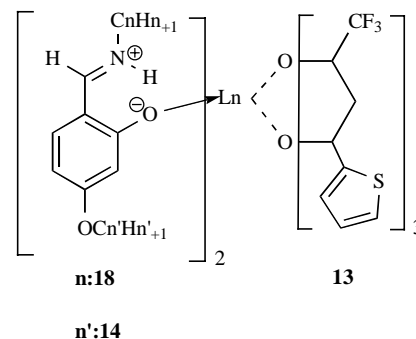


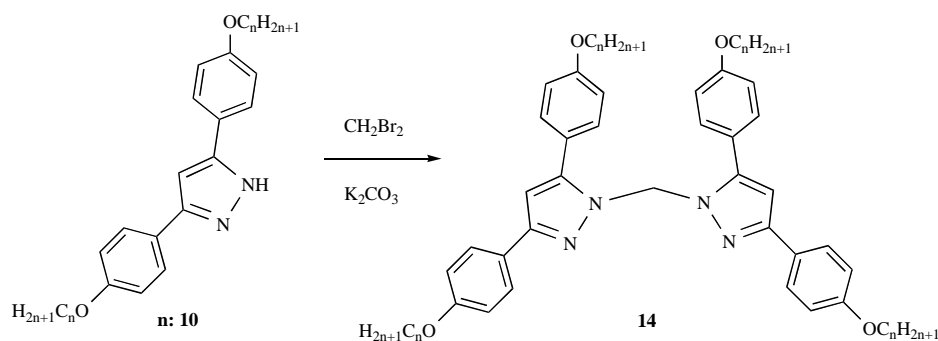
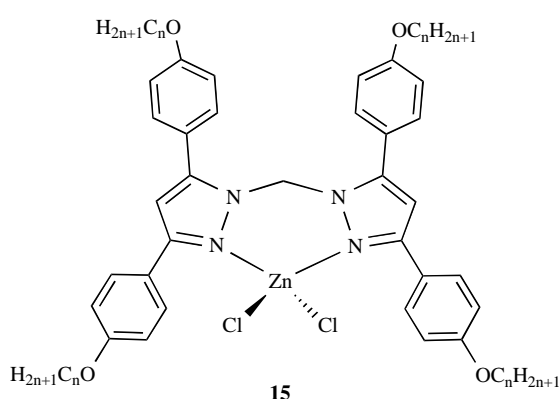
Fig. (14). Structure of 13.

4. BIDENTATE SYSTEMS

N,N-donors. Bidentate alkane-rich ligands with two *N*-donor groups comprise a wide variety of ligand systems. One of the most recent is the ligands developed by Gimenez and co-workers, which are based on the bis(pyrazolyl)methane derivatives (14) [37]. They were made from 3 via the reaction shown in Fig. (15).

The Zn(II) complex of 14 was prepared from the reactions of $ZnCl_2$ and 14 in THF and the tetrahedral complex with general formula $[Zn(14)Cl_2]$ (15) was isolated, Fig. (16). These complexes self-organize in the ionic melt state and generate schematic A and columnar phases between 79 – 115 °C.

The alkane-rich phenanthroline ligand (16), which in addition of incorporating six $C_{12}H_{25}$ groups per ligand, it also has a C_{60} group, has been prepared [60]. The ligand com-

Fig. (15). Structure and synthesis of **14**.Fig. (16). Structure of **15**.

prised four alkoxy groups ($C_{12}H_{25}$) and its synthesis is shown in Fig. (17).

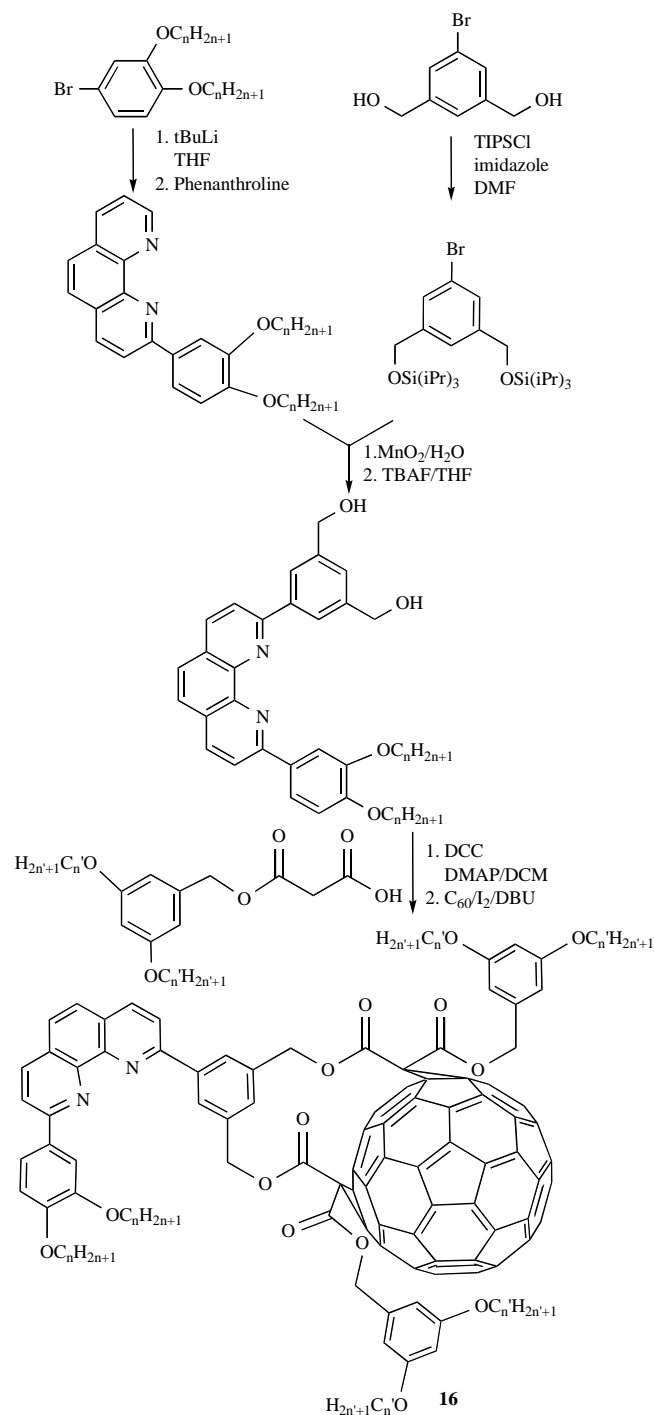
The Cu(I) *bis* complex of **16** has been prepared. Reactions of Cu(I) tetrafluoroborate salts and **16** in a mixture of acetonitrile:dichloromethane (1:5) under anaerobic conditions gave bis(2,9-diphenyl-1,10-phenanthroline)Cu(I) complex (**17**), Fig. (18). The self-assembly properties of **17** have not been investigated.

Other alkane-rich phenanthroline ligands have been reported [61]. For example, ligand **18** comprises the phenanthroline ligand moiety and four alkoxy groups varying in length C_nH_{n+1} ($n = 8, 12, 16$) and attached to the 3rd and 5th positions of the pendant aryl groups (Fig. 19). In addition of having coordination- and alkane-directing groups, these ligands have hydrogen bonding (donor and acceptor) capabilities via the carboxamide groups. The synthesis for these derivatives is shown in Fig. (19).

The Cu(I) complex of **18** has been prepared. It was formed from the anaerobic reaction of **18** with Cu(I) salts in acetonitrile at room temperature and gave the *bis* complex $[Cu(18)_2]^+$ (**19**), Fig. (20). The complex self-organizes into cubic phases between 90 and 140 °C.

The phenanthroline ligand **20** has been prepared [62]. It consists of an imidazo[4,5]-1,10-phenanthroline core functionalized with three alkoxy groups ($C_{14}H_{29}$). The synthesis of this molecule is shown in Fig. (21).

The reaction of **20** with $UO_2(CF_3SO_3)_2$ in warm ethanol gave the uranyl complex **21**, (Fig. 22). Both of the potential optical isomers of **21** formed during the reaction. This complex self-organizes into columnar phases between 95–181 °C.

Fig. (17). Structure and synthesis of **16**.

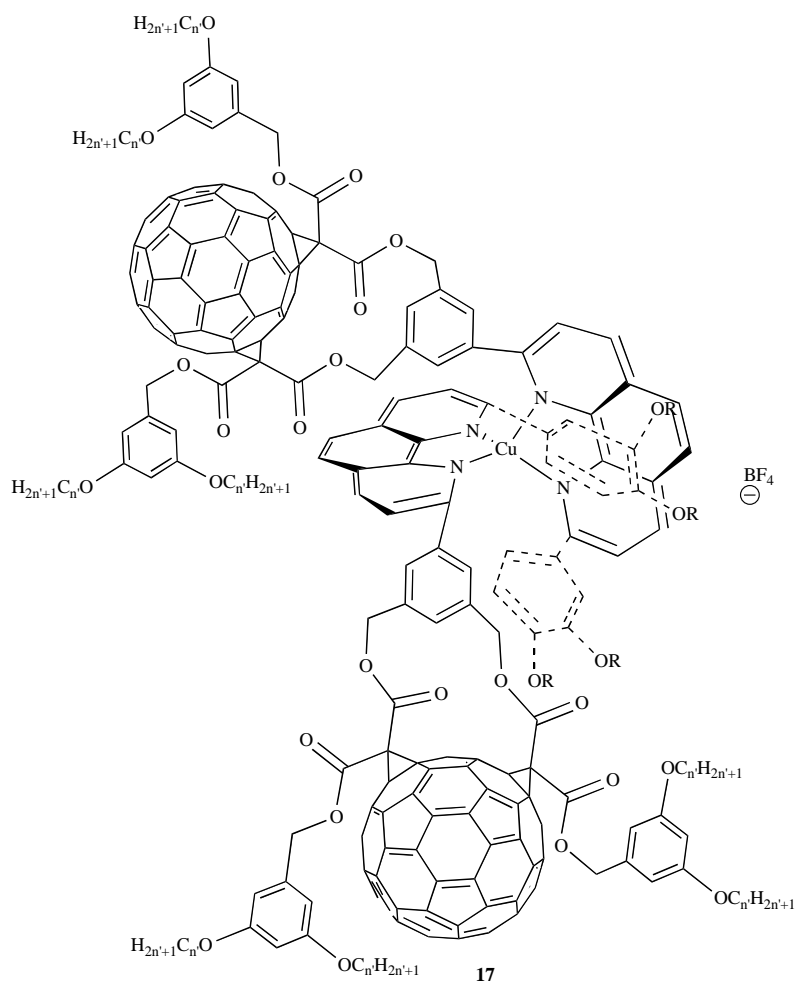


Fig. (18). Structure of 17.

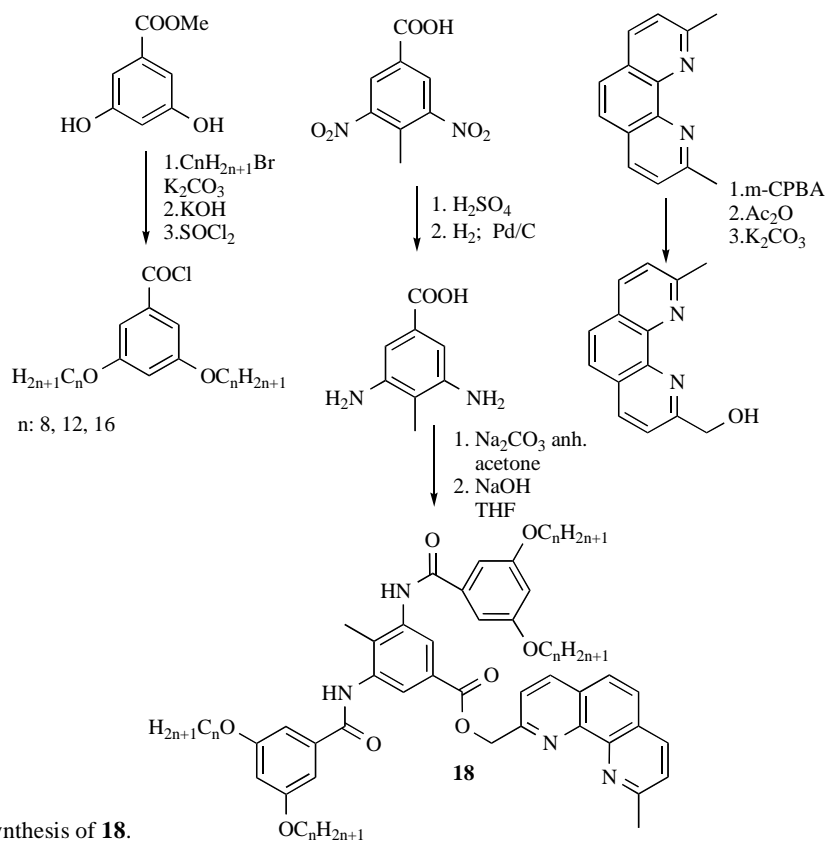


Fig. (19). Structure and synthesis of 18.

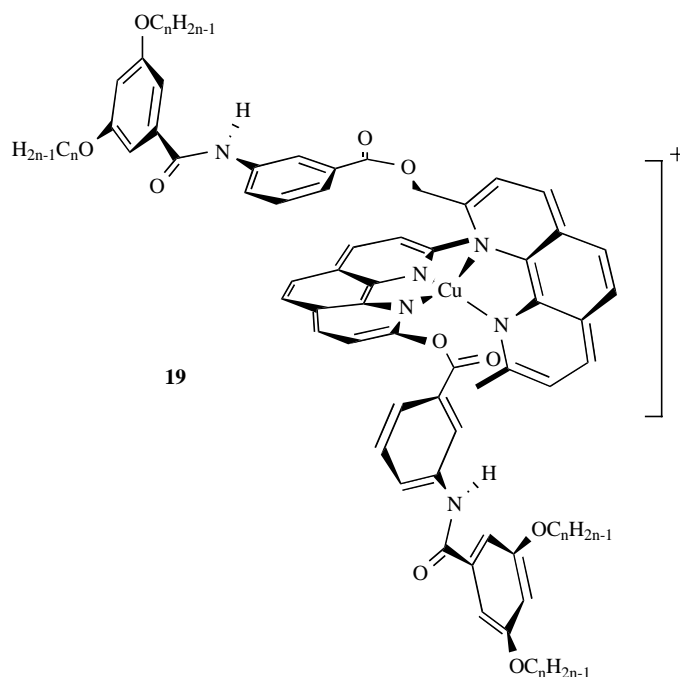


Fig. (20). Structure of 19.

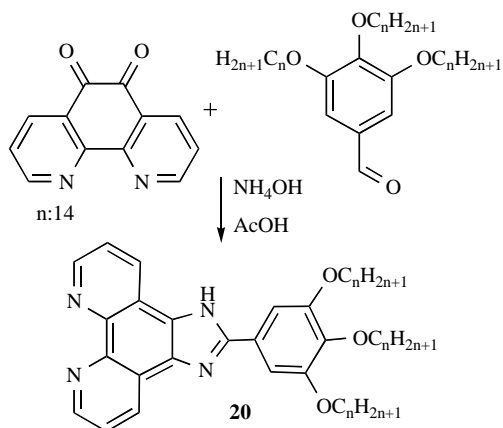


Fig. (21). Structure and synthesis of 20.

Alkane-rich ligands with N,N-donors based on picoline substituted imino compounds (**22**) have been prepared [63]. They comprise three alkoxy groups per molecule with variations in their hydrocarbon length C_nH_{n+1} ($n = 8, 12, 16$). The synthesis for ligand **22** is shown in Fig. (23).

The Cu(I) complexes of **22** were prepared from reactions between the ligand and Cu(I) tetrafluoroborate salts in acetonitrile at room temperature, and gave the tetrahedral *bis* complex $[Cu(22)_2]^+$ (**23**), Fig. (24). These complexes self-organize into columnar liquid crystalline phases of hexagonal symmetry between 30 – 160 °C.

Alkane-rich dipyrindyl ligands were originally prepared by Gaines and co-workers (**24**) [64]. These were based on 5,5'-dialkyl-2,2'-bipyridine compounds that comprised two alkyl groups of $C_{18}H_{37}$ and $C_{19}H_{39}$ in length. The synthesis of

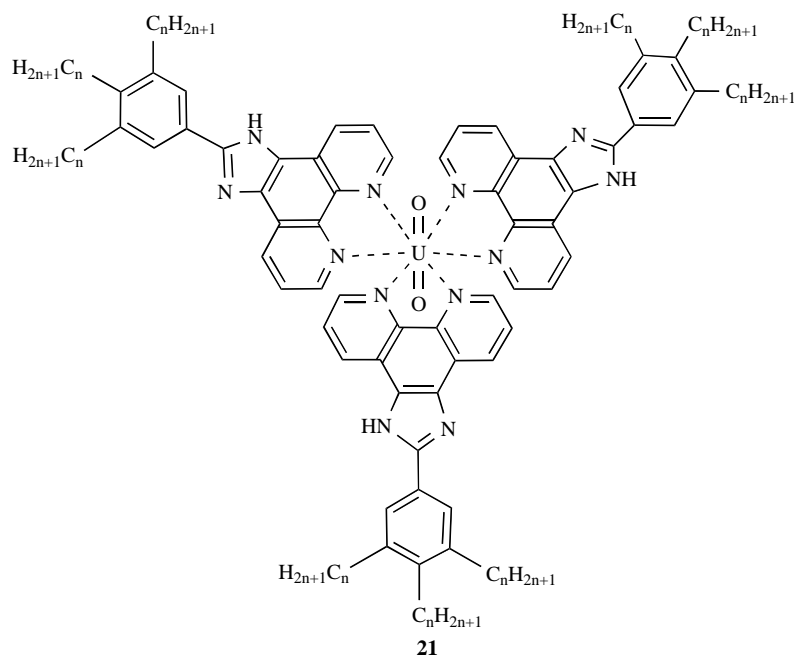
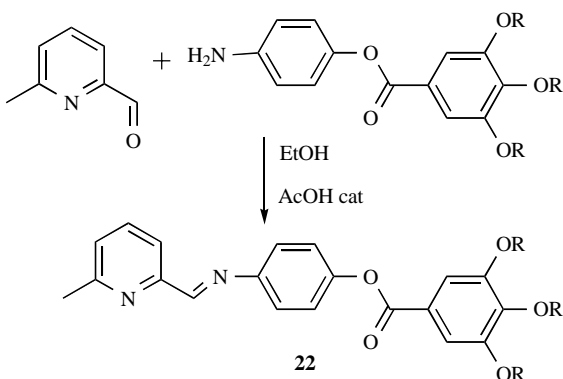
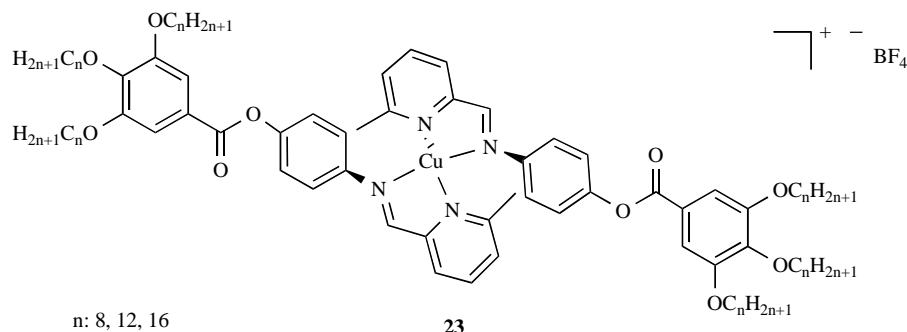
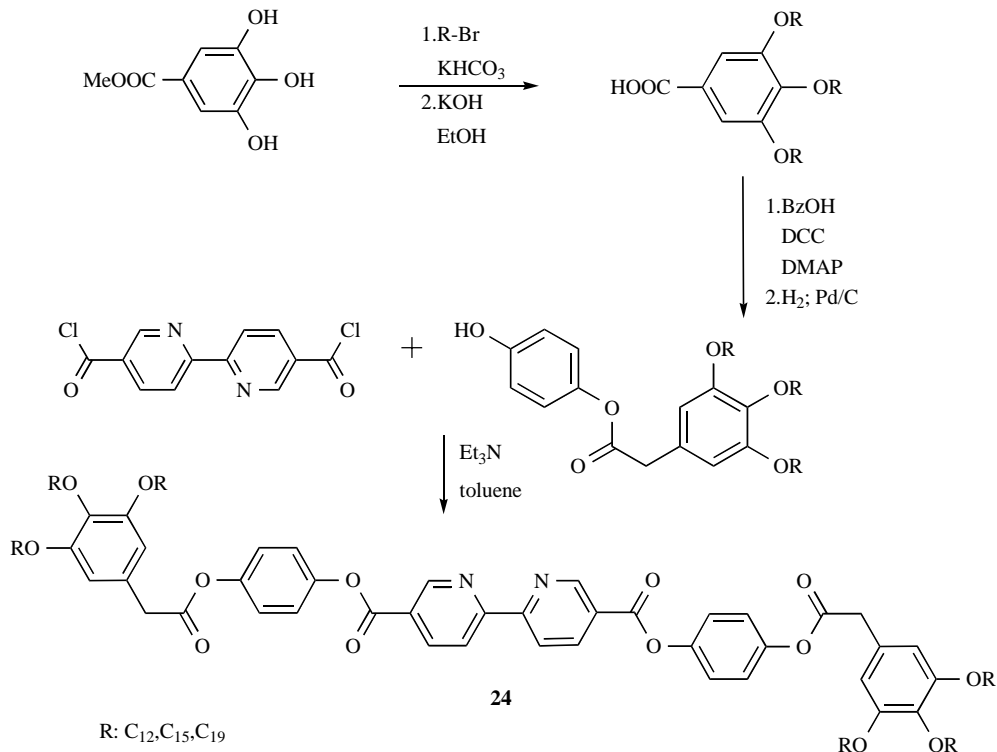


Fig. 22. Synthesis of 21.

Fig. (23). Structure and synthesis of **22**.Fig. (24). Synthesis of **23**.Fig. (25). Structure and synthesis of **24**.

24 is shown in Fig. (25). Similar alkane-rich dipyriddy ligands bearing hydrocarbons of C_nH_{n+1} (n = 12, 15, 19) have been made more recently [65-67].

The Ru(I) [68], Ru(II) [66,69] and Fe(II) [70] complexes of derivatives of **24** have been prepared. For example, the

bipyridyl ligands were reacted with *cis*-[RuCl₂(bipy)₂] under reflux conditions in 2-propanol to give product [Ru(**24**)(bipy)₂]²⁺ (**25**), (Fig. 26). Complex derivatives of **25** were reported to undergo a spontaneous self-organization into elliptical micelles in water. However, when two equivalents of **24** was reacted with *cis*-[RuCl₂(bipy)] salts, the reaction gave the corresponding *cis*-[Ru(**24**)₂(bipy)]²⁺ (**26**) complex. This product self-organizes into Langmuir-Blodgett films [69] and inverted micelles in organic media [71]. However, Ru(I) complexes with bipyridyl ligands have also been reported [68] Similarly, the corresponding iron(II) complex ligated to two molecules of **24**-like ligands and two cyanide ions, namely [Fe(**24**)₂(CN)₂] (**27**), self-assemble into metall-ovesicles in water and redox-active films on surfaces [70].

Alkane-rich ligands with the N,N-donor set based on the diazabutadiene core (**28**) were first prepared by Bruce and coworkers [72]. They incorporate one or two alkoxy groups varying in hydrocarbon length C_nH_{n+1} of n = 8, 10, 12. The synthesis of **28** is shown in Fig. (27).

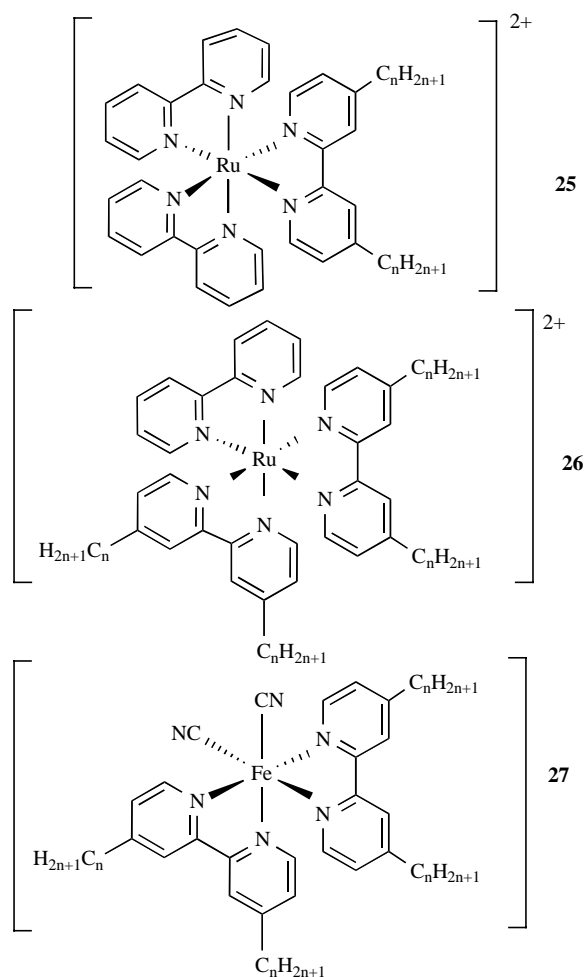


Fig. (26). Structure of 25 - 27.

The Re(I) complex of **28** has been prepared. Reactions of **28** with bromopentacarbonyl-rhenium (I) in toluene:heptane

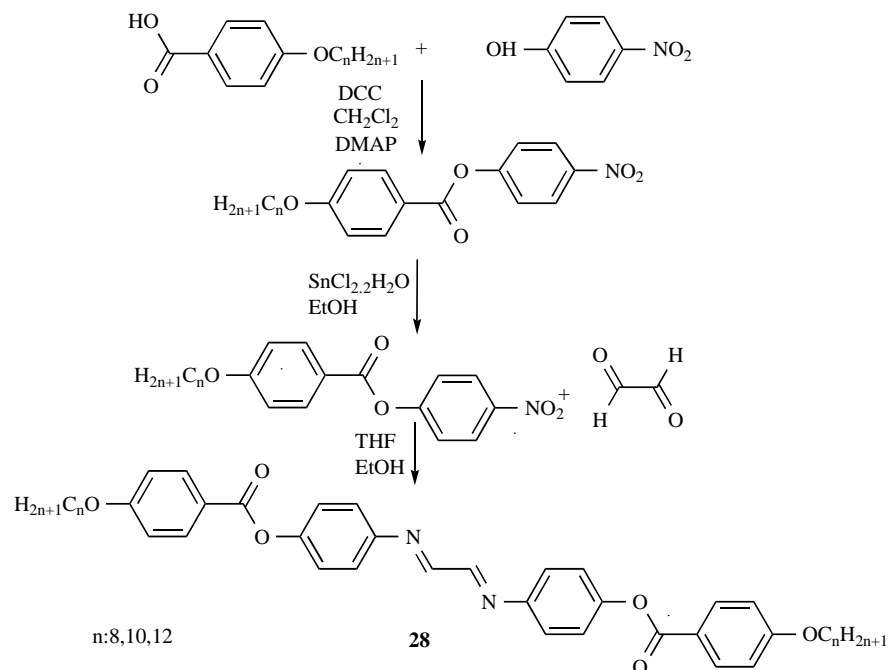


Fig. (27). Structure and synthesis of **28**.

(2:3) mixtures at 80°C gave the product [Re(**28**)(CO)₃Br] (**29**), Fig. (**28**). The self-organization properties of derivatives of **29** were the formation nematic liquid crystalline phases between 167 – 252 °C.

N,O-donors. The bidentate alkane-rich ligand **30** with N,O-donor groups based on the aryloxazoline core and comprising six dodecyloxy groups per molecule has been prepared [73]. The synthesis of **30** is shown in Fig. (**29**).

The Cu(II) and Pd(II) complexes of **30** have been prepared. The ligand was reacted with Cu(II) acetate or Pd(II) acetate salts in ethanol at room temperature and generated the corresponding bis-oxazoline complexes [Cu(**30**)₂] (**31**) and [Pd(II)(**30**)₂], respectively, (Fig. **30**). These complexes form supramolecular columnar structures between 3 – 70 °C.

The bidentate alkane-rich ligand **32** with N,O-donor groups based on the salicylaldimine Schiff bases has been prepared. They comprise derivatives that use alkyl, alkoxy, and alkyloxybenzyloxy hydrocarbon substituents varying in length C_nH_{n+1} (n = 7 – 18) [74-75]. In addition, a salicylaldimine Schiff bases comprising as an alkyl group a cholesteryl ester unit have been prepared [76-77]. The ligand synthesis of a typical ligand (**32**) is shown in Fig. (**31**).

The Cu(II), Pd(II), Zn(II), and V(IV) complexes of derivatives of **32** have been prepared [78-79]. For example, mixtures of **32** and Cu(II) acetate in hot methanol gave the bis complex [Cu(**32**)₂] (**33**), Fig. (**32**). Moreover, the addition of Cu(II) chloride to **33** gave the dinuclear complex [Cu₂(**32**)₂] (**34**). These complexes self-organize in the ionic melt state between 60 and 160 °C, where smectic A, C, and E phases form, depending on the alkane length and position in the molecular structure. Similar phases were achieved for derivatives of the dinuclear complex **34**, where the self-organization occurs between 52 – 145 °C.

The bidentate alkane-rich ligands with N,O-donor groups based on the β-enaminoketone moiety were first prepared by Ovchinnikov and co-workers [80]. They have been recently

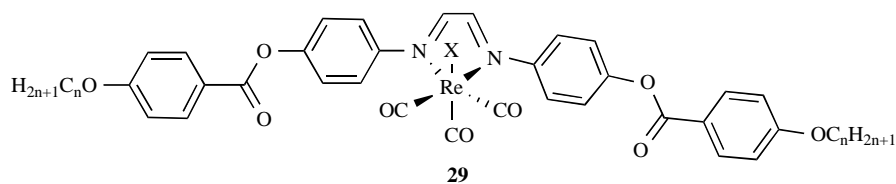


Fig. (28). Structure of 29.

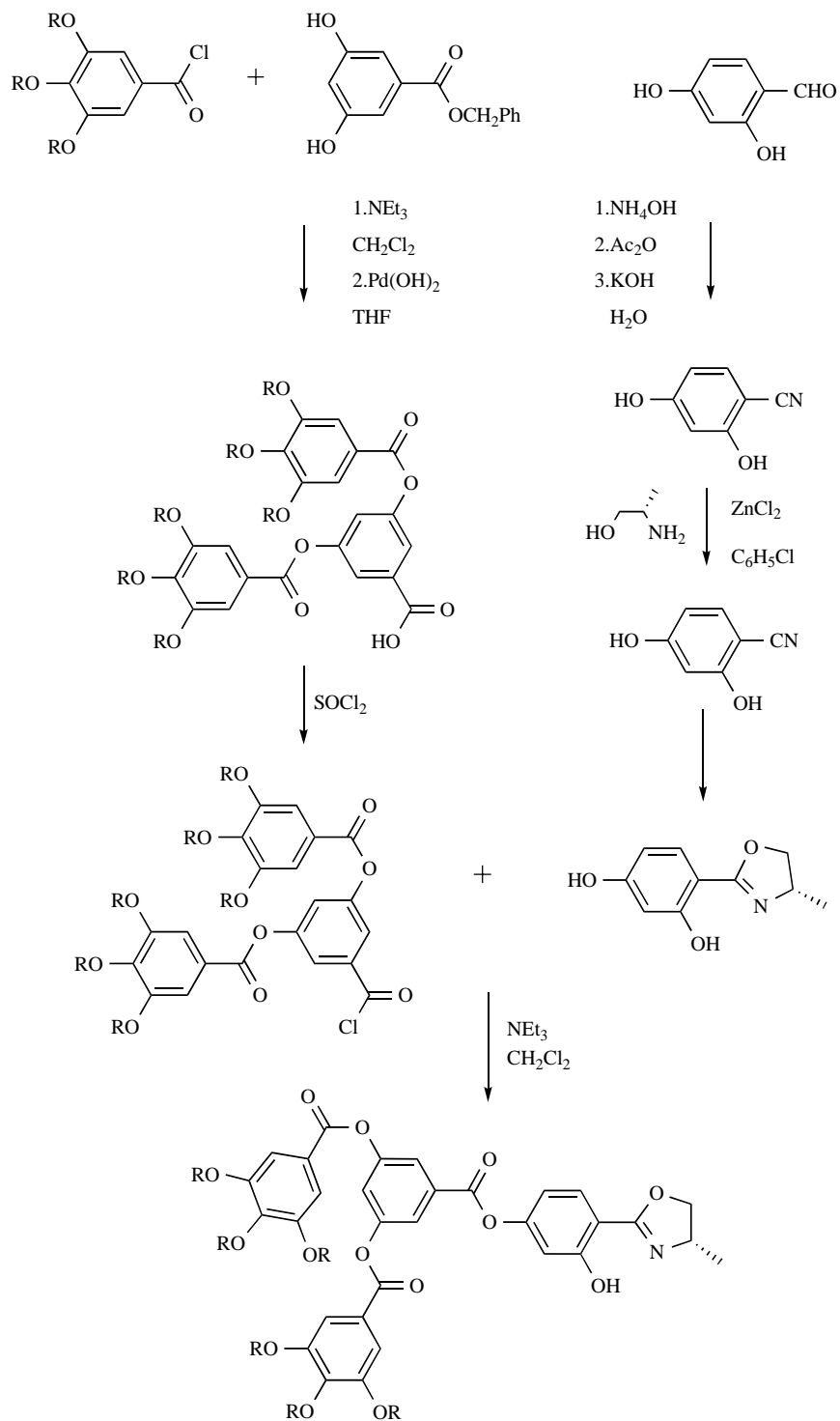
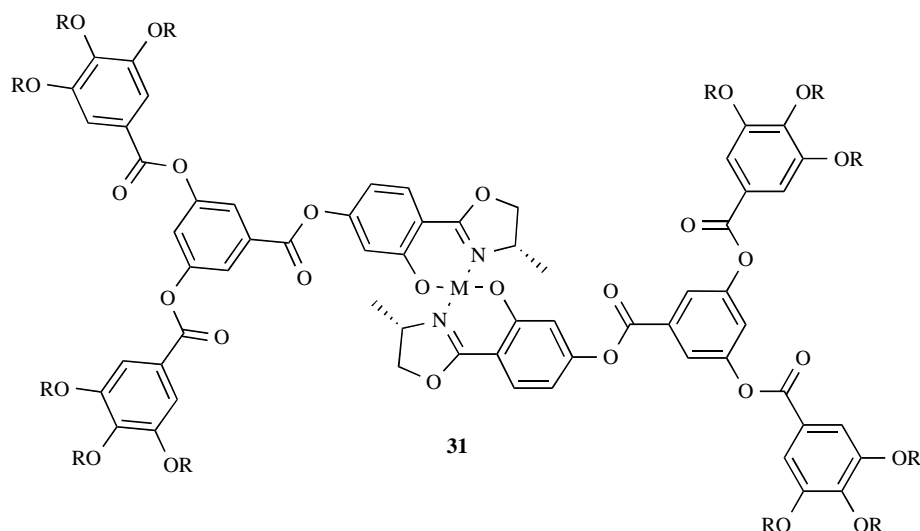
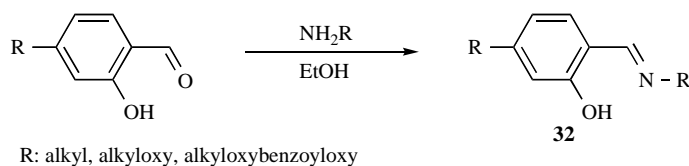
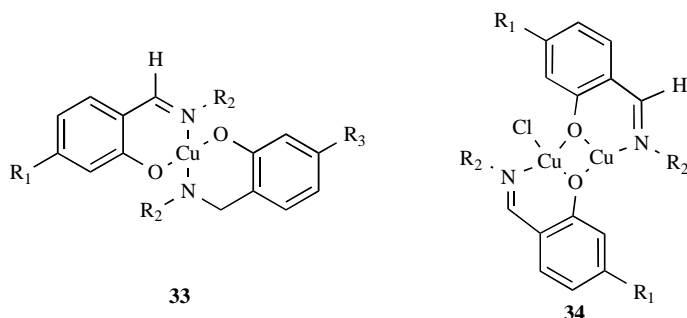
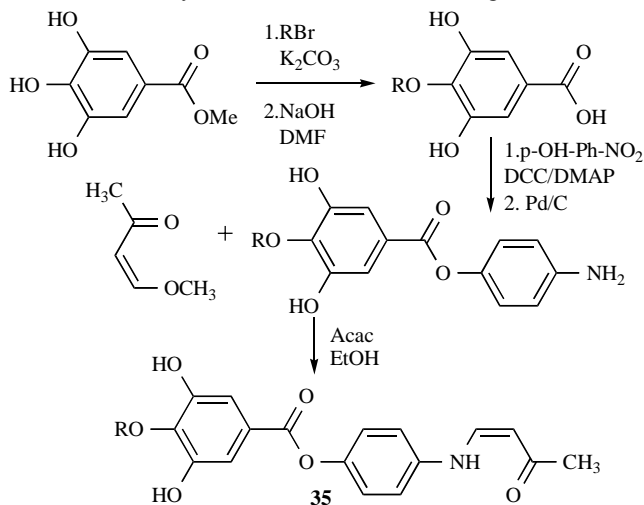


Fig. (29). Structure and synthesis of 30.

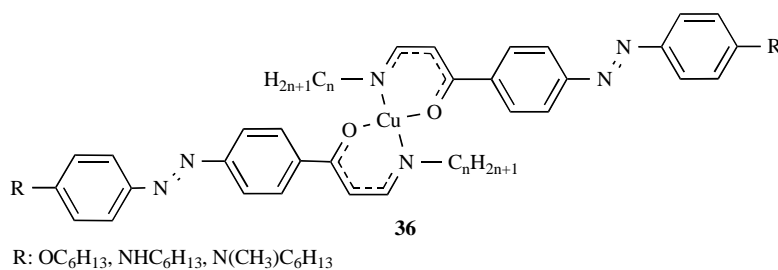
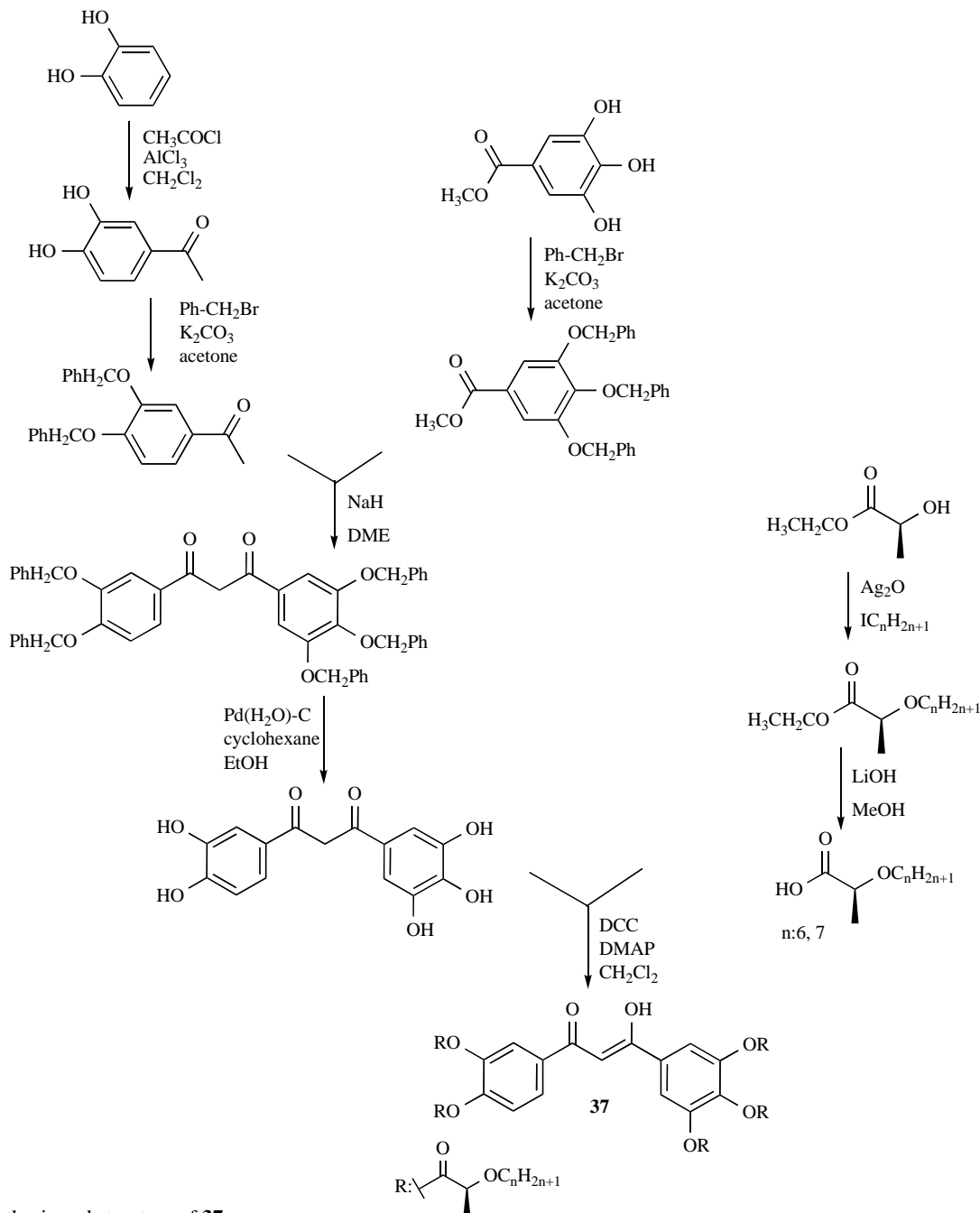
Fig. (30). Structure of **31**.Fig. (31). Structure and synthesis of **32**.Fig. (32). Structure of **33** and **34**.

prepared with systematic variations in their structure (**35**), where the hydrocarbon length varies in length C_nH_{n+1} ($n = 8 - 18$) [81]. The synthesis of **35** is shown in Fig. (33).

Fig. (33). Synthesis and structure of **35**.

The Cu(II) [82-86], Ni(II) [87], Co(II) [88], and Pd(II) [66] *bis* complexes with derivatives of **35** have been prepared. For example, reactions of **35** with Ni(II) acetate in hot ethanol gave the corresponding complexes $[Ni(\mathbf{35})_2]$ (**36**), Fig. (34). The self-organization properties of these complexes generally occurs at high temperatures in the ionic melt state between 130 and 180 °C, where nematic, smectic A and C phases form, depending on the metal ion and the alkane length and position.

O,O-donors. The bidentate alkane-rich ligands with an O,O donor set based on the β -diketonates framework were originally prepared by Bulkin and co-workers [89]. Early β -diketonates were based on the 1,3-*bis*(*p*-substituted-phenyl)- β -diketonates, where the hydrocarbon length was C_nH_{n+1} ($n = 7, 13$) [90]. More recently, the 1,3-diphenylpropanedione ligands (**37**) bearing five alkoxy substitutions per molecule, where the hydrocarbon length was C_nH_{n+1} ($n = 6, 7$) have been prepared [91]. Similar alkane-bearing β -diketonates have been prepared with four alkoxy of C_nH_{n+1} ($n = 10, 12$) [92], and with one alkoxy per molecule [93]. The synthesis of **37** is shown in Fig. (35).

Fig. (34). Structure of **36**.Fig. (35). Synthesis and structure of **37**.

The β -diketones *bis* complexes of Cu(II), Pd(II) and V(IV), and the *tris* complexes of Cr(III), Mn(III), Co(III), and Fe(III) have been prepared. For example, reactions of Cu(II) acetate and ligand derivatives of **37** in absolute etha-

nol gave the *bis* complex [Cu(II)(**37**)₂] (**38**) or the *tris* complex [Cu(II)(**37**)₃] (**39**), Fig. (36). The *bis* complex **38** self-organizes into columnar phases at room temperature, where as the *tris* complexes **39** also forms columnar phases except

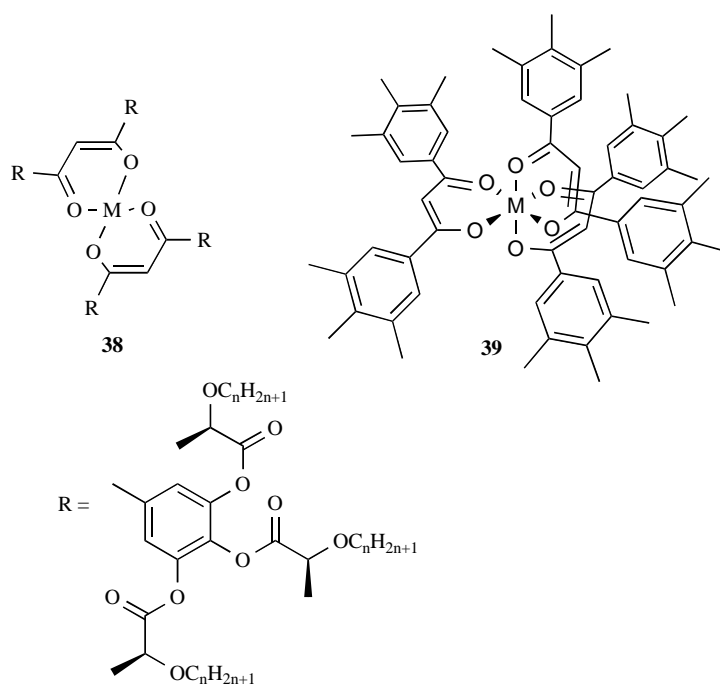


Fig. (36). Structure of **38** and **39**.

between 62 – 108 °C. Scanning tunneling microscopy study of bis β -diketones Pd(II) complexes confirmed the columnar phase arrangement of these materials [94].

The bidentate alkane-rich ligands with O,O-donor groups based on the tropolone framework were originally prepared by Seto and coworkers [95], and the first demonstration of their metal-binding behavior was by Sinn and coworkers [96]. Derivatives of the tropolone structure (**40**) using alkoxy groups with varying hydrocarbon groups C_nH_{n+1} ($n = 10, 12, 14, 16$) have been prepared. The synthesis of **40** is shown in Fig. (37).

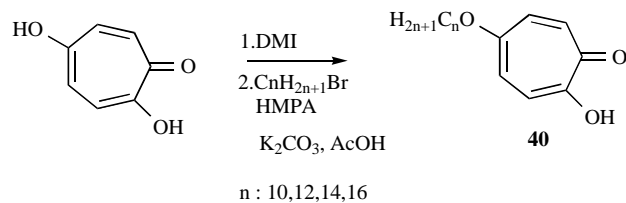


Fig. (37). Synthesis and structure of **40**.

The *bis* complexes of Cu(II), Zn(II), Ni(II), V(IV), Mn(II) and U(VI) of derivatives of **40** have been prepared [97-98]. For example, reactions between Cu(II) acetate and **40** in hot ethanol gave the complex [Cu(II)(**40**)₂] (**41**), Fig. (38). Interestingly, only complexes of tropolone with Cu(II) ions exhibit self-organizing behavior and forms smectic B and C phases at high melting temperatures between 232 – 269 °C.

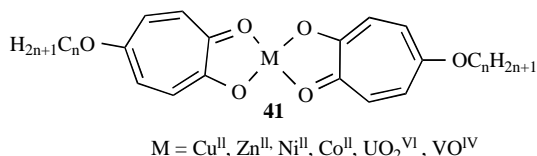


Fig. 38. Structure of **41**.

N,C-donors. Alkane-rich ligands that chelate metals with a C,N donor set are based on the 4-alkoxy-N-(4'-alkoxyphenyl) benzylidene framework (**42**). Derivatives comprising two alkoxy groups with C_nH_{n+1} , $n = 4, 6, 8,$ and $12,$ have been prepared [99-101]. The synthesis of a typical ligand of this type is shown in Fig. (39).

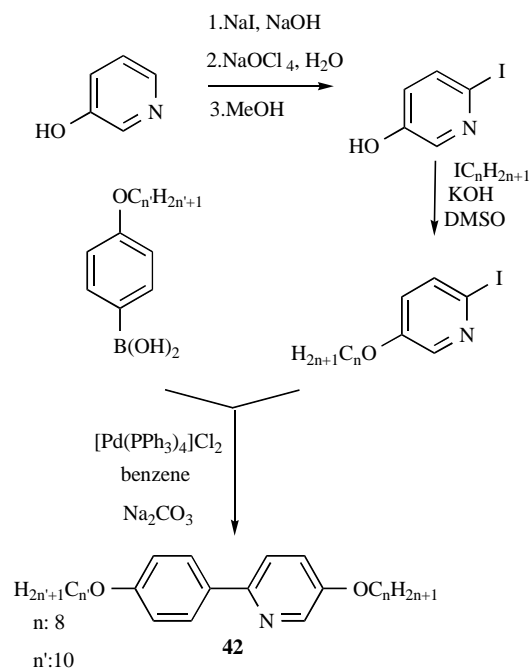


Fig. (39). Synthesis and structure of **42**.

The Pd(II), Re(II), [99-101] and Pt(II) [102] complexes of derivatives of **42** have been prepared. For example, the Pd(II) complex was prepared from reactions between Pd(II) acetate and the ligand in acetic acid. Subsequent reactions

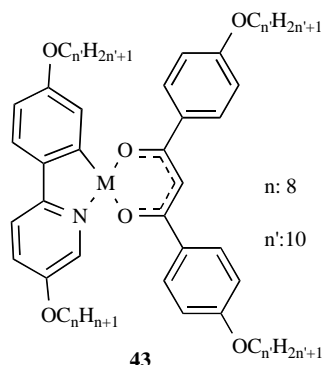


Fig. (40). Structure of **43**.

led to the asymmetrical complex **43**, Fig. (40). The Pd(II) complex **43** self-organizes into simple cubic phases between 46 – 98 °C.

5. TRIDENTATE SYSTEMS

N,N,N-donors. Tridentate alkane-rich ligands with three N-donor groups based on the 2,6-bis(benzimidazol-2'-yl)pyridine core (**44**) were originally prepared by Piguet and coworkers [103]. Derivatives comprising two alkoxy groups

per ligand bearing C_nH_{n+1} groups with $n = 12$ and 16 have been prepared. The synthesis of **44** is shown in Fig. (41).

The trivalent lanthanide (La to Lu) [104,105] and Zn(II) [106] complexes of derivatives of **44** have been prepared. For the synthesis of the lanthanide complexes (**45**) was achieved from reactions between **44** and the nitrate salts of the metals in acetonitrile-dichloromethane mixtures, Fig. (21). The lanthanide complexes melt at temperatures between 190 – 269 °C without any evidence of self-organization. However, when six alkoxy groups of $C_{12}H_{25}$ are incorporated to the complex, the lanthanide systems self-organize into columnar phases between 130 – 160 °C [107]. Similar self-organized behavior between 131 - 157 °C was observed for the Zn(II) complexes having six alkoxy groups per molecule.

Tridentate alkane-rich ligands with three N-donor groups based on the 2,2',2''-terpyridine core (**46**) with alkyl substitutions at the 6' position were originally prepared by Bruce and coworkers [108]. The ligand was prepared with C_nH_{n+1} groups of $n = 19$ and 31 . The synthesis of **46** is shown in Fig. (43).

The Ru(II) salts of **46** were prepared from [Re(terpy)Cl₂], where terpy = 2,2',2''-terpyridine and generated the corresponding *bis* complex [Re(II)(terpy)(**46**)]²⁺ (**47**), Fig.

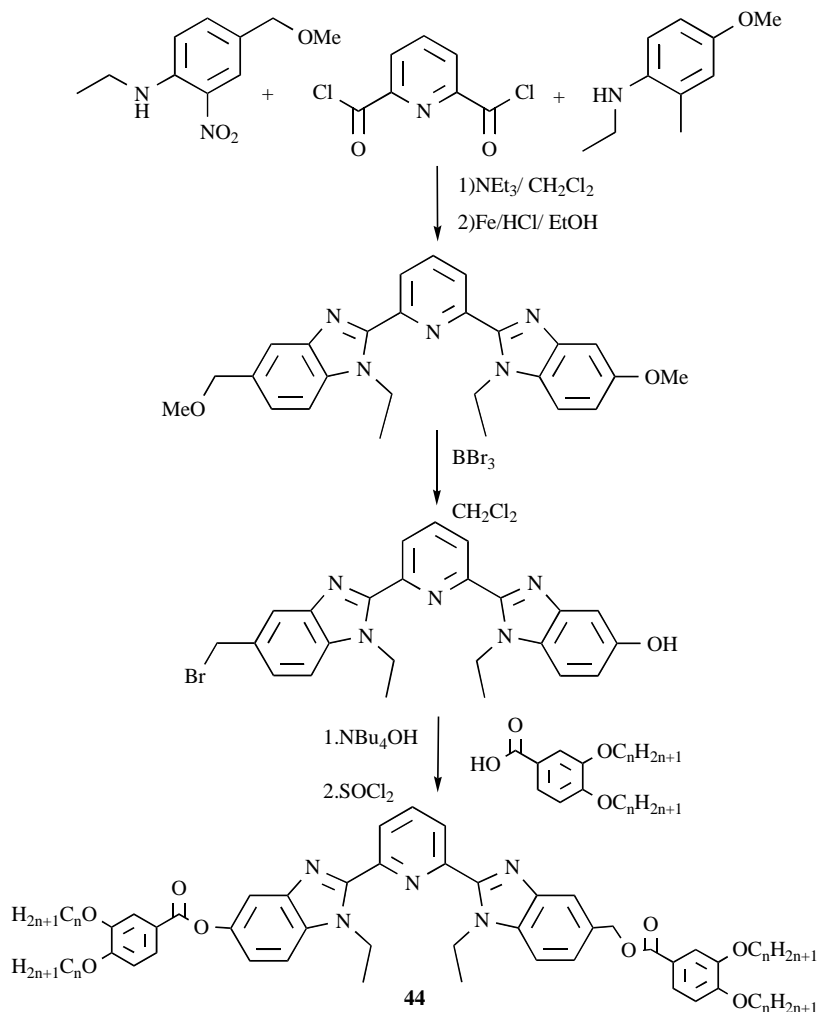
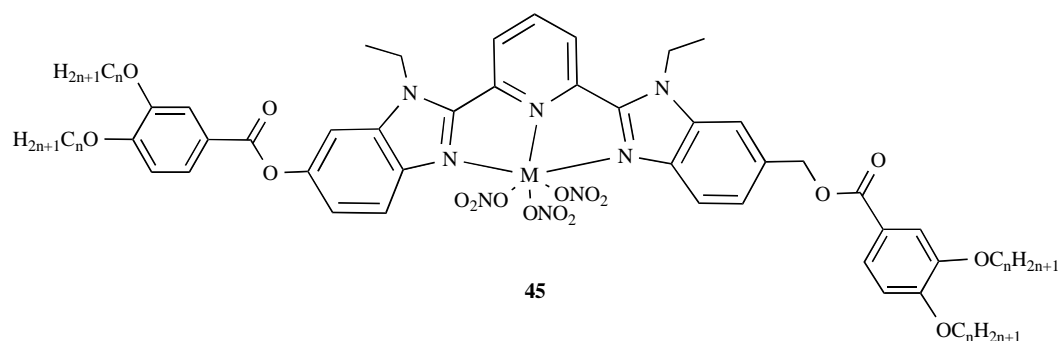
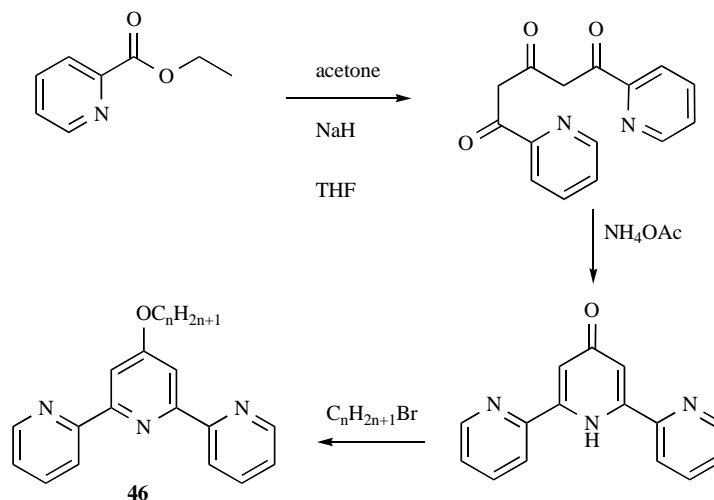
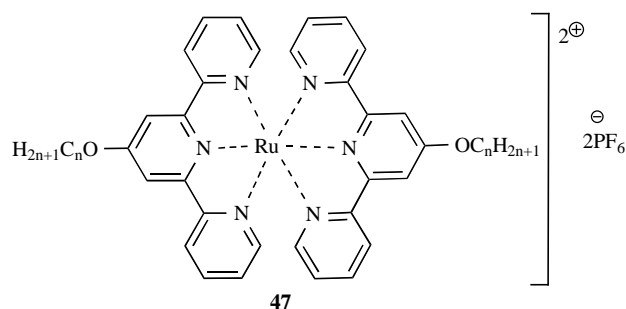


Fig. (41). Synthesis and structure of **44**.

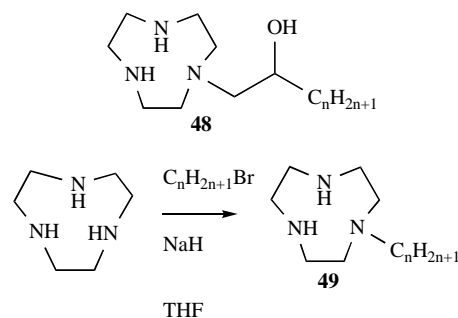
**Fig. (42).** Structure of **45**.**Fig. (43).** Synthesis and structure of **46**.

(44). These complexes self-organize into multi-lamellar structures on surfaces.

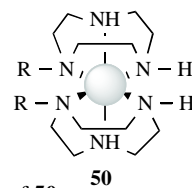
**Fig. (44).** Structure of **47**.

Tridentate alkane-rich ligands with three N-donor groups based on the 1,4,7-triazacyclononane core were first prepared by Wendorff and coworkers [109]. The ligand comprises three N-substitutions with arylalkoxy groups bearing $C_{10}H_{21}$ groups (**48**). Other derivatives using this core comprise one N-substitution with alkane groups of C_nH_{n+1} $n = 12$ and 18 (**49**) [110]. The synthesis of **49** is shown in Fig. (45).

The Ni(II)¹⁰⁹ and Cu(II)¹¹⁰ complexes of alkane-containing 1,4,7-triazacyclononane derivatives have been prepared. For example, Cu(II) triflate salts, where triflate = trifluoromethanesulfonate, were reacted with two equivalents

**Fig. (45).** Structure of **48** and synthesis **49**.

of **49** in acetonitrile-chloroform (5:1) mixtures and gave the *bis* complex $[Cu(II)(\mathbf{49})_2]^{2+}$ (**50**), Fig. (46). The derivatives of **50** self-organize into metallo-liposomes in water and are able to condense DNA plasmids and deliver them into the nucleus of eukaryotic cells [110]. On the other hand, the Ni(II) complex of ligand **48** self-organizes into columnar phases in the ionic melt state.

**Fig. (46).** Structure of **50**.

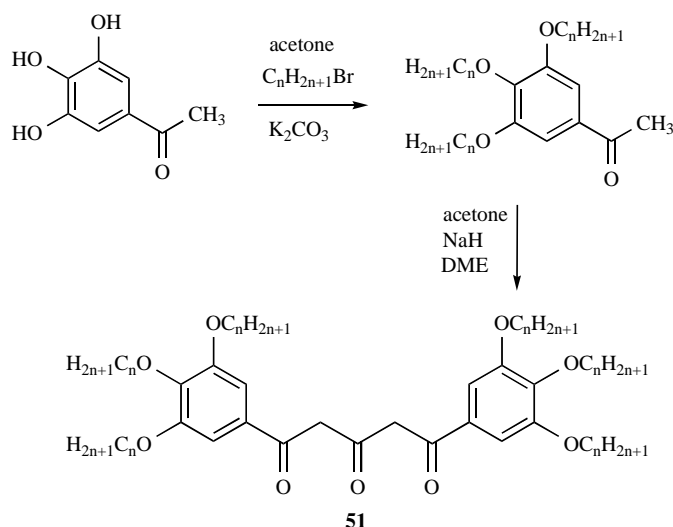


Fig. (47). Synthesis and structure of **51**.

O,O,O-donors. Tridentate alkane-rich ligands with three O donor groups based on 1,3,5-triketone framework (**51**) were originally prepared by Swager and coworkers [111,112]. Derivatives of this ligand comprising two and four alkoxy groups C_nH_{n+1} $n = 5, 6, 7, 8, 10, 12, 14,$ and 16 have been prepared. The synthesis of **51** is shown in Fig. (47).

Reactions between derivatives of **51** and Cu(II) acetate in chloroform-methanol (1:5) mixtures gave the corresponding dinuclear product $[Cu_2(51)_2]$ (**52**), Fig. (48). Similar complexes with Ni(II) and Pd(II), as well as heteronuclear bimetallic complexes with these metals were prepared. All these dinuclear complexes exhibit self-organized behavior and form columnar phases in the melt state between $55-135^\circ C$.

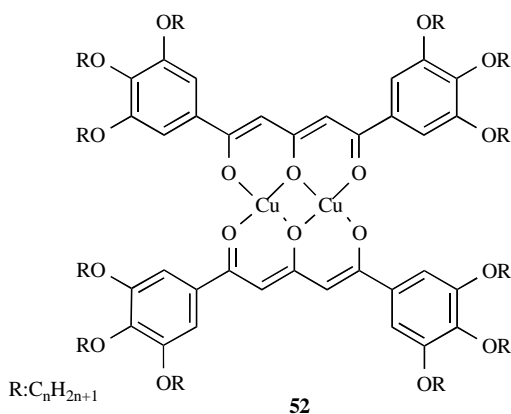


Fig. (48). Structure of **52**.

N,S,S-donors. Tridentate alkane-rich ligands with one N-donor and two thiolato S donor groups based on pyridine-2,6-bis(thiocarboxylic) acids (**53**) were originally prepared by Espinet and coworkers [113]. Derivatives comprising one alkoxy or alkylsulfanyl groups per ligand bearing C_nH_{n+1} groups with $n = 4, 8, 12$ have been reported. The synthesis of **53** is shown in Fig. (49).

Reactions of **53** with Pd(II) acetate in acetonitrile gave the mononuclear complex **54**, which exists in equilibrium in

solution with its corresponding dinuclear complex **55**, Fig. (50). Similar complexes replacing the thiocarboxylate moiety with carboxylate groups were also prepared and displayed similar monomer-dimer equilibrium in solution. The equilibrium between **54** and **55** could be shifted to mononuclear complexes upon reactions with alkane-rich monodentate ligands such as 4-decyloxy-4'-stilbazole, 4-decyloxy-*N*-(4-pyridylmethylene)-anilines, decyl 4-pyridinecarboxylate, 4-(4'-decyloxyphenyl)pyridinecarboxylate, 4-(3',4',5'-tridecyloxybenzyl)pyridinecarboxylate, 4-isocyano-1-decyloxybenzene, or 4-isocyano-4'-decyloxybiphenyl, which substitute the solvent molecule of complex **54** and give products that self-organize into smectic C and nematic phases between $150-260^\circ C$.

5. TETRADENTATE SYSTEMS

N₄-donors. Tetradentate alkane-rich ligands with four N-donor groups based on the 2,3,9,10,16,17,23,24-octakis(alkoxymethyl)phthalocyaninato framework were originally prepared by Piechocki and coworkers [114]. These complexes are made from the fragment **56**. Synthesis of this precursor is shown in Fig. (51). The corresponding macrocyclic compounds containing alkyl [115-118] alkoxy [118-122] and alkylthio [124-125] groups that vary the hydrocarbon length by C_nH_{n+1} $n = 4, 5, 6, 8, 9, 10, 12, 14, 15, 16,$ and 18 .

The trivalent lanthanide (Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Co(II), Ni(II), Cu(II), and V(IV) [126-127]. complexes of derivatives of **56** have been prepared. Transition metal complexes of the first row tend to form mononuclear porphyrin-like systems (**57**), whereas lanthanide complexes form bis-complexes (**58**), Fig. (52). The complexes were formed from reactions of the ligands and the acetate salts of the metal ions under reflux conditions in high boiling point solvents (hexanol for the lanthanides and 2-dimethylaminoethanol for transition metals). Complexes with transition metals self-organize into columnar phases between $50-75^\circ C$, whereas the lanthanide *bis*-complexes self-organize into columnar phases between $43-202^\circ C$.

N₂O₂-donors. Tetradentate alkane-rich ligands with two N-donor and two O-donor groups based on the *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxopropenyl]ethylenediamine

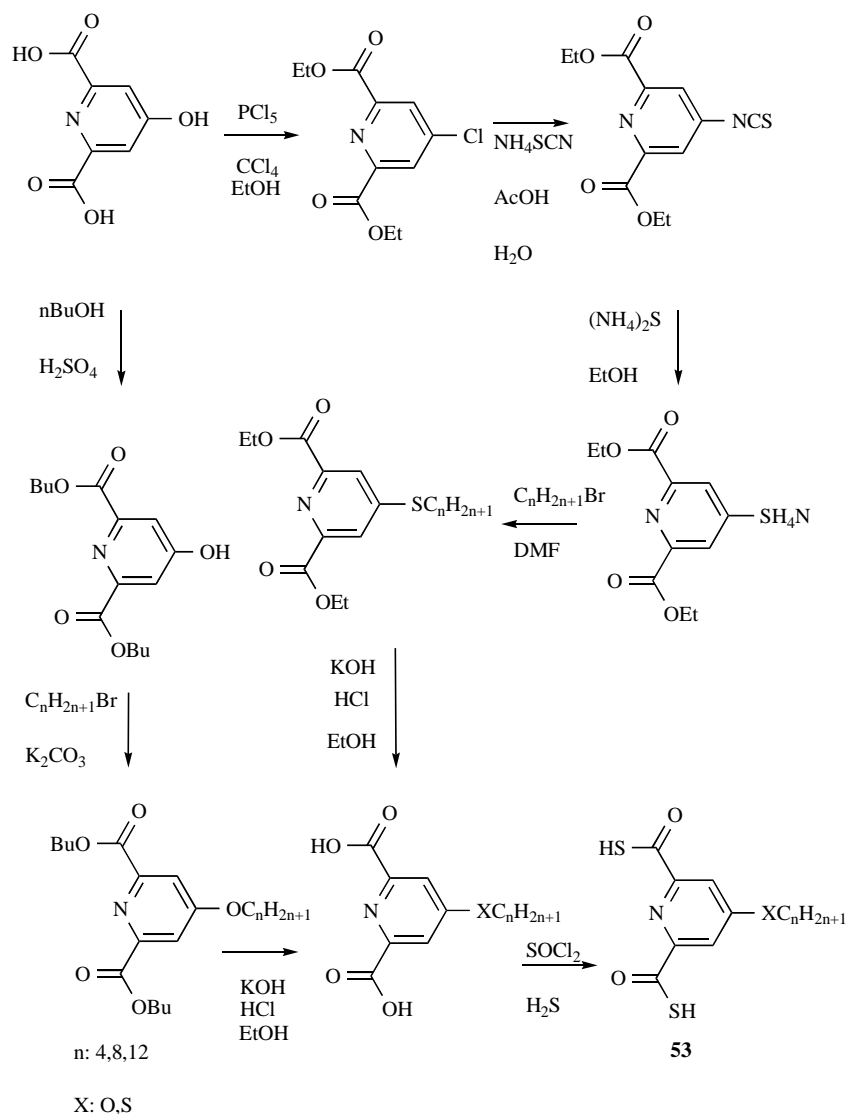


Fig. (49). Synthesis and structure of **53**.

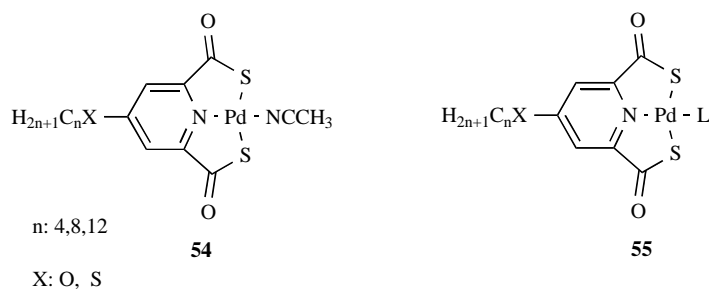


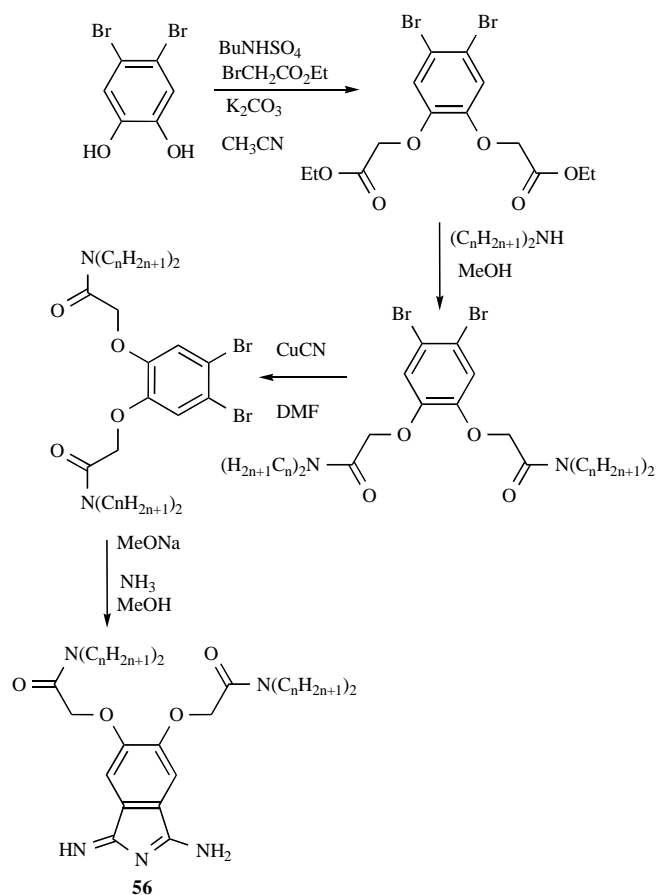
Fig. (50). Structure of **54** and **55**.

framework (**59**) were prepared by Lai and coworkers [128-130]. These ligands incorporate C_nH_{n+1} groups with $n = 8, 10, 12, 14, 15,$ and 16 . The synthesis for **59** is shown in Fig. (**53**).

The Cu(II), Pd(II), Co(II), and V(IV) complexes with derivatives of **59** have been prepared. For example, the Co(II) complex of **59**, namely $[\text{Co}(\mathbf{59})]$ (**60**), is shown in Fig. (**54**). In a typical reaction, the ligand was reacted with the acetate salt of the corresponding metal ion in alcohol under reflux

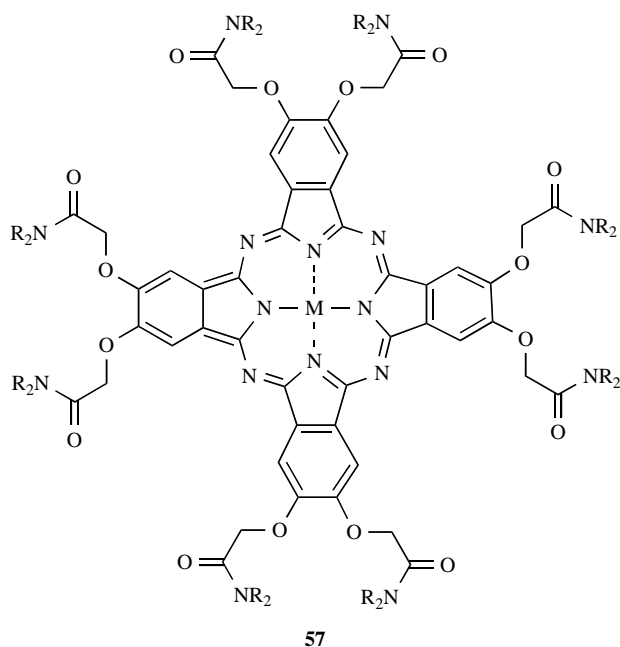
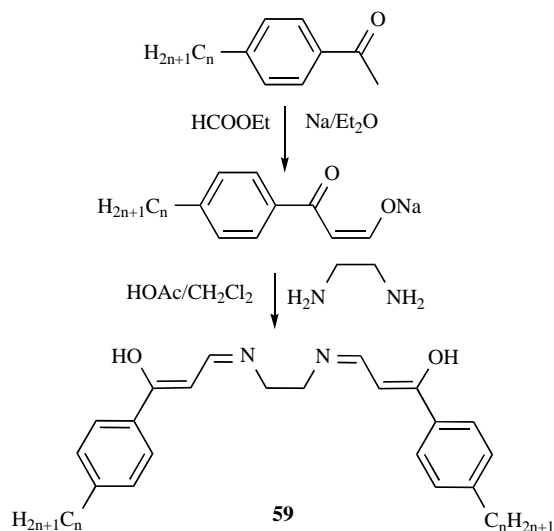
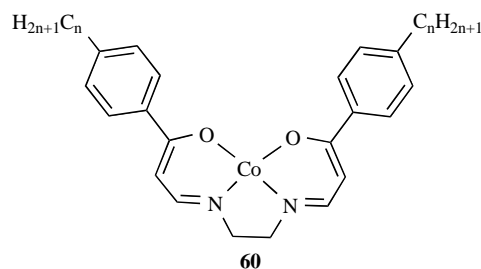
conditions. These complexes form columnar supramolecular structures between $40 - 150^\circ\text{C}$, depending on the metal type and the length and number of hydrocarbons.

Tetradentate alkane-rich ligands with two N-donor and two O-donor groups based on the salicylaldimine Schiff bases were originally prepared by Gray and coworkers [131]. These ligands comprised two groups of C_nH_{n+1} with $n = 4 - 8$. Derivatives of these ligands comprising two C_nH_{n+1} $n = 5, 6, 7, 9$ groups (**61**) [132] and six C_nH_{n+1} $n = 14$ groups [133]

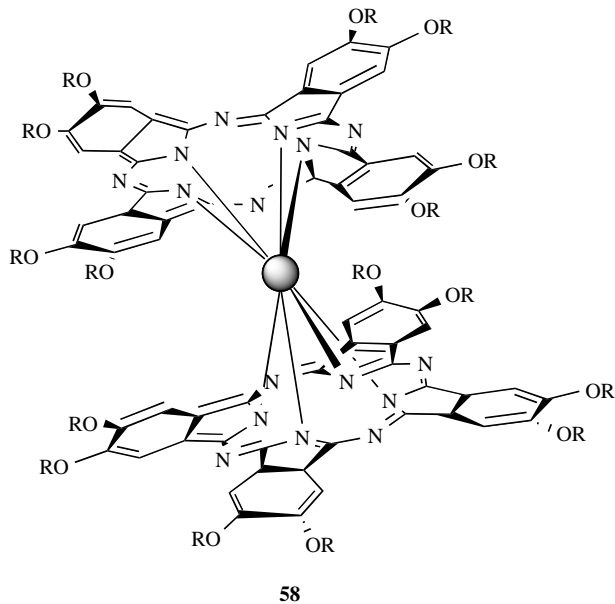
Fig. (51). Synthesis and structure of **56**.

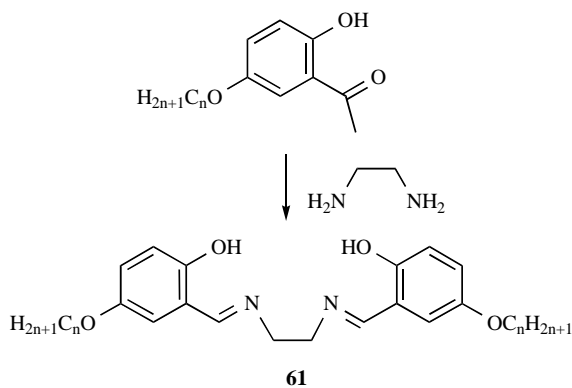
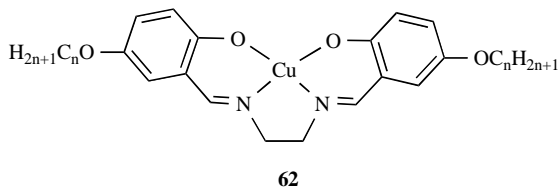
have been reported. The synthesis of **61** is shown in Fig. (55).

The Cu(II) complex (**62**) using the ligand derivatives of **61** have been prepared (Fig. 56). Similarly, the VO(IV) and

Fig. (52). Structure of **57** and **58**.Fig. (53). Synthesis of **59**.Fig. (54). Structure of **60**.

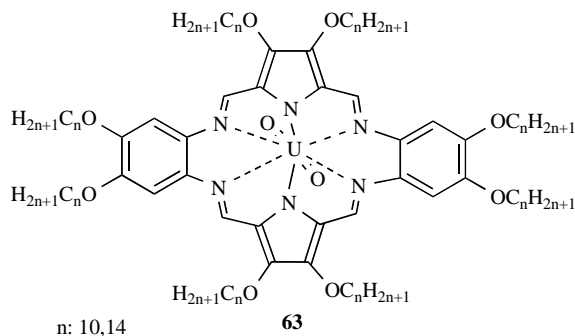
Ni(II) of the early tetradentate salicylaldehyde Schiff bases ligands were reported. These complexes form columnar supramolecular structures between 55 – 120 °C, depending on the metal type and length and number of hydrocarbons.



Fig. (55). Synthesis and structure of **61**.Fig. (56). Structure of **62**.

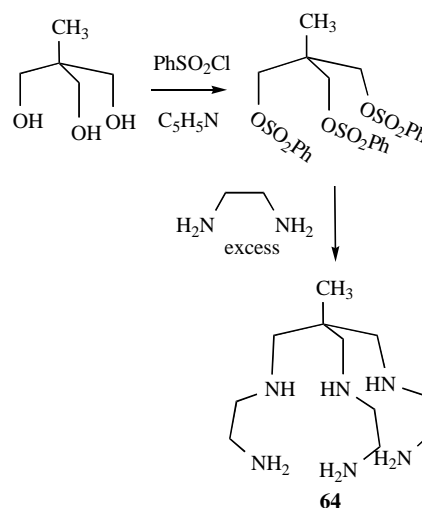
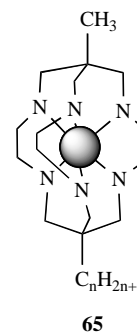
5. POLYDENTATE (>5) SYSTEMS

***N*₆-donors.** The hexadentate alkane-rich ligands with six N-donor groups based on expanded porphyrin frameworks were originally prepared by Sessler and coworkers [134,135]. They comprise eight alkoxy groups varying in C_nH_{n+1} $n = 6, 10, \text{ and } 14$. The ligand forms from the in situ reaction using $[UO_2(OAc)_2]$ as template in hot methanol and the complex **63**, Fig. (57). The uranyl complexes derivatives of **63** self-organize into columnar phases between 106 – 135 °C.

Fig. (57). Structure of **63**.

The hexadentate alkane-rich ligands with six N-donor groups based on 4,4',4''-ethylidynetris(3-azabutan-1-amine) frameworks (**64**) were originally prepared by Walker and coworkers [136]. The synthesis for **64** is shown in Fig. (58).

The Co(III) complex of **65** has been prepared and comprised one alkyl group varying the hydrocarbon unit as C_nH_{n+1} $n = 8, 12, \text{ and } 16$, Fig. (59). The complex was formed the cryptan complex **65** in situ during the incorporation of the alkyl groups on the ligand and the Co(III) served as template. The Co(III) complexes self-organize into Langmuir-Blodgett films on surfaces and metallo-liposomes in water.

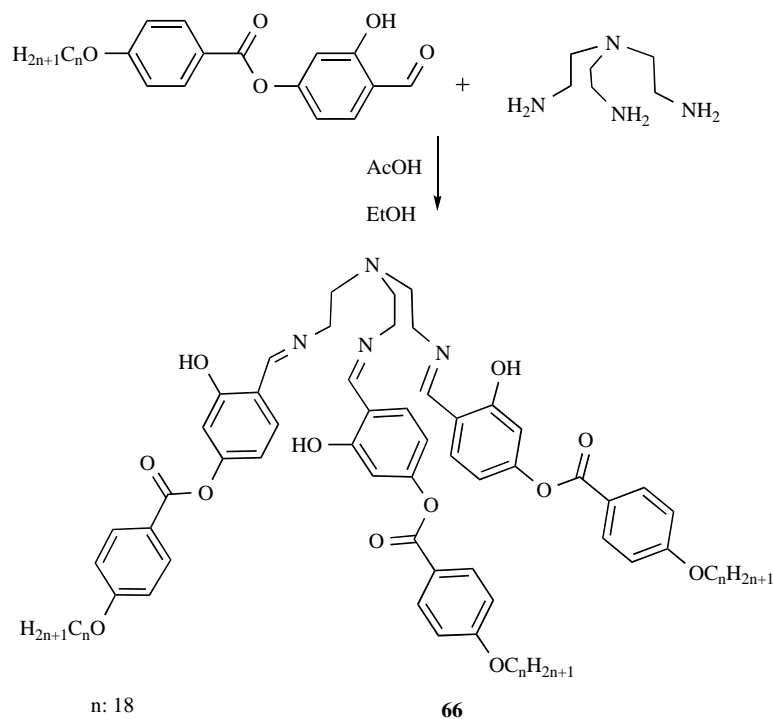
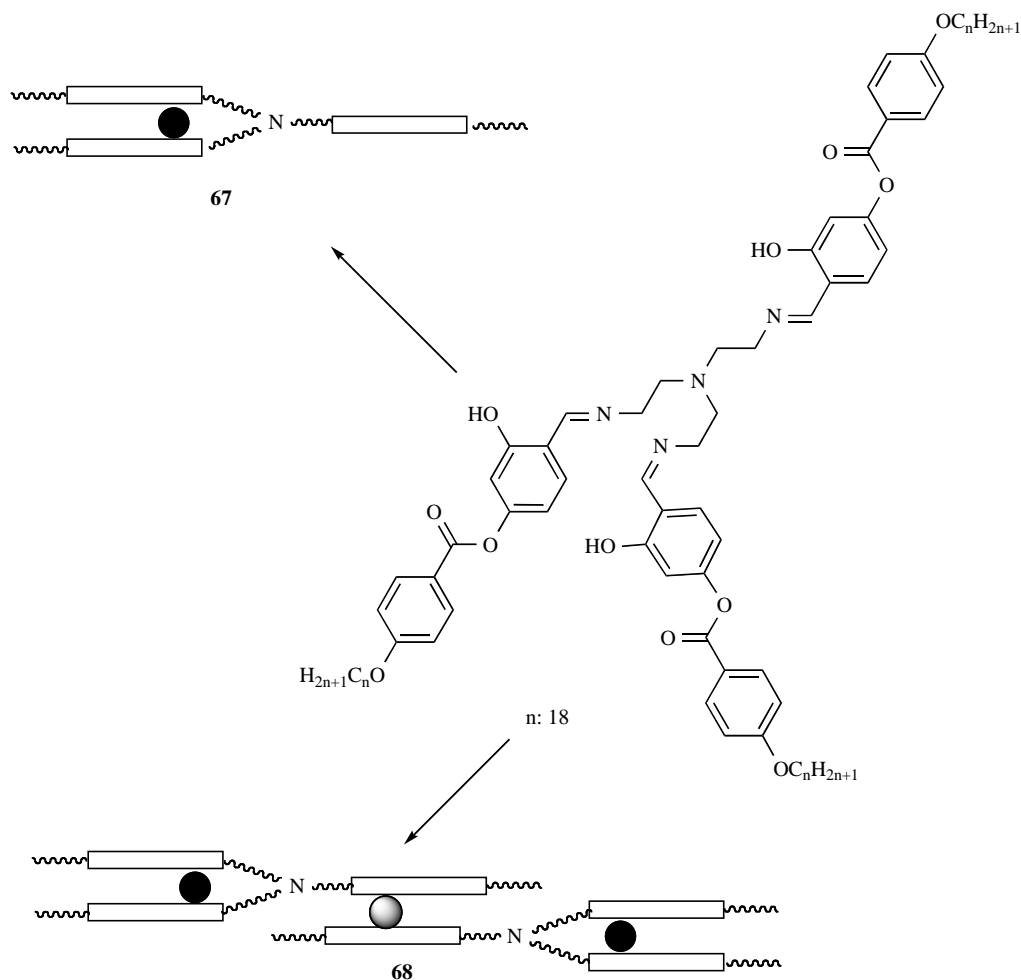
Fig. (58). Synthesis and structure of **64**.Fig. (59). Structure and self-assembly of **65**.

The multidentate alkane-rich ligand (**66**) based on derivatives of salicylaldehyde Schiff bases were prepared by Serrano and coworkers [137]. They comprise a potential coordination sphere of N_4O_3 and three alkoxy groups of $C_{18}H_{37}$. The synthesis for **66** is shown in Fig. (60).

The Cu(II), Ni(II), VO(IV), and Pd(II) complexes of **66** have been prepared as the mononuclear and heteronuclear composites. For example, the ligand was reacted with the acetate salts of the metals in hot ethanol and the corresponding complexes $[Cu(66)]$ (**67**), Fig. (61). The heteronuclear complexes such as $[CuNi_2(66)]$ (**68**) were prepared by subsequent stoichiometric additions of the metal ions to **67**. These complexes self-organize into smectic C phases between 80 – 160 °C.

CONCLUDING REMARKS

The design of molecules that self-organize into supramolecular architectures is at the dawn of its potential. This research is paving the way to molecular materials that may become the core architectures of integrated nanotechnology systems of the future with medical or commodity product applications. Alkane-rich metal complexes provide for an ingenious path to self-organized molecular systems that reach the nanometer and micron scales. It is now evident that small changes on their molecular structure impact their supramolecular chemistry. These molecules are able to self-organize in the neat liquid state (liquid crystals), in aqueous

Fig. (60). Synthesis and structure of **66**.Fig. (61). Structure and self-assembly of **68** and **69**.

media (metallomicelles and metalloliposomes), and on surfaces (Langmuir-Blodgett films). Future research on alkane-rich metal complexes will include investigations of (1) the use of coordination networks of increasing complexity within liquid crystalline phases, (2) the use of heterometallic and hierarchical systems, (3) dynamic supramolecular systems with reversible and quasi-reversible phases, (4) novel supramolecular architectures in aqueous media with applications in biomaterials and drug delivery, and (5) surface interfaces with applications in electrical and optical engineering science.

ACKNOWLEDGEMENTS

We thank the University of Texas at El Paso, the National Science Foundation Grant 0649020, ACS-PRF 44703-GB3, the Lizanell-Colbert Coldwell Foundation and the Ralph Ponce de Leon Boarder Health Research Fund for financial support.

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