



Synthesis and mesomorphic behavior of a homologous series of N-(4-n-alkoxysalicylidene)-4-n-alkoxy anilines and their Copper (II) complexes

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Abstract

Series of metal (Cu) complexes with bidentate Schiff-bases viz. N-(4-n-alkoxy salicylidene)-4-n-alkoxyanilines, obtained by the 1:1 condensation of 4-n-alkoxy salicylaldehyde and 4-n-dodecyloxyaniline, 4-n-hexyloxyaniline, 4-n-octyloxyaniline, 4-n-decyloxyaniline, 4-n-dodecyloxyaniline, 4-n-tetradecyloxyaniline and 4-n-hexadecyloxy aniline, have been prepared and characterized. The synthesis of the ligands N-(4-n-hexyloxysalicylidene)-4-n-alkoxyanilines as well as the complexes and characterization by thermal microscopy for mesomorphism are presented. The ligands are found to exhibit interesting smectic phases (mostly tilted phases in addition to nematic phases and polymorphism, while the complexes showed-orthogonal smectic A, and tilted smectic phases. The mesomorphic range as well as the polymorphism decreases with an increase in chain length. The complexation of these ligands with Cu(II) salt leads to thermally stable metallomesogens possessing larger mesomorphic range and reduced number of mesomorphic phases.

Keywords: Copper complexes, Schiff bases, liquid crystals, metallomesogens, mesomorphism.

Introduction

In the last two decades the investigation of metal containing liquid crystals popularly known as metallomesogens has been one of the most active research areas of material chemistry in particular liquid crystals [1-9]. The importance of metallomesogens gained momentum in a multi fold way because of its multifaceted characteristics viz., variety of molecular geometries which are unknown of organic molecular structures and potential application abilities in optoelectronics and photonic devices. Although, the great potential of metallomesogens as advanced molecular materials has been recognized, the mesomorphic properties of transition metal complexes have not been fully exploited [1-3]. The Schiff bases in particular N-salicylideneaniline with extended aromatic or substituted or unsubstituted aliphatic end chains either at either ends or one end of the molecule is a very important organic moiety which can serve as coordinating ligand and when coordinated with different

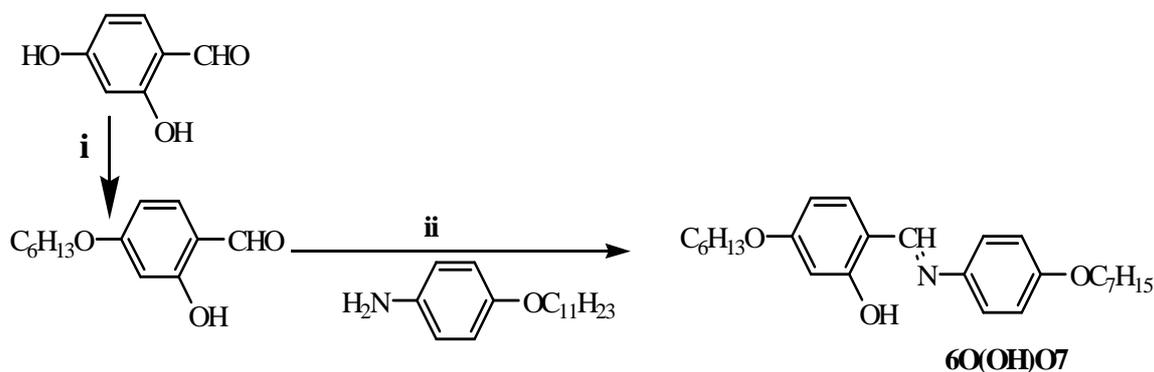
metals belonging to d-block and f-block elements exhibit calamitic liquid crystalline phases and possess potential application abilities. Moreover the characteristic properties of metal ions as well as the complex but subtle mesomorphic properties of the Schiff base ligands in the reported examples [4-9] motivated a systematic study of mesomorphic properties viz., characterization of the ligands, the influence of the complexation of a metal with the ligands to form coordination compounds, thereby affecting the mesomorphic properties of the ligands, which can establish not only the molecular structure-function relationships but also the molecular design principles toward specific functional materials. A variety of substituted N-salicylidene anilines complexes with Cu (II) have been reported [10-18] exhibiting nematic, smectic A, smectic C, smectic C*, smectic B and smectic E phases.

Several research reports appeared on the organo-metallic compounds of Palladium with N (4-n-alkoxybenzylidene)-4'-n-alkylanilines viz., binuclear ortho palladated complexes formed with different bridging groups exhibit ordered mesophases [19-21]. However the introduction of ortho-hydroxyl functional group in benzylidene moiety manifesting the intra-molecular H-bonding not only enhances the stability of the imines but also promotes the tilted smectic phases due to lateral dipole moment. The reported complexes till date are derived from N(4-n-alkoxysalicylidene)-4'-n-alkylanilines or n-alkoxyanilines (hereafter abbreviated as **nO(OH)m** compounds [10-11] with n=12, m=14, 6 and 8; n=m=2,6,10 and 14; n=2,6 and 14, m=10, n=10, m=2,4,6 and 14 and n=7, m=4; with metals of Cu(II) [10-16], Ni(II), VO(II) [17] and Pd(II) [18], or **nO(OH)Om** compounds [22] with n=8 and m=12, m=7,8,10, 12 and 14) coordinated to mono and binuclear copper complexes. As the studies in literature on these compounds are meager [10,11,22-24] and staggered, systematic studies on Schiff base copper (II) complexes containing alkyl / alkoxy anilines are required to understand the structure property relationship.

The anisotropic dispersion forces of the molecules not only contribute to enhance the liquid crystalline behavior but also stabilize the liquid crystalline phases. The shape of the molecule and the presence of polar atoms or groups in the molecule, which manifest the molecular polarizability, contribute the liquid crystalline properties. Our earlier studies on lower homologues N(4-n-butyloxy salicylidene) 4'-n-alkylanilines **4O(OH)6**, **4O(OH)7** and **4O(OPH)8** and their complexes with copper (II) [23], revealed that the ligands exhibit exotic mesophases while the complexes exhibit thermally stable mesophases possessing large thermal ranges and reduced phase variants (number of mesomorphic phases) and only orthogonal mesophases. The introduction of oxygen atom in the aniline moiety of the molecule enhances the polarizability of the molecule and enhances transverse dipole moment of the molecule. The mesomorphism of the complexes of such ligands is not well studied. Hence as a part of our studies on these materials, we present here the synthesis of some homologues N-(4-n-hexyloxysalicylidene)-4'-n-alkoxyanilines **6O(OH)Om** (m = 7, 8, 10, 12, 14, 16) and their complexes with copper (II), phase transition temperatures and characterization of the phases.

The compounds **6O(OH)Om** (m=7,8,10,12,14,16; **2a-f**) were synthesized in a two step reaction as described in scheme 1, in which the hydroxyl group in the 4-position of 2,4-dihydroxybenzaldehyde and 4-acetamidophenol is first replaced by an alkoxy chain. The 4-n-alkoxyanilines obtained after the hydrolysis of relate 4-acetamidopheno; The Schiff base imines were prepared by the reaction of the appropriate 4-n-alkoxyaldehyde with 4-n-alkoxy aniline following the procedures well documented in literature and is presented in scheme1. The complexes were synthesized treating the ligand with copper acetate in presence

of a base. The complexes were isolated in good yields, which are soluble in chloroform, toluene, and dioxane but insoluble in ethanol, methanol and hexane.



Scheme I i. C_6H_5Br , $KHCO_3$, KI, dry acetone, reflux, 48h,
ii. Acetic acid, absolute Ethanol, reflux, 4 h

The new imine compounds presented here were characterized by spectroscopic methods, (1H NMR, IR) and elemental analysis. The molecular structures are in full agreement with the formulae and spectroscopic data. The copper (II) complexes were characterized by IR spectroscopy and elemental analysis. The disappearance of the **OH** band of free ligands in copper (II) complexes indicated that the OH band has deprotonated and coordinated to the metal ions as $-O$. The stretching mode of imine (C=N) group shifted to a lower frequency by around $12-15\text{ cm}^{-1}$ in comparison to free ligand, indicating that the azomethine N atom is involved in the metal-nitrogen bond formation. The results of C=N stretching frequency of both the ligands and the corresponding copper complexes in IR spectra which appeared at 1623 cm^{-1} and 1609 cm^{-1} respectively, are in good agreement with reported results [10,22,23] on similar copper complexes. These observations and elemental analysis confirm the empirical molecular formula and the coordination of the ligand to CU (II) through 2N and 2O, in the 2:1 ratio. The data are also consistent with the expected square planar structure or nearly square planar structure for these types of complexes reported earlier. 1H NMR spectroscopy gives the information of the nature and environment of the proton located in different chemical environments. The imine proton appeared as a singlet at $\delta=8.73$. The hydroxyl group ortho to imine group of the benzylidene ring plays an important role in the thermal stability of these compounds with the formation of strong H-bonding to form a six member ring and reduce the basic character of the nitrogen atom in the imine thereby stabilizing the structure. The phenolic proton in ortho position appeared as a broad singlet at $\delta=13.95$ indicating the strong intramolecular H-bonding. The values δ of linked hydrogen and phenolic hydrogen for the ligands is in good agreement with the reported results on similar salicylideneanilines.

Mesomorphism of the ligands

The thermal behavior viz., phase transition temperatures and mesomorphism of ligands as well as metal complexes, was investigated by combining differential scanning calorimetry, thermal microscopy and miscibility tests with standard reference compounds and the results are summarized in table 1 and table 2. The ligands and complexes are highly stable and transition temperatures are reproduced after several repeated DSC scans. The ligands nO(OH)Om compounds exhibit higher transition temperatures than their counterparts nOm compounds with out hydroxyl groups.

Ligands

The lower homologues **6O(OH)O7** and **6O(OH)O8** exhibit nematic, smectic A, smectic C, smectic I and smectic J phases. The compounds **6(OH)O10**, **6O(OH)O16** exhibited and additional smectic I phase. The lower homologues exhibited nematic and /or smectic A phases over a very narrow thermal range ($\sim 1^{\circ}\text{C}$), followed by smectic C ($\sim 15^{\circ}\text{C}$), smectic I (large phase region of $>30^{\circ}\text{C}$), and smectic J ($\sim -10^{\circ}\text{C}$) phases. This is an indication of the influence of end aliphatic alkyl chain length and their competition with lateral outboard dipolar forces of the molecules. The melting temperatures of imine compounds as observed in DSC increase with increasing chain length of the alkyloxy group. The details of the observation of microscopic textures is presented for two compounds **6O(OH)O8** and **6O(OH)O12** as representative examples since other compounds also exhibited identical phase variant except a change in transition temperatures.

6O (OH) O8, 2b:

The differential scanning calorimetry spectrum of the compound **6O(OH)O8, 2b** has shown four transitions at 62.6°C , 64.1°C , 127.0°C and 127.90°C and at 127.1°C , 126.0°C , 54.4°C and 50.3°C in the heating and cooling cycles respectively. In thermal microscopy the compound **6O(OH)O8** on cooling exhibited a nematic phase (N) at 128.1°C which was identified by its characteristic marble or schlieren (figure 1) texture and less viscous fluid in nature. On further cooling, at 126.4°C the transformation of nematic to smectic A phase is characterized by the formation of focal conic fan texture or homeotropic regions. The temperature range of smectic A phase (0.5°C) is very small. On further cooling the smectic A to smectic C phase is marked by the appearance of familiar fingerprint region characteristic of smectic C phase by slow growth of fine filament lines across the schlieren texture (figure 2) from the homeotropic regions at 125.9°C . These lines have been interpreted [25] as layer undulations caused by stresses due to thermal contraction and the contraction may be exceptionally large because of large increase in tilt angle upon cooling in Sc phase. Such sudden increase in tilt angle leading to layer contraction at the onset of Sc phase is observed earlier [25, 26]. The contraction of the smectic layers of the tilted phase may be exceptionally large because of sudden manifestation of large tilt upon cooling. Moreover the strong possibility of intermolecular H-bonding in these compounds are likely to promote the spiral or helical structure in smectic phase to exhibit striped or domain like texture in smectic C phase. The striped texture resembles those that are exhibited by the racemic (R^* , S^*) compounds possessing helical structure in smectic c^* phase [27]. This texture is paramorphic in nature. The nematic –smectic A and smectic A-smectic C phase transitions are second order and hence could not be detected by differential scanning calorimetry. Even the observation of smectic A phase between nematic and smectic C phases was found to be difficult because of very small thermal range (0.5°C). However, on further cooling, at 110.1°C a platelet texture characteristic of smectic I phase was observed at a different location of the slide supported by the presence of paramorphic schlieren texture ruling out the possibility of smectic F phase. Further cooling of the sample yielded a mosaic texture at 55.1°C characterizing the phase as smectic J rather than smectic G since the expected phase below smectic I is smectic. Even though it is conceivable that it is a smectic G phase by its characteristic mosaic texture such phenomena is ruled out due to the absence of smectic F phase with the observed characteristic textures and also confirmed from miscibility studies.

The compound **6O(OH)O7, 2a** also exhibited identical phase variant NACU with characteristic textures of the respective phases.

6O(OH)O12,2d:

The differential scanning calorimetry spectrum of the compound **6O(OH)O12, 2d** on heating has shown two transitions at 76.9⁰C and 125.2⁰C in heating and at 123.4⁰C and 55.2⁰C in cooling cycles. In the cooling cycle the samples transition temperatures are different which is due to super cooling of the liquid crystalline phases. The sample on cooling exhibited a smooth focal conic fan texture below 125.2⁰C in S₁ phase characteristic of smectic A phase. On further cooling the phase transformed into another phase S₂, at 124.8⁰C and exhibited broken focal conic fan texture with lines across the fans, which is characteristic of smectic C phase. The other compounds **2c**, **2e** and **2f** also exhibited similar textures confirming the smectic A and C phases. The compound **2f**, in addition to smectic A and C phases. Exhibited a platelet texture characteristic of smectic I phase. The observed transition temperatures are in good agreement with the microscopic data. However the phase transition between smectic A (S₁) and smectic C (S₂) which is a second order transition observed by thermal microscopy is not detected by DSC.

Mesomorphism of the Cu (II) complexes:

All the new copper (II) complexes are microcrystalline solids at room temperature and exhibit liquid crystalline behaviour like the previously reported complexes of analogous molecular structures [10, 11, 23, and 24]. Moreover they exhibit higher clearing temperatures and smaller mesomorphic ranges than those of corresponding ligands. All the compounds exhibit enantiotropic liquid crystalline smectic A and smectic C phases.

Cu[6O(O)O10]₂, 3c:

The differential scanning calorimetry spectrum of the compound Cu [6O (O) O10], 3c on heating has shown three transitions at 140.4⁰C (42.7 kJ/mol), 146.3⁰C (0.03 kJ/mol) and 164.8⁰C (10.2 kJ/mol) in heating and at 163.7⁰C (10.2 kJ/mol), 145.1⁰C (0.04 kJ/mol) and 109.0⁰C (33.6 kJ/mol) in cooling cycles. However the observation of smectic C-smectic A phase transition with low enthalpy value and also by thermal microscopic observation of the transition in the compound Cu [6O (O) O10]₂ is missed in an earlier report. In the cooling cycle the samples transition temperatures are different which is due to super cooling of the liquid crystalline phases. The sample on cooling exhibited a smooth focal conic fan texture below 166.1⁰C in S₁ phase characteristic of smectic A phase (figure 5). On further cooling the phase transformed into another phase S₂, at 145.1⁰C and exhibited broken focal conic fan texture (figure 6), which is characteristic of smectic C phase. The focal conic fan and broken focal conic fan textures exhibited by compound 3e characterizing the textures as smectic A and smectic C phases respectively are shown in figures 7 and 8. The other compounds 3a and 3d also exhibited similar textures to confirm the smectic A and C phases. The smectic A-smectic C phase transition could be detected by differential scanning calorimetry in some cases but with a very low value of enthalpy indicating a weak first order transitions. Further the effect of the alkyl chain length on the melting points of the complexes show the opposite trend with respect to the ligands, i.e. a consistent decrease of melting points is observed. However, the compound, 3f, exhibited smectic A and smectic E phases. The complexes in general melt at higher temperatures than the ligands indicating their thermodynamic stability. All the compounds exhibited super cooling and exhibited the smectic phases over a thermal range of 50~ 60⁰C. Further our results are in good agreement with the reported [22] observation of smectic A and smectic C phases in mono nuclear copper complexes of **8O(OH)Om(m=10,12,14)** and lower homologues of **10O(OH)Om (m=7,8,10,12)** and **12O(OH)Om (m=7)** homologue series.

Conclusion

The introduction of oxygen atom in the aniline moiety promoted tilted liquid crystalline phases like smectic C and smectic I phases. The nematic and /or smectic A phases have been observed over a narrow thermal range of ~ 1 °C in homologues even with a chain length which is apparent from the phase range of around 10 °C in C14 and C16 homologues. In general the lateral outboard dipole moment promotes tilted liquid crystalline phases. The increase in chain length promotes molecular segregation leading to smectic phases. The unsubstituted homologue [28] with out ortho hydroxyl group (N-14-n-hexyloxybenzylidene]-4-n-octylaniline, exhibits the phase variant NABG, while ortho hydroxyl substituted homologues **6O(OH)2** [29], **6O(OH)6** [30] and **6O(OH)8** [31] exhibit N, NC and NAC phase variants respectively. However the compounds **6O(OH)7** and **6O(OH)8** possessing of oxygen atoms at both ends exhibit NACU phase variant. Hence the apparent change in phase behaviour viz., increase in thermal range of smectic A phase in higher homologues, indicate the influence of lateral dipole moment (promoted by hydroxyl group aided by end oxygen atoms) and the role of competing influence between the chain length promoting segregation and end oxygen atoms promoting polarizability in deciding the phase variant.

As it can be seen form the data presented in table 2, the copper compounds of different ligands posses similar liquid crystalline properties viz. smectic A and smectic C phases. Marcos et al [10] reported smectic A phase only in **Cu[6O(O)O10]₂** while we observed smectic A and smectic C phases. In our earlier studies [23] we observed only orthogonal phases in the copper complexes, **Cu[4O(O)6]₂** exhibiting smectic A phase only, while the other two complexes **Cu[4O(O)7]₂** and **Cu[4O(O)8]₂** exhibit ABE variant] where the oxygen atom is absent in aniline moiety. Analogous results are also reported about the observation of smectic A phase in other homologues of copper complexes of **nO(OH)6** (**n=6,8,10,12,16 and 18**) and **12O(OH)m** (**m=1-4,6 and 8**). However in the present study tilted smectic C phase in addition to smectic A phase is observed and the results are in.

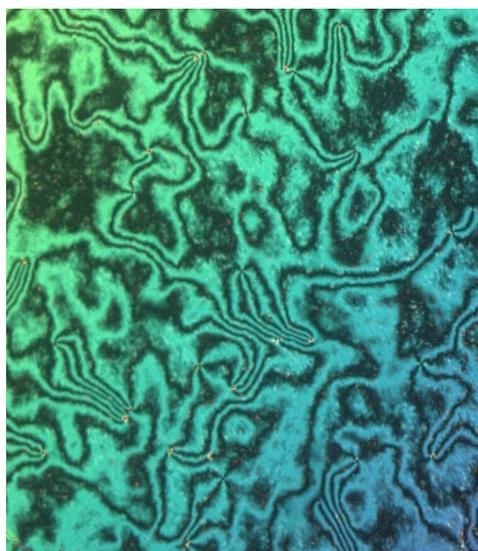


Figure 1: Schlieren texture of nematic phase of **6O(OH)O8** at 127.9°C

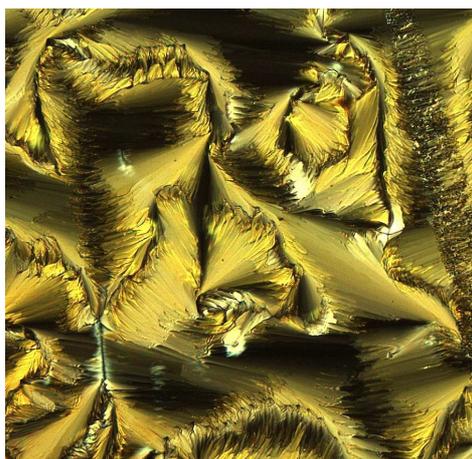


Figure 2: Smectic C schlieren texture with undulation lines of 6O(OH)O8 at 125.8°C

6O(OH)O7;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{\max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{\max} = 403 \text{ nm}$, $\epsilon = 3.90 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 0.88 (t, 6H, CH_3), 1.20–1.80 (m, 18H, CH_2), 3.99 (t, $J = 6.5\text{Hz}$, 4H, CH_2O), 6.45 (d, $J = 0.9 \text{ Hz}$, 1H, H), 6.47 (dd, $J = 0.9, 8.8\text{Hz}$, 1H, H), 6.93 (d, $J = 8.8 \text{ Hz}$, 2H, H), 7.22 (d, $J = 8.8\text{Hz}$, 2H, H), 7.26 (d, $J = 8.8\text{Hz}$, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $\text{C}_{26}\text{H}_{37}\text{NO}_3$: C, 75.80; H, 9.21; N, 3.41. Found: C, 75.87; H, 9.06; N, 3.40.

6O(OH)O8;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{\max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{\max} = 401 \text{ nm}$, $\epsilon = 3.33 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 0.88 (t, 6H, CH_3), 1.20–1.80 (m, 20H, CH_2), 3.99 (t, $J = 6.5\text{Hz}$, 4H, CH_2O), 6.45 (d, $J = 0.9 \text{ Hz}$, 1H, H), 6.47 (dd, $J = 0.9, 8.8\text{Hz}$, 1H, H), 6.93 (d, $J = 8.8 \text{ Hz}$, 2H, H), 7.22 (d, $J = 8.8\text{Hz}$, 2H, H), 7.26 (d, $J = 8.8\text{Hz}$, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $\text{C}_{27}\text{H}_{39}\text{NO}_3$: C, 76.51; H, 9.24; N, 3.22. Found: C, 76.20; H, 9.24; N, 3.29.

6O(OH)O10;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{\max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{\max} = 400 \text{ nm}$, $\epsilon = 3.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 0.88 (t, 6H, CH_3), 1.20–1.80 (m, 24H, CH_2), 3.99 (t, $J = 6.5\text{Hz}$, 4H, CH_2O), 6.45 (d, $J = 0.9 \text{ Hz}$, 1H, H), 6.47 (dd, $J = 0.9, 8.8\text{Hz}$, 1H, H), 6.93 (d, $J = 8.8 \text{ Hz}$, 2H, H), 7.22 (d, $J = 8.8\text{Hz}$, 2H, H), 7.26 (d, $J = 8.8\text{Hz}$, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $\text{C}_{29}\text{H}_{43}\text{NO}_3$: C, 76.22; H, 9.71; N, 3.09. Found: C, 76.78; H, 9.55; N, 3.09.

6O(OH)O12;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{\max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{\max} = 399 \text{ nm}$, $\epsilon = 3.95 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 0.88 (t, 6H, CH_3), 1.20–1.80 (m, 28H, CH_2), 3.99 (t, $J = 6.5\text{Hz}$, 4H, CH_2O), 6.45 (d, $J = 0.9 \text{ Hz}$, 1H, H), 6.47 (dd, $J = 0.9, 8.8\text{Hz}$, 1H, H), 6.93 (d, $J = 8.8 \text{ Hz}$, 2H, H), 7.22 (d, $J = 8.8\text{Hz}$, 2H, H), 7.26 (d, $J = 8.8\text{Hz}$, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $\text{C}_{31}\text{H}_{47}\text{NO}_3$: C, 77.09; H, 9.39; N, 3.14. Found: C, 77.29; H, 9.83; N, 2.91.

6O(OH)O14;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{\max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{\max} = 403 \text{ nm}$, $\epsilon = 2.77 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 0.88 (t, 6H, CH_3), 1.20–1.80 (m, 32H, CH_2), 3.99 (t, $J = 6.5\text{Hz}$, 4H, CH_2O), 6.45 (d, $J = 0.9$

Hz, 1H, H), 6.47 (dd, $J=0.9$, 8.8Hz, 1H, H), 6.93 (d, $J=8.8$ Hz, 2H, H), 7.22 (d, $J=8.8$ Hz, 2H, H), 7.26 (d, $J=8.8$ Hz, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $C_{33}H_{51}NO_3$: C, 77.42; H, 9.89; N, 2.59. Found: C, 77.45; H, 10.08; N, 2.75.

6O(OH)O16;

A yellow solid; yield: 90%; IR (KBr Pellet): ν_{max} in cm^{-1} 2955, 2919, 2849, 1626, 1577, 1250; UV-vis: $\lambda_{max} = 405$ nm, $\epsilon = 2.87 \times 10^4$ L mol⁻¹ cm⁻¹; ¹H NMR (400MHz, CDCl₃): δ 0.88 (t, 6H, CH₃), 1.20–1.80 (m, 34H, CH₂), 3.99 (t, $J=6.5$ Hz, 4H, CH₂O), 6.45 (d, $J=0.9$ Hz, 1H, H), 6.47 (dd, $J=0.9$, 8.8Hz, 1H, H), 6.93 (d, $J=8.8$ Hz, 2H, H), 7.22 (d, $J=8.8$ Hz, 2H, H), 7.26 (d, $J=8.8$ Hz, 2H, H), 8.49(s, 1H, H) 13.95(s, 1H, H); anal.calcd for $C_{35}H_{55}NO_3$: C, 78.59; H, 10.21; N, 2.98. Found: C, 78.16; H, 10.31; N, 2.60.

Cu[6O(O)O7]₂: A brown solid; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2850, 1604, 1436 and 1176; anal.calcd for $C_{52}H_{72}N_2O_6$: C, 70.45; H, 8.10; N, 3.05. Found: C, 70.60; H, 8.20; N, 3.17.

Cu[6O(O)O10]₂: A brown solid; IR (KBr pellet): ν_{max} in cm^{-1} 2922, 2851, 1603, 1436 and 1176; anal.calcd for $C_{58}H_{84}N_2O_6$: C, 71.88; H, 8.80; N, 2.80. Found: C, 71.90; H, 8.74; N, 2.89.

Cu[6O(O)O12]₂: A brown solid; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2852, 1602, 1436 and 1176; anal.calcd for $C_{62}H_{92}N_2O_6$: C, 72.61; H, 9.10; N, 2.79. Found: C, 72.65; H, 9.05; N, 2.73.

Cu[6O(O)O14]₂: A brown solid; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2850, 1604, 1436 and 1176; anal.calcd for $C_{66}H_{100}N_2O_6$: C, 73.30; H, 9.30; N, 2.69. Found: C, 73.33; H, 9.32; N, 2.59.

Cu[6O(O)O16]₂: A brown solid; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2853, 1603, 1436 and 1176; anal.calcd for $C_{70}H_{108}N_2O_6$: C, 73.85; H, 9.59; N, 2.40. Found: C, 73.93; H, 9.57; N, 2.46.

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