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Ionic hexagonal columnar metallomesogens derived from tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine

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A series of transition metal (Ni, Cu, Pd) complexes derived from macrocyclic tetrabenzo-[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine (TAAB) was synthesized and their mesomorphic properties studied by differential scanning calorimetry, polarized optical microscopy and X-ray powder diffraction (XRD). These compounds have eight alkoxy side chains attached around the central molecular core and form disc-like molecules. All the derivatives exhibited columnar mesophases over a wide range of temperature. The mesomorphic behaviour was found to be dependent on the incorporated metal and the carbon length of the alkoxy side chains. The clearing temperatures decreased in the order $M = \mathrm{Ni} > \mathrm{Pd} > \mathrm{Cu}$; this decrease was probably due to the size of the metal ions. Some derivatives with shorter side chains ($n = 10, 12$) were room temperature liquid crystals. All compounds were found to exhibit hexagonal columnar ($\mathrm{Col_h}$) phases which were confirmed by powder XRD.

1. Introduction

Metallomesogens have attracted much attention in the generation of unique structures and novel physical properties due to the rich intrinsic properties of metal ions [1 *a*, *b*]. Incorporation of metal ions into mesogenic structures often alters the molecular geometries, distinct from the organic moiety, this change in molecular shape might generate a contrasting mesomorphism. The presence of metal ions can induce dative interaction between neighbouring molecules, affecting the molecular packing pattern between layers. On the other hand, mesomorphic properties might be totally destroyed upon incorporation of the metal ions due to the formation of a large central core. Several types of macrocyclic structures have been studied, and most of these discotic molecules were found to exhibit interesting columnar phases [1, 2]. Typical examples included (*a*) tridentate ligands, e.g. 1,4,7-triazacyclononanes [2 *a*]; (*b*) tetradentate ligands, e.g. phthalocyanines [2 *b–d*], porphyrins [2 *e*, *f*], tetra-azaporphyrins [2 *g*], tetraazacyclotetradecanes [2 *h*]; (*c*) hexadentate ligands, e.g. hexaazacyclooctadecanes [2 *h*]; and (*d*) octadentate ligands, e.g. bisphthalocyanines [2 *i*, *j*]. The central metal ions used to generate mesogenic compounds were various, including most transition metals (Co, Ni, Pd, Cu, Zn, Pt, Pb, Cr, Mo, W, Lu). Most of these metallomesogenic compounds exhibited hexagonal or rectangular columnar phases as predicted for discotic molecules. Recently another new group of macrocyclic derivatives, the tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]-tetraazacyclohexadecines (TAAB) have been prepared by a unique procedure and their mesomorphic properties studied [3]. These metal-free macrocyclic compounds were found to exhibit hexagonal columnar mesophases as expected. However, no studies of their transition metal complexes was performed. In this paper we report the preparation of three series of metal (Cu, Ni, Pd) complexes derived from these disk-like TAAB derivatives, and the effect of metal ion incorporation on their mesomorphism.

2. Results and discussion

2.1. *Synthesis and characterization*

The synthetic procedures for diprotonated-TAAB derivatives were obtained from the literature [3, 4]. These compounds were prepared by the self-condensation of 3,4-dialkoxy-2-aminobenzaldehydes in the presence of 50% aqueous HBF_4. The overall reaction yields were relatively low, in the range 25–38%, due to the production of other polycyclic compounds [4]. The TAAB derivatives were isolated as light yellow crystals and were characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectroscopic data in $CDCl_3$ showed one characteristic peak at 8.12 ppm which was assigned to imine-H (C=N−H). The metal complexes were obtained by the reaction of the TAAB derivatives with copper(II), nickel(II) or palladium(II) acetate under reflux in

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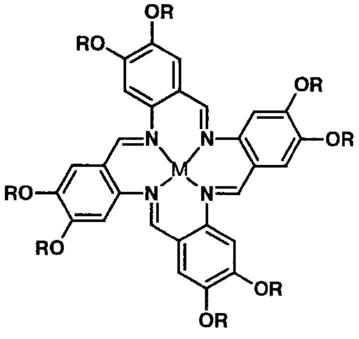
CH_2Cl_2/CH_3OH. The yields were fairly low, in the range 28–35%. All these complexes were characterized by UV-Vis spectroscopy and gave satisfactory elemental analyses.



$1^{2+}(BF_4^-)_2$
M = Cu, Ni, Pd; R = $(CH_2)_nH$

2.2. *Mesomorphic properties*

The mesomorphic properties of the metal-free diprotonated-TAAB derivatives have been studied by Kim *et al.* and the mesophases identified as hexagonal disordered columnar mesophases (Col$_{hd}$) [3]. The columnar mesophases, as predicted, existed over a wide range of temperature including room temperature; the clearing points ranged from 249 to 271°C depending on the alkoxy side chain length (n = 8, 10, 12). In order to study the difference in mesomorphic properties from metal-free derivatives three series of metal complexes—Cu, Ni and Pd—were prepared and studied. These prepared complexes (**1**) were all structurally similar to the metal-free TAAB derivatives; they were all disk-like molecules with eight alkoxy side chains attached to the central core. The formation of columnar mesophases was expected. In fact all these complexes exhibit liquid crystalline behaviour, characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The phase-transition temperatures of the various complexes are given in table 1, each of them showed an enantiotropic columnar mesophase. The crystal-to-mesophase transition temperatures were determined by DSC analysis, however columnar-to-isotropic transition temperatures were not detected by DSC. The absence of the DSC isotropic peak might be due to a relatively low transition enthalpy change for the transition, indicating that the columnar phase was a highly disordered phase. All the clearing temperatures in table 1 were therefore observed by POM. This phenomenon was also observed in metal-free compounds and is probably a nature of the macrocycle ring regardless of the presence or absence of a metal ion.

Table 1. Phase behaviour of metal complexes **1**. n = No. of carbons in the side chain; Cr = crystal phase; Col$_h$ = columnar hexagonal phase; I = isotropic. The transition temperatures were observed by polarizing optical microscopy.

Cu, n = 10		Col$_h$ $\underset{185.4}{\overset{196.2}{\rightleftharpoons}}$ I
12		Col$_h$ $\underset{178.8}{\overset{193.5}{\rightleftharpoons}}$ I
14	Cr $\xrightarrow{25.8}$	Col$_h$ $\underset{180.7}{\overset{190.1}{\rightleftharpoons}}$ I
16	Cr $\underset{38.2}{\overset{58.1}{\rightleftharpoons}}$	Col$_h$ $\underset{186.1}{\overset{195.2}{\rightleftharpoons}}$ I
18	Cr $\underset{43.8}{\overset{66.1}{\rightleftharpoons}}$	Col$_h$ $\underset{176.5}{\overset{183.2}{\rightleftharpoons}}$ I
Ni, n = 10		Col$_h$ $\underset{287.5}{\overset{290.3}{\rightleftharpoons}}$ I
12		Col$_h$ $\underset{267.5}{\overset{270.4}{\rightleftharpoons}}$ I
14	Cr $\underset{20.1}{\overset{27.9}{\rightleftharpoons}}$	Col$_h$ $\underset{262.5}{\overset{265.3}{\rightleftharpoons}}$ I
16	Cr $\underset{54.2}{\overset{59.4}{\rightleftharpoons}}$	Col$_h$ $\underset{236.5}{\overset{238.0}{\rightleftharpoons}}$ I
18	Cr $\underset{43.6}{\overset{51.5}{\rightleftharpoons}}$	Col$_h$ $\underset{230.4}{\overset{233.6}{\rightleftharpoons}}$ I
Pd, n = 10		Col$_h$ $\underset{258.1}{\overset{261.4}{\rightleftharpoons}}$ I
12		Col$_h$ $\underset{246.5}{\overset{250.3}{\rightleftharpoons}}$ I
14		Col$_h$ $\underset{235.6}{\overset{238.1}{\rightleftharpoons}}$ I
16	Cr $\underset{26.3}{\overset{41.6}{\rightleftharpoons}}$	Col$_h$ $\underset{220.2}{\overset{223.8}{\rightleftharpoons}}$ I
18	Cr $\xrightarrow{49.3}$	Col$_h$ $\underset{197.5}{\overset{201.2}{\rightleftharpoons}}$ I

Increasing the carbon lengths of the complexes has in all cases a similar effect of lowering the clearing points and decreasing the mesophase temperature range. These complexes exhibited relatively high clearing points (183–290°C) depending on the metal ion, and they were relatively stable without any decomposition above the clearing temperature. The clearing temperatures decreased in the order Ni > Pd > Cu. Compared with analogous metal-free TAAB derivatives (n = 10, 12) copper complexes have lower clearing temperatures by *c.* 55–67°C; however, nickel complexes have higher temperatures by *c.* 21–27°C. Palladium complexes have clearing temperatures close to those of metal-free TAAB derivatives. This difference in clearing temperatures was probably due to a combination of the size of the metal ions and the possibility of dative coordination of metal ions to neighbouring molecules; which factor played a major part was uncertain. In addition, some complexes with shorter side chains (n = 10, 12) were in fact room temperature liquid crystals. The columnar mesophase temperature range for all the complexes is wide, decreasing as the side chain length increases. In POM these compounds displayed an pseudo focal-conic optical texture, typical of hexagonal columnar structures.

Powder XRD was performed to confirm the structure of the mesophases. A summary of diffraction peaks and lattice constants for the complexes is given in table 2. All compounds displayed the diffraction pattern of a two-dimensional hexagonal lattice, with one intensive peak and two weaker peaks (see the figure). These are characteristic of columnar (Col_h) phases with a *d*-spacing ratio of 1, $(1/3)^{1/2}$ and $(1/4)^{1/2}$, corresponding to Miller indices (1 0 0), (1 1 0) and (2 0 0), respectively. The hexagonal lattices also correlated well with increasing side chain lengths and with the size of the metal ions. However, the absence of a distinct peak for more ordered columnar phases at wide angle is consistent with the DSC analysis of low enthalpies for the columnar-to-isotropic transition.

3. Summary and conclusion

Transition metal (Ni, Cu, Pd) complexes derived from macrocyclic tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine (TAAB) were synthesized and their mesomorphic properties studied. These compounds exhibit hexagonal columnar phases over a wide range of temperatures. The clearing temperatures decrease in the order of Ni > Pd > Cu, this decrease being due probably to the size of the metal ions. Some derivatives were room temperature liquid crystals.

4. Experimental

All chemicals and solvents were reagent grades from Aldrich Chemical Co. The solvents were dried by standard techniques. ^1H and ^{13}C NMR spectra were measured on a Bruker DRS-200 spectrometer. DSC analysis was carried out on a Perkin-Elmer DSC-7 instrument at a scan rate of 10.0°C min^{-1}. POM was carried out on Nikkon MICROPHOT-FXA with a Mettler FP90/FP82HT hot stage system. XRD studies were performed on an INEL MPD-diffractometer with a 2.0 kW CuK_α X-ray source equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace with an accuracy of ± 0.1°. Elemental analysis for carbon, hydrogen, and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyser; the results are listed in table 3. The dialkoxybenzaldehydes [5], 3,4-dialkoxy-2-nitrobenzaldehydes, 3,4-dialkoxy-2-aminobenzaldehydes and diprotonated-octaalkoxy(tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine) tetrafluoroborates [3] were prepared according to literature procedures. Typical syntheses are described below.

4.1. *3,4-Didecanoxybenzaldehyde*

Yield 93%, white solid. ^1H NMR (ppm, $CDCl_3$): 0.85 (t, $J = 6.79$ Hz, $-CH_3$, 6H), 1.23–1.43 (m, $-CH_2$, 28H),

Table 2. Variable temperature XRD data for metal complexes **1**.

Complex		Mesophase	Lattice spacing/Å	*d*-Spacing/Å obs. (calc.)	Miller indices
Cu,	$n = 14$	Col_h 180°C	49.50	42.87 (42.87)	(1 0 0)
				24.86 (24.75)	(1 1 0)
				19.71 (21.43)	(2 0 0)
	16	Col_h 180°C	55.05	47.68 (47.68)	(1 0 0)
				27.63 (27.52)	(1 1 0)
				21.50 (23.84)	(2 0 0)
	18	Col_h 170°C	59.26	51.32 (51.32)	(1 0 0)
				29.86 (29.63)	(1 1 0)
				23.58 (25.66)	(2 0 0)
Ni,	14	Col_h 180°C	48.24	41.78 (41.78)	(1 0 0)
				24.21 (24.12)	(1 1 0)
				19.17 (20.89)	(2 0 0)
	16	Col_h 180°C	54.58	46.86 (46.82)	(1 0 0)
				27.13 (27.06)	(1 1 0)
				22.29 (23.43)	(2 0 0)
	18	Col_h 230°C	59.94	51.91 (51.91)	(1 0 0)
				30.04 (29.97)	(1 1 0)
				23.14 (25.95)	(2 0 0)
Pd,	14	Col_h 180°C	51.88	44.93 (44.93)	(1 0 0)
				26.02 (25.94)	(1 1 0)
				20.87 (22.46)	(2 0 0)
	16	Col_h 170°C	56.86	49.24 (49.24)	(1 0 0)
				28.51 (28.43)	(1 1 0)
				25.04 (26.22)	(2 0 0)
	18	Col_h 190°C	62.90	54.84 (54.84)	(1 0 0)
				31.53 (31.45)	(1 1 0)
				25.40 (27.24)	(2 0 0)

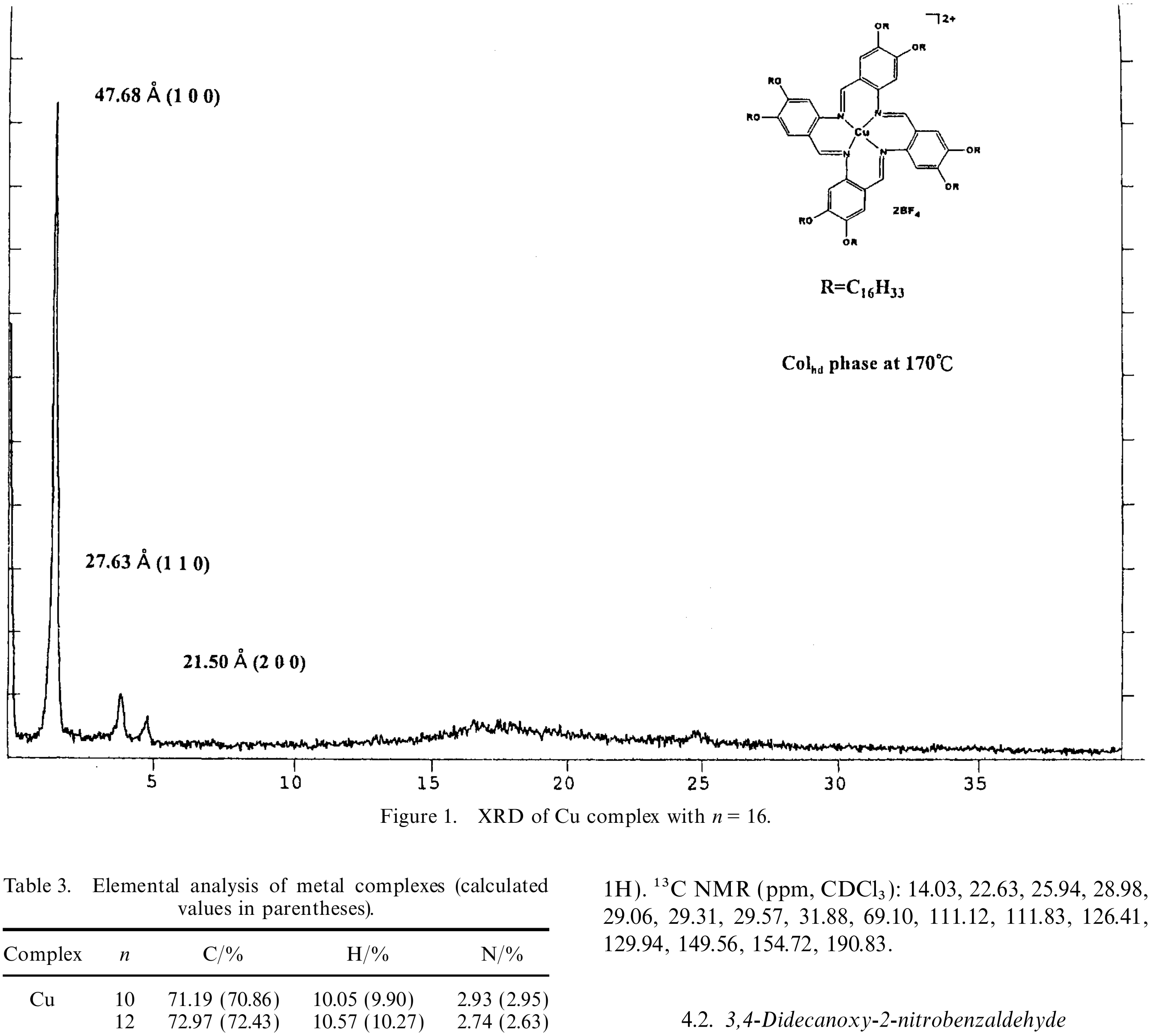


Figure 1. XRD of Cu complex with $n = 16$.

Table 3. Elemental analysis of metal complexes (calculated values in parentheses).

Complex	*n*	C/%	H/%	N/%
Cu	10	71.19 (70.86)	10.05 (9.90)	2.93 (2.95)
	12	72.97 (72.43)	10.57 (10.27)	2.74 (2.63)
	14	73.59 (73.52)	10.73 (10.39)	2.48 (2.38)
	16	73.95 (73.70)	11.05 (10.86)	2.20 (2.14)
	18	75.52 (75.63)	11.38 (11.30)	2.02 (2.00)
Ni	10	68.47 (68.50)	9.66 (9.50)	2.86 (2.95)
	12	72.62 (72.58)	10.25 (10.29)	2.68 (2.64)
	14	73.85 (73.85)	10.80 (10.78)	2.41 (2.39)
	16	75.31 (75.65)	11.03 (10.88)	2.25 (2.18)
	18	76.27 (75.75)	11.27 (11.32)	1.94 (2.01)
Pd	10	67.03 (66.82)	9.54 (9.28)	3.01 (2.88)
	12	68.98 (68.77)	9.98 (9.79)	2.71 (2.59)
	14	63.01 (62.58)	9.02 (8.92)	2.54 (2.35)
	16	71.68 (72.34)	10.71 (10.69)	1.98 (2.10)
	18	72.66 (72.79)	10.98 (10.86)	2.02 (1.97)

1.74–1.86 (m, $-CH_2$, 4H), 4.03 (tt, $J = 1.81$ Hz, $-OCH_2$, 4H), 6.96 (d, $J = 8.63$ Hz, $-C_6H_3$, 1H), 7.36 (s, $-C_6H_3$, 1H), 7.48 (d, $J = 1.81$ Hz, $-C_6H_3$, 1H), 9.79 (s, $-CHO$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.03, 22.63, 25.94, 28.98, 29.06, 29.31, 29.57, 31.88, 69.10, 111.12, 111.83, 126.41, 129.94, 149.56, 154.72, 190.83.

4.2. *3,4-Didecanoxy-2-nitrobenzaldehyde*

A solution of 3,4-didecanoxybenzaldehyde (10.0 g, 0.024 mol) in 50 ml of CH_2Cl_2 was added to a mixture of $NaNO_2$ (1.65 g, 0.024 mol) and conc. HNO_3 (10.0 ml, 0.024 mol). The mixture was stirred at room temperature for 6 h. The solution was washed three times with water, and the organic layer was collected and dried over anhydrous $MgSO_4$. The solution was evaporated to give a yellow solid which was purified by chromatography (silica gel; hexane/CH_2Cl_2, 1 : 1). Recrystallization from CH_2Cl_2/MeOH gave yellow platelet crystals; yield 58%. ^1H NMR (ppm, $CDCl_3$): 0.88 (t, $-CH_3$, 6H), 1.47 (m, $-CH_2$, 28H), 1.91 (m, $-CH_2$, 4H), 4.13 (t, $-OCH_2$, 4H), 7.36 (s, $-C_6H_2$, 1H), 7.56 (s, $-C_6H_2$, 1H), 10.41 (s, $-CHO$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.51, 23.08, 26.25, 29.16, 29.31, 29.68, 29.73, 29.94, 32.30, 69.85, 108.53, 111.03, 125.66, 143.98, 152.69, 153.60, 188.34.

4.3. *3,4-Didecanoxy-2-aminobenzaldehyde*

A mixture of 3,4-didecanoxy-2-nitrobenzaldehyde (5.0 g, 0.01 mol) and palladium on carbon (0.20 g, 10%) in 100 ml CH_2Cl_2 was added dropwise to a solution of $HCOONH_4$ (3.40 g, 0.05 mol) in 20 ml of CH_3OH. The solution was stirred at room temperature for 30 min. The reaction solution was filtered through Celite 405 to remove solid Pd/C and the filtrate was extracted with water. The solution was dried over $MgSO_4$, then concentrated to give a brown solid. This was purified by column chromatography (silica gel; CH_2Cl_2), and yellow crystals were obtained after recrystallization from CH_2Cl_2/MeOH; yield 82%. ^1H NMR (ppm, $CDCl_3$): 0.89 (t, $-CH_3$, 6H), 1.44 (m, $-CH_2$, 28H), 1.84 (m, $-CH_2$, 4H), 3.98 (t, $-OCH_2$, 4H), 6.05 (s, $-C_6H_2$, 1H), 6.90 (s, $-C_6H_2$, 1H), 9.62 (s, $-CHO$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 13.91, 22.50, 25.79, 29.32, 29.98, 31.73, 68.60, 70.74, 99.02, 111.35, 120.22, 140.32, 147.40, 156.86, 191.25.

4.4. *Diprotonated-octadecanoxy(tetrabenzo[b,f,j,n]-[1,5,9,13]tetraazacyclohexadecine) tetrafluoroborate*

3,4-Didecanoxy-2-aminobenzaldehyde (3.0 g, 0.007 mol) was dissolved in hot ethanol (100 ml), and to the solution was slowly added 5 drops of 50% aqueous HBF_4. The solution was heated under gentle reflux for 6 h. The solution was filtered while hot and a black solid collected after the solution was cooled to room temperature. The solid was washed several times with ethanol; yield 28%. ^1H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 24H), 1.52 (m, $-CH_2$, 112H), 1.76 (m, $-CH_2$, 16H), 3.94 (q, $-OCH_2$, 16H), 6.58 (s, $-C_6H_2$, 4H), 6.72 (s, $-C_6H_2$, 4H), 8.12 (s, $-CHO$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 14.53, 23.15, 26.56, 29.75, 29.94, 30.31, 69.36, 69.65, 99.85, 117.62, 119.84, 138.40, 149.25, 154.66, 157.54. IR (KBr): 2954.4, 1280.3, 1229.5, 1124.8, 1083.5, 1054.5 cm^{-1}.

4.5. *Octadecanoxy(tetrabenzo[b,f,j,n][1,5,9,13]-tetraazacyclohexadecine) copper(II) tetrafluoroborate*

A mixture of diprotonated-octadecanoxy- TAAB tetrafluoroborate (0.50 g, 0.28 mmol) dissolved in 50 ml of CH_2Cl_2, and copper(II) acetate monohydrate (0.03 g, 0.28 mmol) dissolved in 10 ml of MeOH, was heated under reflux for 12 h. The reaction mixture was concentrated to dryness and the solid redissolved in CH_2Cl_2. The solution was filtered and evaporated to give an orange–brown solid. A light orange–brown solid were obtained after recrystallization from CH_2Cl_2/ethyl acetate; yield 43%. IR (KBr): 2955.7, 2924.8, 2853.4, 1614.8, 1587.8, 1553.1, 1516.4, 1462.4, 1366.0, 1283.0, 1229.0, 1119.0, 1084.3, 1057.3 cm^{-1}. Elemental analysis: calc. for $C_{172}H_{308}N_4O_8B_2F_8Cu$ C 75.63, H 11.30, N 2.00; found C 75.52, H 11.38, N 2.02%.

4.6. *Octadecanoxy(tetrabenzo[b,f,j,n][1,5,9,13]-tetraazacyclohexadecine) nickel(II) tetrafluoroborate*

Yield 27%. IR (KBr): 2959.5, 2919.0, 2847.6, 1612.9, 1591.7, 1564.7, 1520.3, 1462.4, 1358.2, 1277.2, 1229.0, 1211.6, 1126.7, 1036.0 cm^{-1}. Elemental analysis: calc. for $C_{172}H_{308}N_4O_8B_2F_8Ni$ C 75.65, H 10.88, N 2.18; found C 75.31, H 11.03, N 2.25%.

4.7. *Octahexadecanoxy(tetrabenzo[b,f,j,n][1,5,9,13]-tetraazacyclohexadecine) palladium(II) tetrafluoroborate*

Yield 39%. IR (KBr): 2559.5, 2919.0, 2851.5, 1618.6, 1585.9, 1556.9, 1518.3, 1466.3, 1362.1, 1279.1, 1230.9, 1124.8, 1036.0 cm^{-1}. Elemental analysis: calc. for $C_{156}H_{276}N_4O_8B_2F_8Pd$ C 72.34, H 10.69, N 2.10; found C 71.68, H 10.71, N 1.98%.

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