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Supramolecular organization in copper(I) isocyanide complexes: copper(I) liquid crystals from a simple molecular structure

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The synthesis, characterization and mesomorphic properties of five series of copper(I) isocyanide complexes [CuCl(CNR)] [R = $C_6H_4C_6H_4OC_nH_{2n+1}$ (L^A), $C_6H_4OOCC_6H_4OC_nH_{2n+1}$ (L^B), $C_6H_4COOC_6H_4OC_nH_{2n+1}$ (L^C), $C_6H_3\{3,4\text{-}(OC_nH_{2n+1})_2\}$ (L^D), $C_6H_2\{3,4,5\text{-}(OC_nH_{2n+1})_3\}$ (L^E); $n = 4, 6, 8, 10, 12$] are described. Although some of the free isocyanides used are not liquid crystals, all the copper isocyanide complexes prepared, except four, are mesogens. The copper derivatives Cu–L^A show smectic A (S_A) and smectic C (S_C) mesophases, the complexes Cu–L^B and Cu–L^C display only S_A phases and the di- and tri-alkoxyphenylisocyanide copper complexes, Cu–L^D and Cu–L^E, display hexagonal columnar mesophases, some of them at room temperature.

These copper isocyanide complexes are compared with the similar gold(I) isocyanide complexes [AuClCNR] and the influence of the metallic atom on the mesogenic behaviour for representative complexes is discussed.

Introduction

Supramolecular self-organized systems have received increasing attention in recent years, due to they fact that they can display special catalytic, optical or electrical properties.[1–4] A good example of this type of behaviour is represented by liquid crystals. The tendency for a given molecule to display a particular liquid-crystalline superstructure is related to its shape, aspect ratio, and polar properties.[5] Rod-like molecules generally assemble into nematic or smectic phases, whereas disc-like molecules tend to display columnar phases. Materials with columnar phases can also be generated from molecules which are not disc-shaped but have shapes which upon aggregation are able to fill circular spaces.[6–10]

In recent years the diversity of metallomesogens has grown to include different types of complexes containing a wide range of metals and ligands.[11–19] Some of them are based on isocyanide complexes: some complexes of Au(I),[7,9,20–27] Pd(II) and Pt(II),[8,27–30] and very recently a few isocyanide complexes of iron(0).[31] In this context and as a continuation of our previous studies on mesomorphic metal isocyanide complexes, we report here the synthesis and liquid crystalline behaviour of copper(I) isocyanide complexes of type [CuCl(CNR)] (R = $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_4COOC_6H_4OC_nH_{2n+1}$, C_6H_4OOC-$C_6H_4OC_nH_{2n+1}$, $C_6H_2\{3,4\text{-}(OC_nH_{2n+1})_2\}$, $C_6H_2\{3,4,5\text{-}(OC_nH_{2n+1})_3\}$; $n = 4, 6, 8, 10, 12$). To the best of our knowledge liquid crystals based on copper(I) isocyanide complexes have not been described before.

Results and discussion

Synthesis and characterization

The copper(I) isocyanide complexes have been prepared by reaction of CuCl with the appropriate isocyanide ligand (Scheme 1), as described in the literature for similar copper(I) isocyanide derivatives.[32]

The C,H,N analyses for the complexes, yields, and relevant IR data are given in the Experimental section. The IR spectra in dichloromethane are all similar, and show one $\nu(C{\equiv}N)$ absorption for the isocyanide group at higher wavenumbers (*ca.* 30 cm^{-1}) than for the free isocyanides, as a consequence of coordination.[32] It is interesting to note that when the IR spectra are recorded in diluted solutions ($\leqslant 10^{-1}$ M), an additional weak band is observed in the $\nu(C{\equiv}N)$ region, at about 2197 cm^{-1}. This high frequency band suggests the presence of a small amount of cationic species of the type $[Cu(CNR)_n]^+$.[33] The observation of this cationic complex is possibly due to some ligand scrambling in solution similar to that described for analogous complexes [AuXL] (X = anionic ligand, X = neutral donor ligand).[34] Related $[Ag(CNR)_2]^+$ complexes are also known.[35,36]

The ^1H NMR spectra of the metal complexes are all very similar within each family. L^A, L^B and L^C derivatives, show, as expected, four somewhat distorted "pseudodoublets" (a deceptively simple pattern arising from the strictly speaking AA′XX′ spin systems) for the two phenyl groups present in the molecule. In addition, the first methylene group of the alkoxy chain is observed as a virtual triplet at 3.9–4.1 ppm. The remaining chain hydrogens appear in the range 0.8–1.8 ppm. The ^1H NMR spectra of the L^D complexes show three signals for the aromatic protons as expected for an AMX spin system. The L^E derivatives show one singlet for aromatic protons, corresponding to the two equivalent protons present in the molecule. Table 1 lists the assignments made for copper isocyanide complexes.

Mesogenic behaviour

All the copper isocyanide complexes prepared are mesomorphic, except the complexes $[CuCl(CNC_6H_4OOC\text{-}C_6H_4OC_4H_9)]$, $[CuCl(CNC_6H_3\{3,4\text{-}(OC_nH_{2n+1})_2\})]$ ($n = 4, 6$) and $[CuCl(CNC_6H_2\{3,4,5\text{-}(OC_4H_9)_3\})]$. Their optical, thermal and thermodynamic data are collected in Table 2. The free isocyanides L^A, L^B, and L^C display nematic and/or smectic A phases in the range 60–90 °C.[29] Their copper derivatives Cu–L^A show smectic A (S_A) and smectic C (S_C) mesophases, while the complexes Cu–L^B and Cu–L^C display only S_A phases. The

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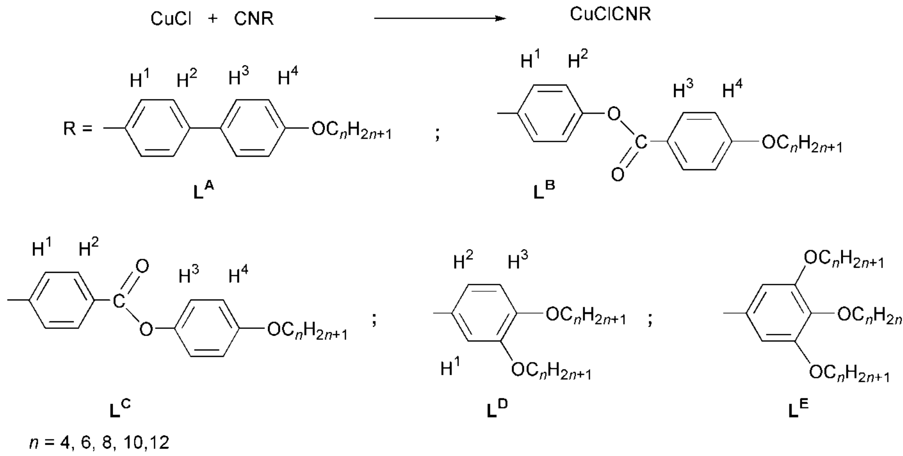

Scheme 1

smectic A (S_A) mesophases have been identified by optical microscopy, by their typical mielinic and homeotropic textures on heating and their focal-conic fan texture on cooling from the isotropic liquid. The S_C mesophases show the typical schlieren texture which does not flash when subjected to mechanical stress, and the broken focal-conic fan texture on cooling from the S_A phase with a focal-conic fan texture. The range of the S_C phase increases, and that of the S_A phase decreases, as the length of the chain increases.

The melting points decrease with increasing length of the alkoxy chain in each series. They also decrease in the order Cu–L^C > Cu–L^B. This same trend observed in Cu–L^C compared to Cu–L^B compounds (which differ only in the position of the ester group) has been found in analogous organic cyanoaryl esters,[35] and in similar mesogenic iron isocyanide complexes.[31]

The coordination of an isocyanide to a metal to give a metal isocyanide complex produces generally an increase of the molecular polarizability, and as a consequence an increase of transition temperatures and the obtention of more ordered mesophases, compared to the free isocyanide.[7,9,21–26] The same trend is observed in the copper complexes described here.

It is also interesting to compare the thermal properties of the copper(I) complexes Cu–L^A with those of the previously reported gold(I) complexes [AuCl(CNC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$) (Fig. 1).[23] It can be seen that, except for the shorter alkoxy chains ($n=4$, 6), the copper complexes show lower melting temperatures than the gold derivatives. Moreoever, the copper complexes show lower clearing points, shorter mesogenic ranges, and an enhancement of smectic C phases.

When the isocyanides used are L^D or L^E, the molecular shape of the metal complexes cannot be considered rod-like any longer. The free isocyanides are not liquid crystals, but again the presence of the metal induces mesomorphism, and most of the di- and tri-alkoxyphenylisocyanide copper complexes (Cu–L^D and Cu–L^E) display enantiotropic liquid crystal behaviour, some of them at room temperature. The optical textures, when viewed with a polarizing microscope on cooling from the isotropic melt, are characteristic of hexagonal columnar phases and display linear birefringent defects, large areas of uniform extinction and fan domains.[7,26,36]

The derivatives [CuCl(CNC$_6$H$_3${3,4-(OC$_n$H$_{2n+1}$)$_2$})] ($n=4$, 6) are not liquid crystals, but exist in two solid polymorphic forms, C and C′ with different melting points, and exhibit the so-called double melting behaviour.[37] When a pristine sample of these compounds is heated at 10 °C min^{-1}, C melts first and a homogeneous mixture of isotropic liquid and solid C′ is obtained. On further heating, the melting of the C′ crystals is observed. On cooling from the isotropic liquid, the compound crystallizes in the C form. A second heating cycle shows that the sample melts completely at the melting temperature of C, but if the temperature is maintained above the melting point of C but below that of C′, the liquid resolidifies to the C′ form. Further heating produces an isotropic liquid at the melting point of C′.

The mesophases of [CuCl(CNC$_6$H$_3${3,4-(OC$_8$H$_{17}$)$_2$})] and [CuCl(CNC$_6$H$_2${3,4,5-(OC$_{12}$H$_{25}$)$_3$})] were identified as columnar hexagonal by X-ray diffraction. The pattern of [CuCl(CNC$_6$H$_3${3,4-(OC$_8$H$_{17}$)$_2$})] at 88 °C contains a set of three sharp reflections in the small-angle region with a reciprocal spacing ratio of $1:\sqrt{3}:\sqrt{7}$, and a diffuse halo in

Table 1 ^{1}H NMR data (CDCl$_3$) for the copper complexes (Cu–L) for $n=12$ (shifts in ppm downfield relative to internal TMS; coupling constants in Hz)

	Aromatic rings						
	H^1	H^2	H^3	H^4	O–CH$_2$ (*para*)	O–CH$_2$ (*ortho*)	–(CH$_2$)$_{n-2}$CH$_3$
Cu–L^A	7.49 (d, 2H) $N_{1,2}=8.64$	7.59 (d, 2H)	7.47 (d, 2H) $N_{3,4}=8.60$	6.98 (d, 2H)	4.00 (t, 2H, $J=6.54$)		1.83–0.86 (m)
Cu–L^B	7.52 (d, 2H) $N_{1,2}=8.92$	7.30 (d, 2H)	8.11 (d, 2H) $N_{3,4}=8.95$	6.97 (d, 2H)	4.04 (t, 2H, $J=6.57$)		1.84–0.85 (m)
Cu–L^C	7.61 (d, 2H) $N_{1,2}=8.63$	8.28 (d, 2H)	7.11 (d, 2H) $N_{3,4}=9.04$	6.93 (d, 2H)	3.96 (t, 2H, $J=6.56$)		1.81–0.85 (m)
Cu–L^D	6.89 (d,1H) $J_{1,2}=2.06$	6.99 (dd, 1H)	6.80 (d, 1H) $J_{2,3}=8.61$		4.00 (t, 2H, $J=6.48$)	3.96 (t, 2H, $J=6.55$)	1.86–0.85 (m)
Cu–L^E	6.62 (s, 2H)				3.95 (t, 2H, $J=6.57$)	3.92 (t, 4H, $J=6.53$)	1.84–0.85 (m)

$N_{1,2}={}^3J_{1,2}+{}^5J_{1,2'}$; $N_{3,4}={}^3J_{3,4}+{}^5J_{3,4'}$.

Table 2 Optical, thermal and thermodynamic data of the copper complexes [CuCl(CNR)]

Compound	*n*	Transition^a	Temperature^b/°C	ΔH^b/KJ mol^{-1}
Cu–L^A	4	C···I	185.0	34.9
		I···S_A	177.4	−2.9
		S_A···C	144.5	−14.4
		C···C′	132.0	−6.7
Cu–L^A	6	C···C′	101.7	−6.1
		C′···S_A	170.7	22.1
		S_A···I	203.8	3.6
Cu–L^A	8	C···S_A	114.3	14.8
		S_A···I	211.9	3.8
Cu–L^A	10	C···S_C	113.3	17.3
		S_C···S_A	133.0^c	
		S_A···I	212.0	2.8
Cu–L^A	12	C···C′	65.7	3.2
		C′···S_C	111.2	17.4
		S_C···S_A	156.0^c	
		S_A···I	212.0	2.2
Cu–L^B	4	C···C′	166.7	4.2
		C′···C″	171.9	4.5
		C″···I	178.5	17.2
Cu–L^B	6	C···S_A	152.1	23.9
		S_A···I	186.4	3.8
Cu–L^B	8	C···C′	115.1	1.8
		C′···C″	134.4	6.1
		C″···S_A	152.6	13.1
		S_A···I	192.5	4.0
Cu–L^B	10	C···C′	131.2	4.5
		C′···S_A	153.9	11.3
		S_A···I	195.0	4.12
Cu–L^B	12	C···C′	126.4	6.7
		C′···C″	135.8	9.1
		C″···S_A	146.3	11.6
		S_A···I	192.6	3.0
Cu–L^C	4	C···S_A	186.2	16.6
		S_A···I	256.3	2.5
Cu–L^C	6	C···S_A	184.5	14.1
		S_A···I	270.0^c	2.8
Cu–L^C	8	C···S_A	176.8	14.5
		S_A···I	275.0^c (dec)	
Cu–L^C	12	C···S_A	166.7	17.0
		S_A···I	256.7 (dec)	1.5
Cu–L^D	4	C+C′···I+C′	71.7^d	5.8
		C′···I	80.3^d	11.1
		I···C	59.7	−9.6
		C···I	68.3	10.6
Cu–L^D	6	C+C′···I+C′	74.1^d	14.3
		C′···I	78.3^d	10.47
		I···C	67.5	−13.8
		C···I	76.0	14.3
Cu–L^D	8	C···Col_h	80.3	19.5
		Col_h···I	96.5	1.0
Cu–L^D	10	C···Col_h	81.4	20.8
		Col_h···I	115.0	1.2
Cu–L^D	12	C···Col_h	86.0	23.5
		Col_h···I	124.0	1.3
Cu–L^E	4	C···C′	82.3	0.5
		C···I	99.1	10.9
Cu–L^E	6	Col_h···I	104.9	1.38
Cu–L^E	8	g···Col_h	3.4	
		Col_h···I	83.6	1.5
Cu–L^E	10	g···Col_h	9.0	
		Col_h···I	75.3	2.1
Cu–L^E	12	C···Col_h	18.1	12.9
		Col_h···I	93.8	2.3

[a] C, crystal; S, smectic; g, glass; I, isotropic liquid. [b] Data refer to the second DSC cycle starting from the crystal. Temperature data as peak onset. [c] Microscopic data. [d] Data refer to the first DSC cycle starting from the crystal.

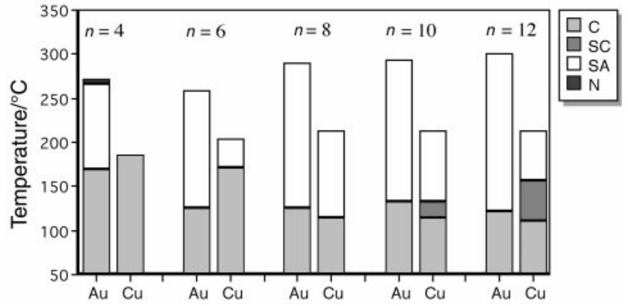

Fig. 1 Comparison of the transition temperatures of [MCl($CNC_6H_4C_6H_4OC_6H_4OC_nH_{2n+1}$)] complexes (M = Au, Cu).

the large-angle region. The reciprocal spacing ratio is consistent with a hexagonal lattice with a lattice constant $a = 30.0$ Å. The broad halo corresponds to a distance of about 4.5 Å and is characteristic of the correlation between the conformationally-disordered chains. Scattering related to the stacking distance is not observed in the pattern. The pattern of [CuCl($CNC_6H_2\{3,4,5\text{-}(OC_{12}H_{25})_3\}$)] at 50 °C contains four sharp reflections in the small-angle region with a reciprocal spacing ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ characteristic of a hexagonal lattice, and a diffuse halo at 4.5 Å characteristic of the molten hydrocarbon chains. This affords a lattice constant $a = 34.3$ Å. The four small-angle maxima are indexed respectively as the (10), (11), (20) and (21) reflections from the two-dimensional hexagonal lattice. The absence of the (20) reflection for [CuCl($CNC_6H_3\{3,4\text{-}(OC_8H_{17})_2\}$)] (see above) is not an uncommom phenomenon in columnar haxagonal mesophases, and it has been shown that the intensity of an X-ray reflection decreases drastically when it corresponds to a minimum of the structure factor.[38]

In these two compounds the columnar structure consists of a central rigid core that contains the halogen and copper atoms and the isocyanide and phenyl groups, and a peripheral flexible cover containing a number of aliphatic chains. It is reasonable to consider that in fact the columns are not generated by staking of discrete molecules but by the supramolecular assembling of somewhat randomly oriented molecules. The absence of an X-ray reflection corresponding to the repeating distance along the columnar axis does not allow one to determine more details about the arrangement of the molecules. However, this point is not relevant, because we assume that there are no discrete discs. Instead, because of the molecular shape, each single molecule is able to fill a portion of the column cross-section and the individual molecules self-assemble into columns which in turn self-assemble in a two-dimensional hexagonal lattice.

It is interesting to compare the thermal behaviour of the trialkoxyphenyl derivatives of copper described here with that of the previously reported similar gold(I) derivatives.[7] For the copper complexes the transition temperatures decrease with increasing length of the alkoxy chain, while for gold(I) derivatives the opposite behaviour is observed. The influence of the length of the terminal alkoxy chains on the thermal behaviour of the material is not a simple matter, but in general an increase of length of the alkoxy chains can cause mainly two opposite effects: an increase of the molecular polarizability leading to higher transition temperatures; and an increase of the degree of disorder of the chains producing lower transition temperatures. Consequently the variation of the transition temperatures upon changing the length of the alkoxy chains depends on the predominant factor. In our copper complexes, where a decrease in the melting point for larger chains is observed, the increase in the degree of disorder of the chain seems to be the dominant factor. In the gold derivatives the increase of the molecular polarizability would be the predominant factor.

In conclusion, the copper(I) isocyanide complexes exhibit mesomorphic properties and provide the first examples of mesogenic copper(I) isocyanide derivatives. Modifications in the organic part of the molecule permit the tuning of the mesomorphic properties. In the case of bulky ligands, such as the di- and tri-substituted isocyanides, the shape of the molecule is dominated by the organic ligand, and columnar mesophases are formed. However, it is important to note that non-mesomorphic isocyanides, di and tri-alkoxyphenyl derivatives, lead to liquid-crystalline materials upon complexation to a CuCl moiety.

Experimental

Literature methods were used to prepare CNR (R = $C_6H_4C_6H_4OC_nH_{2n+1}$,[25] $C_6H_4COOC_6H_4OC_nH_{2n+1}$,[29] $C_6H_4OOCC_6H_4OC_nH_{2n+1}$,[29] $C_6H_2\{3,4,5\text{-}(OC_nH_{2n+1})_3\}$;[7] $n = 4$, 6, 8, 10, 12), and CuCl.[39] Dialkoxyphenylisocyanides $C_6H_2\{3,4\text{-}(OC_nH_{2n+1})_2\}$ have not been reported before and were prepared by the same procedure described for trialkoxyphenyl isocyanides starting from 3,4-dialkoxyphenylamine.[40] Instrumentation was as described elsewhere.[31] Only example procedures are described, as the syntheses were similar for the rest of the compounds. Yields, IR, and analytical data are given for all the copper complexes.

Preparation of 3,4-di(dodecyloxy)phenylisocyanide

To a solution of *N*-[3,4-di(dodecyloxy)phenyl]formamide (6.71 mmol, prepared by reaction of 3,4-dialkoxyphenylamine with formic acid), and triethylamine (13.40 mmol) in 50 ml of CH_2Cl_2 was added dropwise a solution of triphosgene (2.23 mmol) in 25 ml of CH_2Cl_2. The mixture was stirred for 1 h and then the solvent was removed on a rotary evaporator. The resulting residue was chromatographed (silica gel, CH_2Cl_2/hexane 2 : 1 as eluent) and the solvent was evaporated to obtain the product as a white solid (70% yield). mp = 70 °C. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2128 s. ^{1}H NMR ($CDCl_3$): δ 6.94, 6.91 and 6.77 (H^2, H^1 and H^3, AMX spin system, $J_{1,2} = 2.3$, $J_{2,3} = 8.5$, Ar–H), 3.96 (m, 4H, CH_2O), 1.86–0.88 (m, 46H, alkyl chains).

Preparation of [CuCl(CNR)] [R = $C_6H_4C_6H_4OC_nH_{2n+1}$, $C_6H_4COOC_6H_4OC_nH_{2n+1}$, $C_6H_4OOCC_6H_4OC_nH_{2n+1}$, $C_6H_2\{3,4\text{-}(OC_nH_{2n+1})_2\}$, $C_6H_2\{3,4,5\text{-}(OC_nH_{2n+1})_3\}$]

To a suspension of CuCl (0.5 mmol) in dichloromethane (40 mL), under an atmosphere of nitrogen, was added a slight excess of the corresponding isocyanide (0.56 mmol). After stirring for one hour, the resulting solution was filtered in air and hexane (10 mL) was added. The solution was concentrated and afforded the corresponding compound as a white solid. For the trialkoxyphenyl derivatives the product appeared as a viscous fluid. Yields, IR and analytical data are as follows:

R = $C_6H_4C_6H_4OC_nH_{2n+1}$ (Cu–L^A). $n = 4$: Yield 96%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2160. Anal. Calcd. for $C_{17}H_{17}ClCuNO$: C, 58.29; H, 4.89; N, 3.40. Found: C, 57.98; H, 4.91; N, 3.90. $n = 6$: Yield 92%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2159. Anal. Calcd. for $C_{19}H_{21}ClCuNO$: C, 60.31; H, 5.59; N, 3.70. Found: C, 60.19; H, 5.45; N, 3.40. $n = 8$: Yield 98%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2160. Anal. Calcd. for $C_{21}H_{25}ClCuNO$: C, 62.06; H, 6.20; N, 3.45. Found: C, 62.30; H, 6.18; N, 3.26. $n = 10$: Yield 92%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2165. Anal. Calcd. for $C_{23}H_{29}ClCuNO$: C, 63.58; H, 6.73; N, 3.22. Found: C, 63.65; H, 6.69; N, 3.18. $n = 12$: Yield 89%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2158. Anal. Calcd. for $C_{25}H_{33}ClCuNO$: C, 64.92; H, 7.19; N, 3.03. Found: C, 64.93; H, 7.09; N, 3.00.

R = $C_6H_4OOCC_6H_4OC_nH_{2n+1}$ (Cu–L^B). $n = 4$: Yield 69%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2169. Anal. Calcd. for $C_{18}H_{17}ClCuNO_3$: C, 54.83; H, 4.35; N, 3.55. Found: C, 54.69; H, 4.37; N, 3.15. $n = 6$: Yield 75%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2165. Anal. Calcd. for $C_{20}H_{21}ClCuNO_3$: C, 56.87; H, 5.01; N, 3.32. Found: C, 56.69; H, 5.06; N, 3.15. $n = 8$: Yield 78%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2165. Anal. Calcd. for $C_{22}H_{25}ClCuNO_3$: C, 58.66; H, 5.59; N, 3.11. Found: C, 58.91; H, 5.66; N, 2.83. $n = 10$: Yield 76%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2163. Anal. Calcd. for $C_{24}H_{29}ClCuNO_3$: C, 60.24; H, 6.11; N, 2.93. Found: C, 59.96; H, 6.16; N, 2.73. $n = 12$: Yield 78%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2163. Anal. Calcd. for $C_{26}H_{33}ClCuNO_3$: C, 61.65; H, 6.57; N, 2.77. Found: C, 61.59; H, 6.55; N, 3.02.

R = $C_6H_4COOC_6H_4OC_nH_{2n+1}$ (Cu–L^C). $n = 4$: Yield 83%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2158. Anal. Calcd. for $C_{18}H_{17}ClCuNO_3$: C, 54.83; H, 4.35; N, 3.55. Found: C, 55.10; H, 4.44; N, 3.44. $n = 6$: Yield 76%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2157. Anal. Calcd. for $C_{20}H_{21}ClCuNO_3$: C, 56.87; H, 5.01; N, 3.32. Found: C, 56.72; H, 5.14; N, 3.32. $n = 8$: Yield 73%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2158. Anal. Calcd. for $C_{22}H_{25}ClCuNO_3$: C, 58.66; H, 5.59; N, 3.11. Found: C, 58.76; H, 5.70; N, 3.04. $n = 12$: Yield 97%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2157. Anal. Calcd. for $C_{26}H_{33}ClCuNO_3$: C, 61.65; H, 6.57; N, 2.77. Found: C, 61.51; H, 6.64; N, 2.65.

R = $C_6H_2\{3,4\text{-}(OC_nH_{2n+1})_2\}$ (Cu–L^D). $n = 4$: Yield 72%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2167. Anal. Calcd. for $C_{15}H_{21}ClCuNO_2$: C, 52.02; H, 6.11; N, 4.04. Found: C, 52.86; H, 6.22; N, 4.08. $n = 6$: Yield 75%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2166. Anal. Calcd. for $C_{19}H_{29}ClCuNO_2$: C, 56.71; H, 7.26; N, 3.48. Found: C, 56.53; H, 7.15; N, 3.52. $n = 8$: Yield 81%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2161. Anal. Calcd. for $C_{23}H_{37}ClCuNO_2$: C, 60.25; H, 8.13; N, 3.06. Found: C, 60.58; H, 8.11; N, 2.99. $n = 10$: Yield 81%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2169. Anal. Calcd. for $C_{27}H_{45}ClCuNO_2$: C, 63.01; H, 8.81; N, 2.72. Found: C, 63.31; H, 8.83; N, 2.63. $n = 12$: Yield 81%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2166. Anal. Calcd. for $C_{31}H_{54}ClCuNO_2$: C, 65.24; H, 9.36; N, 2.45. Found: C, 65.58; H, 9.39; N, 2.37.

R = $C_6H_2\{3,4,5\text{-}(OC_nH_{2n+1})_3\}$ (Cu–L^E). $n = 4$: Yield 65%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2167. Anal. Calcd. for $C_{19}H_{29}ClCuNO_3$: C, 54.54; H, 6.99; N, 3.35. Found: C, 54.69; H, 6.81; N, 3.20. $n = 6$: Yield 58%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2170. Anal. Calcd. for $C_{25}H_{42}ClCuNO_3$: C, 59.74; H, 8.22; N, 2.79. Found: C, 59.51; H, 8.06; N, 2.71. $n = 8$: Yield 55%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2169. Anal. Calcd. for $C_{31}H_{54}ClCuNO_3$: C, 63.46; H, 9.10; N, 2.39. Found: C, 64.46; H, 8.93; N, 2.48. $n = 10$: Yield 65%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2167. Anal. Calcd. for $C_{37}H_{66}ClCuNO_3$: C, 66.24; H, 9.77; N, 2.09. Found: C, 66.57; H, 9.27; N, 2.96. $n = 12$: Yield 83%. IR (CH_2Cl_2) ν(C≡N)/cm^{-1}: 2170. Anal. Calcd. for $C_{41}H_{78}ClCuNO_3$: C, 68.40; H, 10.28; N, 1.86. Found: C, 68.57; H, 9.85; N, 1.76.

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