CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800128

Self-Organization of Dendritic Supermolecules, Based on Isocyanide–Gold(I), –Copper(I), –Palladium(II), and –Platinum(II) Complexes, into Micellar Cubic Mesophases

**Silverio Coco,*[a] Carlos Cordovilla,[a] Bertrand Donnio,[b] Pablo Espinet,*[a]
María Jesús García-Casas,[a] and Daniel Guillon[b]**

Dedicated to the memory of Naomi Hoshino, a pioneer in the study of metallomesogens

Abstract: First- and second-generation dendrimers with an isocyanide group as the focal functional point (CN-G^n; *n*: 1,2) and their corresponding organometallic complexes [MCl(CN-G^n)] (M: Au, Cu), [{CuCl(CN-G^n)$_2$}$_2$], and *trans*-[MI_2(CN-G^n)$_2$] (M: Pd, Pt) have been synthesized. The free ligands and the first-generation complexes do not show mesogenic behavior, but all of the second-generation complexes display a thermotropic micellar cubic mesophase, over a large temperature range, and some of them directly at room temperature. The structure of the mesophase consists of the packing of two, discrete polyhedral micellar aggregates in a three-dimensional cubic $Im\bar{3}m$ lattice.

Keywords: dendrimers • isocyanides • liquid crystals • metallomesogens • self-assembly

Introduction

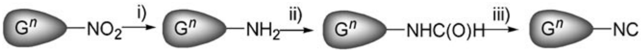
Many dendrimers have been synthesized, and molecular design and synthesis of dendritic systems with new structures and unique physical and chemical properties have emerged as one of the most important topics in supramolecular chemistry.[1] This is particularly true in metallodendrimers,[2] which combine the properties of transition metals, such as catalytic activity,[3] dichroism, paramagnetism, high birefringence, or color,[4] and those derived from the dendrimeric architecture, such as site isolation,[5] recyclability,[6] and possible cooperative effects. Active metallic moieties can be incorporated into different parts of a dendrimer,[7] including the branching points,[8] core,[9] and periphery,[10] to give metallodendrimers with desired functionality, and they may be used in many fields including materials science. In this respect, a great variety of liquid-crystalline dendrimers have been reported,[11,12] with only a few as metal-containing systems.[12,13]

A simple and well-known synthetic route to prepare metallodendrimers is the use of metals as linking groups, by coordination of functionalized dendritic fragments that can act as ligands. Isocyanides are versatile functionalities in organic synthesis and interesting ligands in organometallic chemistry, owing to their coordination ability to give very stable complexes with many transition metals.[14] Isocyanide–metal complexes are catalysts for polymerization[15] and for activation of Si–Si bonds,[16] or molecules used for one-dimensional electric conductors[17] and for liquid crystals.[18,19] This makes isocyanides very promising building blocks to prepare dendritic systems, but examples of dendrimers based on isocyanides have not been reported.

Here we report two families (first ($n=1$)- and second ($n=2$)-generation) of dendritic isocyanides and their stable gold, copper, palladium, and platinum complexes: [MCl(CN-G^n)], (M = Au, Cu), [{CuCl(CN-G^n)$_2$}$_2$], and *trans*-[MI_2(CN-G^n)$_2$] (M = Pd, Pt). Although the free highly branched isocyanides and the CN-G^1–metal complexes are not liquid crystals themselves, all CN-G^2–metal complexes show a cubic mesophase, with the $Im\bar{3}m$ lattice group, in a wide range of temperature, some of them at room temperature.

Results and Discussion

Synthesis and structural characterization: Polyarylester monodendrons bearing an isocyanide function at the focal point CN-G^n ($n=1$, 2) have not been reported yet. We have prepared them starting from the nitro dendritic compounds in three steps, involving first their reduction into the corresponding amines H_2N-G^n ($n=1$, 2) by hydrogen with a palladium-on-carbon catalyst, then by their subsequent transformation into *N*-formamides by formylation, and finally by their dehydration with triphosgene (“bis(trichloromethyl)-carbonate”) and triethylamine (Scheme 1). At room temperature they are white (CN-G^1) or yellow waxy (CN-G^2) solids not particularly smelling that can be stored for long periods in the freezer.



Scheme 1. Reagents and conditions: i) H_2, Pd/C, CH_2Cl_2; ii) formic acid, toluene, reflux; iii) triphosgene, NEt_3, CH_2Cl_2, 0 °C.

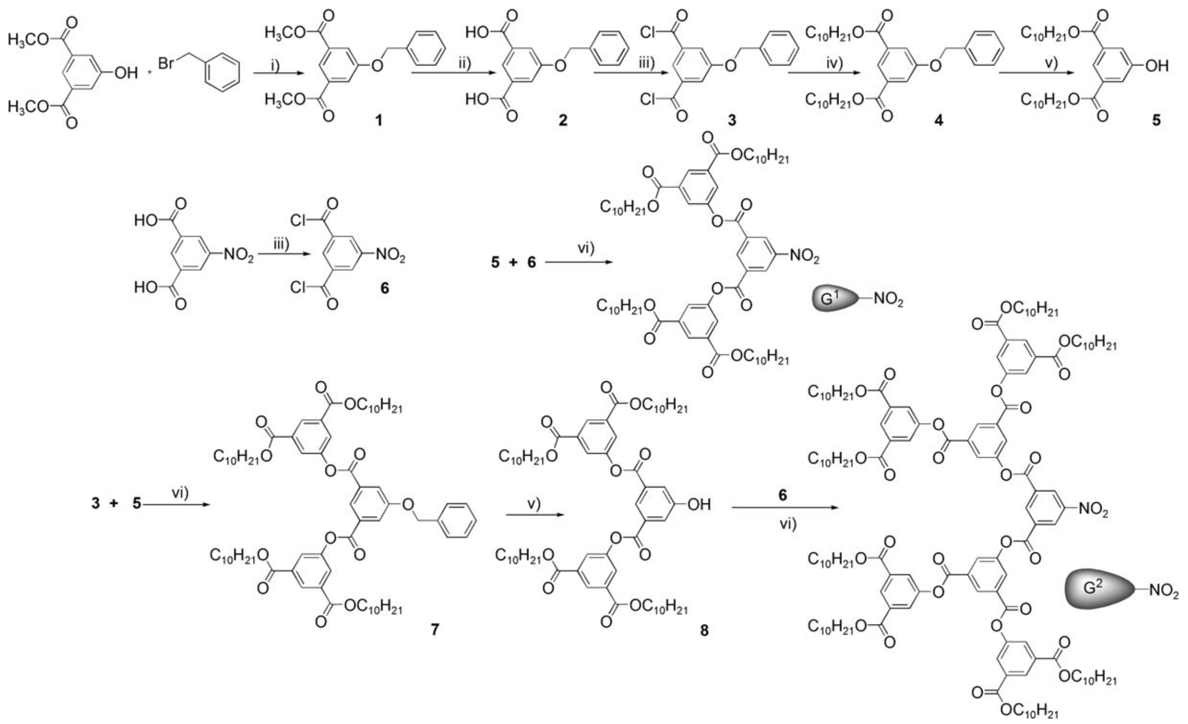
The nitro derivative NO_2-G^1 was prepared starting from dimethyl 5-hydroxyisophthalate in five steps (Scheme 2). Dimethyl 5-hydroxyisophthalate was alkylated with bromomethylbenzene to give the protected phenol **1**. Saponification of the ester groups was carried out with potassium hydroxide to afford 5-benzyloxyisophthalic acid (**2**). Treatment of **2** with thionyl chloride yielded 5-benzyloxy-

---

[a] Dr. S. Coco, Dr. C. Cordovilla, Prof. P. Espinet,
Dr. M. J. García-Casas
IU CINQUIMA/Química Inorgánica
Facultad de Ciencias, Universidad de Valladolid
47071 Valladolid, Castilla y León (Spain)
Fax: (+34) 983-423013
E-mail: scoco@qi.uva.es
espinet@qi.uva.es

[b] Dr. B. Donnio, Dr. D. Guillon
Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS)
UMR 7504 (CNRS-ULP), 23 rue du Loess, BP 43
67034 Strasbourg Cedex 2 (France)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains general procedures and instrumentation, representative DSC traces, and small-angle X-ray patterns of the mesophases of the metallodendrimers.



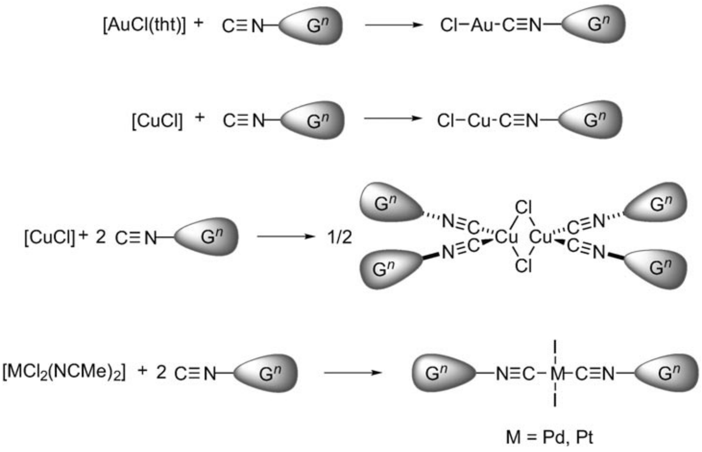
Scheme 2. Reagents and conditions: i) acetone, DMSO, K_2CO_3, reflux; ii) KOH, EtOH/H_2O, reflux; iii) $SOCl_2$, DMF, toluene, reflux; iv) $C_{10}H_{21}OH$, NEt_3, dioxane; v) H_2, Pd/C, CH_2Cl_2; vi) NEt_3, dioxane.

isophthaloyldichloride (**3**), which was etherified with 1-decanol to yield, after deprotection of phenol group, didecanoyl-5-hydroxyisophthalate (**5**). Finally esterification of 5-nitro-isophthaloyldichloride (**6**) with **5** produced the desired nitro derivative NO_2-G^1. The NO_2-G^2 derivative was obtained analogously as summarized in Scheme 2.

The C, H, N analyses, yields, IR and ^{1}H NMR data for the isocyanides and their complexes are given in the Experimental Section. The IR spectra in KBr of the isocyanide monodendrons show a strong $\nu(C\equiv N)$ absorption in the region of 2130 cm^{-1}, and a strong and broad $\nu(C{=}O)$ stretching band at 1725 cm^{-1} supporting the existence of ester groups.

^{1}H NMR spectroscopy of CN-G^n ($n=1$, 2) shows the resonances of two or three AB_2 spin systems corresponding to the aryl hydrogen atoms present in the G^1 and G^2 molecules, respectively. In addition, a triplet is observed at approximately $\delta = 4.36$ ppm, corresponding to the first methylene group of the $COOC_{10}H_{21}$ moieties. The remaining chain hydrogen atoms appear in the range $\delta = 0.8$–1.8 ppm.

The isocyanide complexes were prepared according to Scheme 3. The reaction of isocyanides CN-G^n ($n=1$, 2) with [AuCl(tht)] (tht = tetrahydrothiophene) or CuCl in dichloromethane gave the white complexes [MCl(CN-G^n)] (M = Au, Cu). In contrast, reaction of two equivalents of the isocyanide derivatives with CuCl yielded the binuclear copper(I) complexes [{CuCl(CN-G^n)$_2$}$_2$], which have an inorganic core formed by two tetrahedra sharing an edge. Similarly, reactions of CN-G^n with [$MCl_2(NCCH_3)_2$] (M: Pd, Pt) and KI in tetrahydrofuran afforded the corresponding *trans*-[MI_2(CN-G^n)$_2$] complexes (M = Pd, Pt). It is interesting to note that reaction of CN-G^n with [$MCl_2(NCCH_3)_2$] (M: Pd, Pt) gave *cis*-[MCl_2(CN-G^n)$_2$] complexes (M = Pd, Pt), which were characterized in solution by IR spectroscopy ($\nu(C\equiv N)$ (in CH_2Cl_2): M = Pd: 2218 (s), 2236 cm^{-1} (sh); M = Pt: 2205 (s), 2240 cm^{-1} (sh)). However these *cis*-dichloro complexes show a low stability, possibly due to the high steric hindrance of the monodendrons in a *cis* disposition, and pure complexes could not be isolated.



Scheme 3. Schematic representation of the various dendritic complexes prepared.

The IR spectra of the metal complexes exhibit $\nu(C\equiv N)$ absorptions for the isocyanide group at higher wavenumbers than for the free ligand, by about 90 cm^{-1} for Au^I, 18–

52 cm^{-1} for Cu^{I}, and 60–80 cm^{-1} for Pd^{II} and Pt^{II} complexes. Linear [MCl(CN-G^{n})] (M = Au, Cu) and *trans*-diiodopalladium and platinum complexes (D_{2h} symmetry) display one ν(C≡N) IR absorption band, while [CuCl(CN-G^{n})$_2$]$_2$ (D_{2h}, B$_{2u}$ + B$_{3u}$ symmetry), and the *cis*-dichloropalladium and platinum complexes (C_{2v} symmetry), have two bands, as reported for similar metal aryl isocyanide compounds.[20–22]

The ^{1}H NMR spectra of the metal complexes are all similar to that of the free isocyanide ligand discussed above. It is worth noting that coordination of the isocyanides produces only a slight deshielding for aromatic protons in *ortho* and *para* positions to the isocyanide group (0.2–0.1 ppm for gold and palladium complexes and less than 0.1 ppm for copper and platinum complexes), suggesting that the isocyanide becomes slightly more p acceptor in character due to the coordination.

Mesomorphic behavior: The thermal behavior of all the compounds was studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS) experiments. Although the first- and second-generation free isocyanides (CN-G^1, CN-G^2) and the first-generation metal complexes do not show mesomorphic properties, all second-generation metallodendrimers display a cubic mesophase, some of them occurring at room temperature. Thermal and thermodynamic data are collected in Table 1. No birefringent texture could be observed for any of the complexes in the explored temperature range, but only the formation of large, black (optically isotropic) and viscous areas on increasing temperature. However, upon mechanical shear, weakly birefringent, transient dendritic patterns with homeotropic contours were observed in a polarizing microscope; these contours disappear when the pressure is released. Isotropization was accompanied by an increase in the fluidity of the complexes; however, most of them underwent some decomposition upon reaching the clearing temperature, due to their very high transition temperatures.

Table 1. Thermal and termodynamic data for dentritic ligands and complexes.

	Transition temperature[a] [°C] (ΔH [kJ mol^{-1}])
CN-G^1	Cr 46 (1.6) Cr′ 67 (14.9) Cr″ 82 (52.9) I
CN-G^2	Cr 31 (7.9) I
[AuCl(CN-G^1)]	Cr 45 (8.7) Cr′ 129 (73.0) I
[AuCl(CN-G^2)]	Cr 94 (32.9) Cub-$Im\bar{3}m$ 260[b] decomp
[CuCl(CN-G^1)]	Cr 112 (41.2) I
[CuCl(CN-G^2)]	Cr 110 (28.9) Cub-$Im\bar{3}m$ 290[b] decomp
[{CuCl(CN-G^1)$_2$}$_2$]	Cr 70 (25.8) I
[{CuCl(CN-G^2)$_2$}$_2$]	Cub-$Im\bar{3}m$ 268[b] decomp
trans-[PdI$_2$(CN-G^1)$_2$]	Cr 32 (97.7) I
trans-[PdI$_2$(CN-G^2)$_2$]	Cub-$Im\bar{3}m$ 150[b] decomp
trans-[PtI$_2$(CN-G^1)$_2$]	I
trans-[PtI$_2$(CN-G^2)$_2$]	Cub-$Im\bar{3}m$ 291.0[b] decomp

[a] Cr, Cr′, Cr″: crystalline phases; Cub-$Im\bar{3}m$: cubic phase; I: isotropic liquid; decomp: decomposition. Data collected from the first heating DSC cycle. The transition temperatures are given as peak onsets. [b] Optical microscopy data.

A cubic mesophase with a $Im\bar{3}m$ symmetry was eventually deduced by SAXS measurements. The small-angle X-ray diffraction patterns for all mesomorphic complexes exhibit six ([AuCl(CN-G^2)], [{CuCl(CN-G^n)$_2$}$_2$], *trans*-[PdI$_2$(CN-G^2)$_2$], *trans*-[PtI$_2$(CN-G^2)$_2$]) or seven ([CuCl(CN-G^2)]) sharp, small-angle reflections, for which the reciprocal *d*-spacings were in the ratios $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{5}{:}\sqrt{6}{:}\sqrt{7}$, pointing to a cubic supramolecular organization $[(h^2+k^2+l^2)^{1/2}=a/d_{hkl})]$ (Table 2). The determination of the cubic symmetry is generally not trivial, but a logical analysis of the data permits us to considerably reduce the possibilities. All non-centrosymmetric groups (groups with the 23, 432 and $-43m$ Laue classes) can be disregarded as a consequence of the Friedel's law,[23,24] thus leaving only 17 cubic space groups to consider out of an initial 36. This sequence of ratios is not compatible with a face centerd cubic network (F) due to the presence of the reflection corresponding to the ratio $\sqrt{7}$. Although, a cubic phase with a primitive Bravais lattice (P) cannot be excluded (the simple cubic space groups with the symmetry $Pm\bar{3}$, $Pn\bar{3}$, $Pm\bar{3}m$, $Pm\bar{3}n$, $Pn\bar{3}n$ or $Pn\bar{3}m$ are all compatible with this sequence of ratios), this option is improbable, since six intermediate, authorized reflections, with $h+k+l=2n+1$, are unexpectedly absent. In contrast, this sequence is perfectly compatible with a body-centered cubic lattice (I type).[25] Indeed, for a body-centered cubic lattice, the considered sequence in this case is $\sqrt{2}{:}\sqrt{4}{:}\sqrt{6}{:}\sqrt{8}{:}\sqrt{10}{:}\sqrt{12}{:}\sqrt{14}$ and the reflections can be indexed as (110), (200), (211), (220), (310), (222), and (321); all satisfied the reflection conditions ($0kl{:}k+l=2n$, $hhl{:}l=2n$, $h00{:}h=2n$), and only the symmetry $Im\bar{3}$ or $Im\bar{3}m$ is theoretically compatible with this set of reflections. An aggregation into the highest symmetry is generally admitted and accordingly, the $Im\bar{3}m$ space group (No. 229)[24] is finally retained.

An additional, very intense, but diffuse, halo was observed in the wide-angle region at about 4.4–4.6 Å over the whole temperature range, and was assigned to the liquidlike order of the molten chains, confirming the liquid nature of the mesophase.

The two dendritic ligands and the first-generation complexes are not mesogenic, whereas all second-generation complexes display liquid crystal behavior. Thus, mesomorphism is induced upon complexation, but the appearance of mesomorphic properties depends on the generation. The melting temperatures of related complexes decrease with increasing of the generation, possibly due to entropy effects derived from the increase of the number of alkoxy chains in the second-generation complexes. Moreover, the transition temperatures into the isotropic liquid are not reached in any of the mesomorphic complexes ($T_{\mathrm{dec}} < T_{\mathrm{iso}}$), and since decomposition occurs at very high temperature, the temperature domains of stability of the cubic phases are much extended. These observations clearly suggests that the size of the dendritic blocks (alkoxy chains and phenyl rings) is in competition with the interactions brought by the presence

Table 2. Structural data from X-ray diffraction experiments for the mesomorphic metal isocyanide complexes.

	T [°C][a]	Indexation[b]					Parameters[c]	
		$d_{hkl(\mathrm{exptl})}$ [Å]	hkl	I	L	$d_{hkl(\mathrm{calcd})}$ [Å]		
[AuCl(CN-G^2)]	105	30.94	110	vs	sh	30.87	a	43.66 Å
		21.89	200	s	sh	21.83	V_{mic}	41 600 Å^3
		17.83	211	s	sh	17.82	V_{mol}	4100 Å^3
		15.35	220	vw	sh	15.43	N	10.1
		13.76	310	w	sh	13.80	S	6382 Å^2
		11.71	321	w	sh	11.67	a_{ch}	39.5 Å^2
		4.4	–	s	br	–		
[CuCl(CN-G^2)]	115	32.23	110	vs	sh	32.21	a	45.55 Å
		22.79	200	s	sh	22.78	V_{mic}	47 250 Å^3
		18.68	211	vw	sh	18.60	V_{mol}	4110 Å^3
		16.07	220	vw	sh	16.11	N	11.5
		14.37	310	w	sh	14.40	S	6946 Å^2
		13.15	222	w	sh	13.15	a_{ch}	37.75 Å^2
		12.16	321	w	sh	12.17		
		4.5	–	s	br	–		
[{CuCl(CN-G^2)$_2$}$_2$]	75	32.50	110	vs	sh	32.51	a	45.98 Å
		23.06	200	m	sh	23.00	V_{mic}	48 600 Å^3
		18.79	211	s	sh	18.77	V_{mol}	15 910 Å^3
		16.19	220	vw	sh	16.25	N	3
		14.59	310	w	sh	14.54	S	7080 Å^2
		13.20	222	w	sh	13.28	a_{ch}	36.85 Å^2
		12.27	321	w	sh	12.29		
		4.6	–	s	br	–		
trans-[PdI$_2$(CN-G^2)$_2$]	70	31.57	110	vs	sh	31.46	a	44.49 Å
		22.32	200	m	sh	22.24	V_{mic}	44 030 Å^3
		18.15	211	s	sh	18.16	V_{mol}	7990 Å^3
		15.57	220	vw	sh	15.73	N	5.5
		14.11	310	w	sh	14.07	S	6630 Å^2
		11.90	321	w	sh	11.89	a_{ch}	37.65 Å^2
		4.5	–	s	br	–		
trans-[PtI$_2$(CN-G^2)$_2$]	30	31.96	110	vs	sh	32.07	a	45.35 Å
		22.66	200	m	sh	22.68	V_{mic}	46 635 Å^3
		18.52	211	s	sh	18.51	V_{mol}	7780 Å^3
		16.05	220	vw	sh	16.03	N	6.0
		14.38	310	w	sh	14.34	S	6885 Å^2
		12.12	321	w	sh	12.12	a_{ch}	35.85 Å^2
		4.5	–	s	br	–		

[a] Temperature of the experiment. [b] $d_{hkl(exptl)}$ and $d_{hkl(calcd)}$ are the measured and calculated diffraction spacing; *hkl* corresponds to the indexation of the reflections, I to the intensity of the reflections (vs: very strong, s: strong ; m: medium; w : weak; vw : very weak), and L to the line-shape (br and sh stand for broad and sharp). [c] a is the lattice parameter of the cubic phase $a=[\Sigma_{hkl}d_{hkl}(h^2+k^2+l^2)^{-2}]/N_{hkl}$ in which N_{hkl} is the number of *hkl* reflections, V_{mic} is the micellar volume ($V_{\mathrm{mic}=}a^3/2$), V_{mol} is the molecular volume calculated from $V_{\mathrm{mol}}(T)=V_{\mathrm{metallic}}+V_{\mathrm{ligand}}(T_0)\times[V_{\mathrm{CH2}}(T)/V_{\mathrm{CH2}}(T_0)]$, in which $V_{\mathrm{CH2}}(T)=26.5616+0.02023\,T$ (T in °C, and $T_0=22\,°\mathrm{C}$), $V_{\mathrm{ligand}}(T_0)=MW_{\mathrm{ligand}}/0.6022$, and $V_{\mathrm{metallic}}=MW_{\mathrm{metallic}}/d_{\mathrm{metallic}}\times 0.6022$. Density (g cm^{-3}) and molecular mass (g mol^{-1}) of the metallic fragments: AuCl (232.42), $\rho=7.4$; CuCl (99.0) and Cu$_2$Cl$_2$ (198) $\rho=4.14$, PdI$_2$ (360.23) $\rho=6.003$; PtI$_2$ (448.89) $\rho=6.403$ (Data taken from Handbook of Chemistry and Physics, 67th edition, CRC Press, Boca Raton, Florida, USA, 1986–1987). N is the aggregation number ($N=V_{\mathrm{mic}}/V_{\mathrm{mol}}$). S is the surface of the elementary truncated octahedron ($S=a^2(6\sqrt{3}+2)/4$), and a_{ch} is the cross-section area of one terminal chain, calculated on the surface S ($a_{\mathrm{ch}}=S/2NN_{\mathrm{ch}}$, in which N_{ch} is the number of terminal chains per dendrimer).

of the metallic moieties, which, when both are appropriately dosed, induce specific molecular conformation able to self-assemble in a liquid-crystal supramolecular structure.

The dendritic complexes of the second-generation all self-assemble into a body-centered cubic phase, likely with the micellar morphology. The gold and copper complexes have a similar thermal behavior, melting into the cubic phase at about 100 °C. In contrast, the other complexes (the dimeric copper and the two *trans* square-planar complexes) exhibit the mesophase at room temperature. In all cases, the mesophase is thermally very stable, the complexes decomposing before clearing. The mesophases freeze at low temperature and crystallization is only observed for the derivatives [MCl(CN-G^2)] (M: Au, Cu). Finally, whatever the complexes considered, the mesophases possess close structural parameters, suggesting a similar arrangement of the complexes within the cubic phase.

Cubic mesophases are ordered three-dimensional supramolecular edifices, with a multicontinuous or a discrete micellar structure, depending on the molecular self-organization within the cubic cell.[11e–g,26] Bi- and tricontinuous cubic structures consist of two or three regular, interwoven, infinite, interconnected rod networks (referred to as $Im\bar{3}m$ (P) and $Im\bar{3}m$ (I) structures, respectively);[27–30] the rods are formed by the rigid part of the molecules, and the networks are separated by lipophilic films (their associated minimal surfaces). The difference between the bicontinuous and the micellar structures lies in the periodic discontinuities along the rods in the *x*,*y*,*z* directions (bicontinuous model) that appear at mid-height of the cubic-cell edges; the junctions between three connecting rods then become the micelle (micellar model). It is therefore not trivial to choose one model preferentially to the other. Although, as far as the bicontinuous structure is concerned, the molecules need to be able to stack to form the columns, and thus a specific molecular conformation is required. For the present systems, on the basis of their molecular conformations and packing considerations, the micellar model appears therefore more appropriate and more likely than the multicontinuous one. Indeed, all these dendritic molecules have a very large volume fraction of aliphatic chains in common, and thus a strong interfacial curvature. This forces the dendrimers to deviate from the planar, fanlike shape (G1) to adopt a conical conformation with the isocyanide group, and later the metallic moiety, located at the apex of the structure. The steric hindrance of adjacent branches in CN-G^2 ligands will further stabilize the conical-shape conformation. The mesogens likely self-assemble head-to-head to form spheroidlike nonpolar supramolecular clusters, since stacking is strongly disfavored with such a conformation. The mesophase then consists of the three-dimensional, periodic and regular packing of such supramolecular ensembles, one located at the corners and one at the center of the cubic cell. This self-organization model is similar to that of the classical dendromesogens[11g] and other thermotropic systems showing such phases.

Recall that for micellar thermotropic cubic phases, the micelles are necessarily inverted; that is, the polar nucleus of the micelles is embedded in an apolar aliphatic shell.[31] The broad scattering measured by SAXS corresponding to the molten organic coating indicates the presence of a continuum between the isolated supramolecular metallic clusters.

In thermotropic systems, it is convenient to describe this phase structure by the geometrical space-filling polyhedron model.[32] As far as the $Im\bar{3}m$ phase is concerned, the symmetry and the complete filling of the space is achieved by two truncated octahedrons, one in the center of the cubic lattice (1×1) and one at the corners (8×1/8). In these idealized geometrical structures, the center of gravity of the polyhedron is therefore occupied by the metallic moieties, embedded in the dendritic continuum, the interface between each supermolecule being represented by the polyhedral faces (square and hexagonal faces, with an edge e; Figure 1).

The geometrical relationships between the cubic lattice and polyhedron characteristics provide us with more insight into the molecular arrangement within these micellar aggregates. The number of complexes required to fill one of this polyhedral micelle was calculated. Thus, each micelle contains approximately either twelve, six, and three molecules of [CuClCN-G^2], [MI$_2$(CN-G^2)$_2$] (M=Pd, Pt), and [{CuCl(CN-G^n)$_2$}$_2$], respectively, meaning that whatever the complex, each aggregate requires about twelve dendritic isocyanide moieties, except for the gold complex in which only ten monodendrons per micelle were found. It is evident that these dendritic molecules will adopt the most adequate molecular conformation, with an average projection of the solid angle of about 30–36° subtended by the conical-like dendrons ($\alpha' = 2\pi/\mu$, in which μ is the number of "dendrons" within the micellar aggregate),[27] compatible with their bond system, so as to self-assemble into such a supramolecular aggregate. The cohesion in the three directions of the space between these polyhedral aggregates according to the space-group symmetry is ensured by the intermicellar-chain interdigitation through square faces along the *x*,*y*,*z* directions for micelles within identical cubic subnetworks (binary and quaternary axes), and through hexagonal faces for the connection between micelles belonging to the two distinct subnetworks (ternary axes). This is evidenced by the rather compact arrangement of the chains at the interface between two micelles (the value of the chain-cross section area lies between 36 and 40 Å^2, Table 2). A plausible proposal is shown in Figure 2.

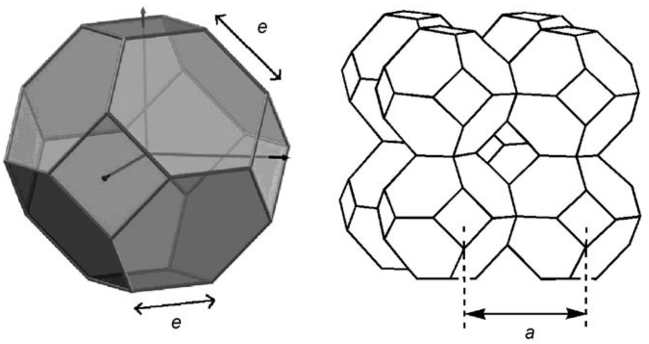


Figure 1. Representation of the truncated octahedron, $a=2\sqrt{2}\times e$; $S=(12\sqrt{3}+6)\times e^2$; $V=8\sqrt{2}\times e^3$. *a*: cubic lattice parameter ; *e*: polyhedron edge. Schematic representation of the body centered (*I*) cubic lattice of $Im\bar{3}m$ symmetry composed of truncated octahedrons.

For the [MI$_2$(CN-G^2)$_2$] and [{CuCl(CN-G^n)$_2$}$_2$] complexes, which contain two and four isocyanide monodendrons, re-

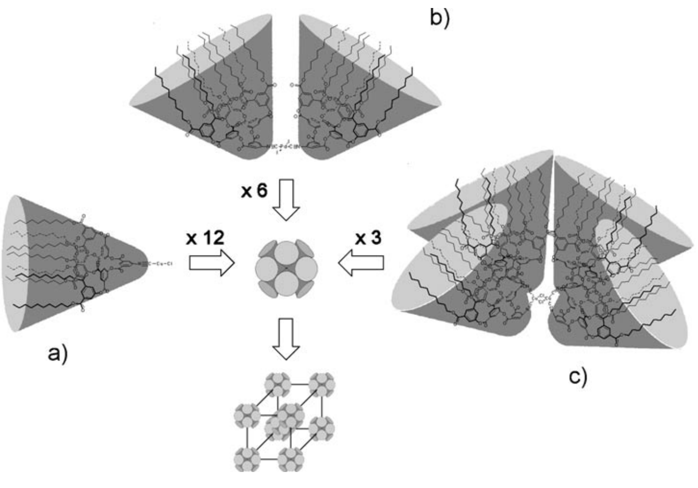


Figure 2. Schematic representation of possible conformations of the dendrimers in each type of molecule, their self-assembling into a supramolecular spherical dendrimer, and the subsequent organization of these spherical dendrimers into a $Im\bar{3}m$ cubic mesophase.

spectively, easily accessible molecular conformations are those that situated the two or four conical monodendrons in a compact arrangement as represented in Figure 2b and c. Ideally, the formation of polyhedral aggregates with similar micellar volume from these structurally very different metal complexes would result from the complementary molecular association of the same number "twleve" of conical monodendrons corresponding respectively to twelve molecules of [CuClCN-G^2] with one isocyanide derivative, six molecules of [MI$_2$(CN-G^2)$_2$] that contain two isocyanide moieties, or three molecules of [{CuCl(CN-G^n)$_2$}$_2$] with four dendritic isocyanides.

As for the gold complex, the necessary number of conical dendrons to fill a micellar aggregate is smaller than for the other complexes (only ten dendrimers), consistent with the lattice contraction, suggesting stronger intermolecular interactions of the metal-containing dendrimer, and consequently a tighter intermicellar packing. The values of the cross-section chain area calculated in each case confirmed the general trend of the packing of these complexes, as all values lie in the same range.

In summary, novel examples of metallodendrimers containing monodendrons with an isocyanide group in the focal point have been prepared. Although the free ligands are not liquid crystals, all second-generation complexes show mesomorphic properties, displaying cubic phases indexed with an $Im\bar{3}m$ lattice, over a wide range of temperatures. Although the metal complexes prepared are structurally very different, the dendrons of the second-generation manage to arrange appropriately despite unfavorable coordination structures.

Experimental Section

Experimental conditions for the analytical, spectroscopic, and XRD studies were as reported elsewhere.[19,25] Literature methods were used to prepare [AuCl(tht)] (tht = tetrahydrothiophene),[33] [MCl$_2$(NCCH$_3$)$_2$] (M = Pd, Pt),[34] and CuCl.[35]

Preparation of dimethyl-5-benzyloxyisophthalate (1): Potassium carbonate (10.52 g, 76.12 mmol) was added to a stirred solution of dimethyl-5-hydroxyisophthalate (8.00 g, 38.06 mmol) and benzyl bromide (5 mL, 41.87 mmol) in acetone/dimethyl sulfoxide (150 mL, 10:1). The mixture was heated to reflux for 22 h. The suspension was filtered and the solvent evaporated under vacuum to yield a white solid (11.43 g, 100 %). ^{1}H NMR (CDCl$_3$): δ = 3.93 (s, 6H; CH$_3$OCO), 5.13 (s, 2H; CH$_2$O), 7.26–7.43 (m, 5H; ArH), 7.83 (t, J = 0.6 Hz, 1H; ArH), 8.28 ppm (d, J = 0.6 Hz, 2H; ArH).

Preparation of 5-benzyloxyisophthalic acid (2): A solution of potassium hydroxide (8.54 g, 152.24 mmol) and **1** (11.43 g, 38.06 mmol) in ethanol/water (300 mL, 95:5) was heated to reflux for 75 min. Then water (300 mL) was added and the solution was acidified with HCl until a pH value of 2 was reached to precipitate a white solid, which was washed with water and dried in vacuo (9.11 g, 88 %). ^{1}H NMR ((CD$_3$)$_2$CO): δ = 5.30 (s, 2H; CH$_2$O), 7.39–7.86 (m, 5H; ArH), 7.86 (d, J = 1.4 Hz, 2H; ArH), 8.30 ppm (t, J = 1.4 Hz, 1H; ArH).

Preparation of 5-benzyloxyisophthaloyl dichloride (3): Dimethyl formamide (1.10 mL, 15.07 mmol) and thionyl chloride (25.45 mL, 348.94 mmol) were added to a solution of **2** (5.00 g, 18.36 mmol) in toluene (100 mL). The solution was heated to reflux for 3 h. Then volatiles were pumped off and the product was isolated as a yellowish solid.

Preparation of didecanoyl 5-benzyloxy-isophthalate (4): A solution of **3** (5.68 g, 18.37 mmol), triethylamine (5.65 mL, 40.42 mmol) and decanol (7.70 g, 40.42 mmol) in dioxane (100 mL) was stirred for 12 h at room temperature. Then water (100 mL) was added to separate an oil, which was extracted with dichloromethane. The organic layer was washed with diluted hydrochloric acid (3×30 mL) and dried over anhydrous magnesium sulfate. The dichloromethane was evaporated to yield an orange oil. The crude product was purified by column chromatography (silica gel, dichloromethane/hexane 2:1) as an orange solid (8.63 g, 85 %). ^{1}H NMR (CDCl$_3$): δ = 0.88–1.77 (m, 36H; AlkH), 4.33 (t, J = 6.7 Hz, 4H; CH$_2$OCO), 5.14 (s, 2H; CH$_2$O), 7.40–7.45 (m, 5H; ArH), 7.83 (d, J = 1.4 Hz, 2H; ArH), 8.29 ppm (t, J = 1.4 Hz, 1H; ArH).

Preparation of didecanoyl-5-hydroxyisophthalate (5): Pd/C (9.00 g, 5 %) was added to a solution of **4** (16.68 g, 30 mmol) in dichloromethane (100 mL) and the mixture was stirred overnight under a hydrogen atmosphere. The reaction mixture was filtered and the solvent evaporated to obtain the product as a white solid (12.63 g, 90 %). ^{1}H NMR (CDCl$_3$): δ = 0.88–1.82 (m, 36H; AlkH), 4.34 (t, J = 6.7 Hz, 4H; CH$_2$OCO), 6.46 (s, 1H; OH), 7.82 (d, J = 1.3 Hz, 2H; ArH), 8.25 ppm (t, J = 1.3 Hz, 1H; ArH).

Preparation of 5-nitro-isophthaloyl dichloride (6): Compound **6** was prepared from 5-nitroisophthalic acid (1.30 g, 6.18 mmol) and thionyl chloride as described for compound **3**. The product was isolated as a yellow oil.

Preparation of NO$_2$-G^1: Compound **5** (6.00 g, 12.97 mmol) and triethylamine (1.80 mL, 12.97 mmol) were added to a solution of **6** (1.53 g, 6.18 mmol) in dioxane (50 mL). The mixture was stirred for 12 h at room temperature, and then water (50 mL) was added. The mixture was extracted with dichloromethane. The organic layer was washed with diluted hydrochloric acid (3×15 mL) and dried over anhydrous magnesium sulfate, and the solvent was removed. The crude product was purified by chromatography (silica, dichloromethane/hexane 2:1) affording a white solid (5.29 g, 78 %). ^{1}H NMR (CDCl$_3$): δ = 0.86–1.81 (m, 72H; AlkH), 4.36 (t, J = 6.6 Hz, 8H; CH$_2$OCO), 8.12 (d, J = 1.5 Hz, 4H; ArH), 8.65 (t, J = 1.5 Hz, 2H; ArH), 9.30 ppm (m, 3H; ArH).

Preparation of G^{1}OCH$_2$C$_6$H$_5$ (7): A solution of **3** (2.43 g, 7.86 mmol), triethylamine (2.4 mL, 17 mmol) and **5** (8.00 g, 17 mmol) in dioxane (100 mL) was stirred for 12 h at room temperature. Water (200 mL) was added and the product extracted with dichloromethane. The organic layer was washed with diluted hydrochloric acid (3×30 mL) and dried over anhydrous magnesium sulfate, and the solvent was removed to give a white solid (7.09 g, 82 %), which was purified by chromatography (silica, dichloromethane/hexane 2:1). ^{1}H NMR (CDCl$_3$): δ = 0.81–1.75 (m, 72H; AlkH), 4.28 (t, J = 6.6 Hz, 8H; CH$_2$OCO), 5.16 (s, 2H; CH$_2$O), 7.31 (m, 5H; ArH), 8.08 (d, J = 7.4 Hz, 2H; ArH), 8.09 (d, J = 1.4 Hz, 4H; ArH), 8.63 (t, J = 1.4 Hz, 2H; ArH), 8.64 ppm (t, J = 1.4 Hz, 1H; ArH).

Preparation of OH-G^1 (8): Pd/C (5 %; 4.00 g) was added to a solution of **8** (7.02 g, 6.05 mmol) in dichloromethane (50 mL). The mixture was stirred overnight under a hydrogen atmosphere. The reaction mixture was filtered and the solvent was evaporated to obtain the product as a white solid (5.81 g, 90 %). ^{1}H NMR (CDCl$_3$): δ = 0.83–1.82 (m, 72H; AlkH), 4.35 (t, J = 6.8 Hz, 8H; CH$_2$OCO), 6.53 (s, 1H; OH), 7.96 (d, J = 1.5 Hz, 2H; ArH), 8.08 (d, J = 1.5 Hz, 4H; ArH), 8.57 (t, J = 1.5 Hz, 1H; ArH), 8.61 ppm (t, J = 1.5 Hz, 2H; ArH).

Preparation of NO$_2$-G^2: Compound **8** (5.60 g, 5.23 mmol) and triethylamine (0.7 mL, 5.23 mmol) were added to a solution of **6** (0.62 g, 2.49 mmol) in dioxane (50 mL). The mixture was stirred for 12 h at room temperature, and then water (50 mL) was added. The mixture was extracted with dichloromethane. The organic layer was washed with diluted hydrochloric acid (3×15 mL) and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified by chromatography (silica, dichloromethane/hexane 2:1) affording a yellow oil (3.69 g, 64 %). ^{1}H NMR (CDCl$_3$): δ = 0.83–1.81 (m, 144H; AlkH), 4.36 (t, J = 6.7 Hz, 16H; CH$_2$OCO), 8.11 (d, J = 1.4 Hz, 8H; ArH), 8.43 (d, J = 1.5 Hz, 4H; ArH), 8.63 (d, J = 1.4 Hz, 4H; ArH), 9.02 (t, J = 1.5 Hz, 2H; ArH), 9.37 ppm (m, 3H; ArH).

Preparation of NH$_2$-G^n: A solution of NO$_2$-G^n (5.45 mmol) in ethanol/dichloromethane (20 mL, 1:1) was stirred overnight at room temperature in the presence of Pd/C (5 %; 3.20 g) under a positive pressure of hydrogen. The mixture was then filtered. The solution obtained was concentrated and cooled to −15 °C to give the product.

NH_2-G^1: White solid (4.92 g, 78 %); ^{1}H NMR ($CDCl_3$): δ = 0.82–1.79 (m, 72 H; AlkH), 4.18 (s, 2 H; NH_2), 4.34 (t, J = 6.7 Hz, 8 H; CH_2OCO), 7.73 (d, J = 1.3 Hz, 2 H; ArH), 8.07 (d, J = 1.3 Hz, 4 H; ArH), 8.37 (t, J = 1.3 Hz, 1 H; ArH), 8.60 ppm (t, J = 1.3 Hz, 2 H; ArH).

NH_2-G^2: Yellow oil (3.20 g, 84 %); ^{1}H NMR ($CDCl_3$): δ = 0.84–1.83 (m, 144 H; AlkH), 4.18 (s, 2 H; NH_2), 4.35 (t, J = 6.8 Hz, 16 H; CH_2OCO), 7.80 (d, J = 1.5 Hz, 2 H; ArH), 8.10 (d, J = 1.4 Hz, 8 H; ArH), 8.39 (d, J = 1.5 Hz, 4 H; ArH), 8.46 (t, J = 1.4 Hz, 1 H; ArH), 8.63 (t, J = 1.4 Hz, 4 H; ArH), 8.97 ppm (t, J = 1.5 Hz, 2 H; ArH).

Preparation of CN-G^n: A solution of bistrichloromethyl carbonate (triphosgene; 1.68 mmol) in dichloromethane (25 mL) was added dropwise to a solution of NHC(O)H-G^n (4.55 mmol), prepared by reaction of the corresponding amine with formic acid and triethylamine (10.8 mmol) in dichloromethane (60 mL) at 0 °C. The mixture was stirred for 1 h and the solvent was removed. The resulting residues were purified by column chromatography (silica gel, CH_2Cl_2/hexane 3:1 as eluent), and the solvent was evaporated to obtain the desired products.

CN-G^1: White solid (3.74 g, 76 %); IR (KBr): $\tilde{\nu}$ = 2133 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.95 (m, 36 H), 4.36 (t, J = 6.7 Hz, 8 H), 8.09 (d, J = 1.5 Hz, 4 H), 8.48 (d, J = 1.6 Hz, 2 H), 8.64 (t, J = 1.5 Hz, 2 H), 9.03 ppm (t, J = 1.6 Hz, 1 H); elemental analysis calcd (%) for $C_{65}H_{93}NO_{12}$: C 72.26, H 8.68, N 1.30; found: C 72.00, H 8.33, N 1.26.

CN-G^2: Yellow waxy solid (7.21 g, 69 %); IR (KBr): $\tilde{\nu}$ = 2125 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.96 (m, 72 H), 4.35 (t, J = 6.8 Hz, 16 H), 8.11 (d, J = 1.4 Hz, 8 H), 8.40 (d, J = 1.5 Hz, 4 H), 8.55 (d, J = 1.6 Hz, 2 H), 8.64 (t, J = 1.4 Hz, 4 H), 9.01 (t, J = 1.5 Hz, 1 H), 9.10 ppm (t, J = 1.6 Hz, 1 H); elemental analysis calcd (%) for $C_{137}H_{189}NO_{28}$: C 71.61, H 8.29, N 0.61; found: C 71.24, H 8.08, N 0.67.

Synthesis of [AuCl(CN-G^n)]: A stoichometric amount of CN-G^n dissolved in dichloromethane (20 mL) was added to a solution of [AuCl(tht)] (0.20 g, 0.18 mmol) in dichloromethane (20 mL). After 30 min the solution was concentrated, acetonitrile was added, and the mixture was cooled.

[AuCl(CN-G^1)]: White solid (0.24 g, 98 %); IR (KBr): $\tilde{\nu}$ = 2229 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.96 (m, 36 H), 4.36 (t, J = 6.8 Hz, 8 H), 8.10 (d, J = 1.0 Hz, 4 H), 8.65 (t, J = 1.0 Hz, 2 H), 8.68 (d, J = 1.1 Hz, 2 H), 9.19 ppm (t, J = 1.1 Hz, 1 H); elemental analysis calcd (%) for $C_{65}H_{93}NAuClO_{12}$: C 59.47, H 7.14, N 1.07; found: C 59.15, H 6.84, N 0.89.

[AuCl(CN-G^2)]: White solid (0.23 g, 80 %); IR (KBr): $\tilde{\nu}$ = 2227 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.96 (m, 72 H), 4.36 (t, J = 6.8 Hz, 16 H), 8.11 (d, J = 1.4 Hz, 8 H), 8.40 (d, J = 1.6 Hz, 4 H), 8.63 (t, J = 1.4 Hz, 4 H), 8.73 (d, J = 1.6 Hz, 2 H), 9.02 (t, J = 1.6 Hz, 2 H), 9.26 ppm (t, J = 1.6 Hz, 1 H); elemental analysis calcd (%) for $C_{137}H_{189}NAuClO_{28}$: C 65.03, H 7.53, N 0.55; found: C 64.69, H 7.49, N 0.53.

Synthesis of [CuCl(CN-G^n)]: CuCl (0.020 g, 0.21 mmol) was suspended in dichloromethane (20 mL) and a stoichometric amount of the appropriate CN-G^n was added. After 1 h the solution was filtered. The crude product was recrystallized in dichloromethane/diethyl ether, [CuCl(CN-G^1)], or dichloromethane/acetone, [CuCl(CN-G^2)].

[CuCl(CN-G^1)]: White solid (0.08 g, 36 %); IR (KBr): $\tilde{\nu}$ = 2179 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.90 (m, 36 H), 4.35 (t, J = 6.8 Hz, 8 H), 8.09 (d, J = 1.5 Hz, 4 H), 8.64 (t, J = 1.5 Hz, 2 H), 8.56 (d, J = 1.5 Hz, 2 H), 9.09 ppm (t, J = 1.5 Hz, 1 H); elemental analysis calcd (%) for $C_{65}H_{93}NClCuO_{12}$: C 66.19, H 7.95, N 1.19; found: C 65.83, H 7.78, N 1.33.

[CuCl(CN-G^2)]: White solid (0.12 g, 37 %); IR (KBr): $\tilde{\nu}$ = 2184 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.96 (m, 72 H), 4.36 (t, J = 6.8 Hz, 16 H), 8.11 (d, J = 1.4 Hz, 8 H), 8.40 (d, J = 1.4 Hz, 4 H), 8.63 (t, J = 1.4 Hz, 4 H), 8.73 (d, J = 1.4 Hz, 2 H), 9.02 (t, J = 1.4 Hz, 2 H), 9.26 ppm (t, J = 1.4 Hz, 1 H); elemental analysis calcd (%) for $C_{137}H_{189}NClCuO_{28}$: C 68.65, H 7.95, N 0.58; found: C 68.74, H 7.88, N 0.91.

Synthesis of [{CuCl(CN-G^n)$_2$}$_2$]: CN-G^n (0.5 equivalents) was added to a suspension of CuCl (0.014 g, 0.14 mmol) in dichloromethane (20 mL). The solvent was removed and the residue washed with pentane, [{CuCl(CN-G^1)$_2$}$_2$], or recristallized in dichloromethane/acetone, [{CuCl(CN-G^2)$_2$}$_2$].

[{CuCl(CN-G^1)$_2$}$_2$]: Yellow waxy solid (0.30 g, 26 %); IR (KBr): $\tilde{\nu}$ = 2147 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.88–1.95 (m, 144 H), 4.36 (t, J = 6.8 Hz, 32 H), 8.09 (d, J = 1.5 Hz, 16 H), 8.61 (d, J = 1.5 Hz, 8 H), 8.64 (t, J = 1.5 Hz, 8 H), 9.10 ppm (t, J = 1.5 Hz, 4 H); elemental analysis calcd (%) for $C_{260}H_{372}N_4Cl_2Cu_2O_{48}$: C 69.09, H 8.30, N 1.24; found: C 68.89, H 8.06, N 1.18.

[{CuCl(CN-G^2)$_2$}$_2$]: Green waxy solid (0.54 g, 43 %); IR (KBr): $\tilde{\nu}$ = 2148 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.78–1.85 (m, 288 H), 4.28 (t, J = 6.7 Hz, 64 H), 8.03 (d, J = 1.5 Hz, 32 H), 8.33 (d, J = 1.4 Hz, 16 H), 8.55 (t, J = 1.5 Hz, 16 H), 8.59 (d, J = 1.5 Hz, 8 H), 8.94 (t, J = 1.4 Hz, 8 H), 9.11 ppm (t, J = 1.5 Hz, 4 H); elemental analysis calcd (%) for $C_{548}H_{756}N_4Cl_2Cu_2O_{112}$: C 70.10, H 8.12, N 0.60; found: C 69.74, H 8.05, N 0.82.

Synthesis of [MI$_2$(CN-G^n)$_2$] (M: Pd, Pt): A solution of [$MCl_2(NCCH_3)_2$] (0.092 mmol)) in tetrahydrofuran (20 mL) was prepared. CN-G^n (2 equiv) and KI (4 equiv) were added. The mixture was stirred for 4 h. The solvent was pumped off and the product extracted in dichloromethane and recristallized in acetone.

[PdI$_2$(CN-G^1)$_2$]: Yellowish solid (0.15 g, 22 %); IR (KBr): $\tilde{\nu}$ = 2199 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.77–1.94 (m, 64 H), 4.37 (t, J = 6.8 Hz, 16 H), 8.11 (d, J = 1.5 Hz, 8 H), 8.66 (m, 32 H), 9.15 ppm (t, J = 1.5 Hz, 2 H); elemental analysis calcd (%) for $C_{130}H_{186}I_2N_2O_{24}Pd$: C 61.93, H 7.44, N 1.11; found: C 61.80, H 7.21, N 1.12.

[PdI$_2$(CN-G^2)$_2$]: Orange waxy solid (0.30 g, 42 %); IR (KBr): $\tilde{\nu}$ = 2201 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.90 (m, 64 H), 4.36 (t, J = 6.8 Hz, 32 H), 8.12 (d, J = 1.5 Hz, 16 H), 8.43 (d, J = 1.6 Hz, 8 H), 8.64 (t, J = 1.5 Hz, 8 H), 8.73 (d, J = 1.5 Hz, 4 H), 9.03 (t, J = 1.6 Hz, 4 H), 9.22 ppm (t, J = 1.5 Hz, 2 H); elemental analysis calcd (%) for $C_{274}H_{378}I_2N_2O_{56}Pd$: C 66.40, H 7.69, N 0.57; found: C 66.66, H 7.79, N 0.62.

[PtI$_2$(CN-G^1)$_2$]: Yellowish waxy solid (0.13 g, 52 %); IR (KBr): $\tilde{\nu}$ = 2188 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.78–1.90 (m, 64 H), 4.37 (t, J = 6.8 Hz, 16 H), 8.12 (d, J = 1.5 Hz, 8 H), 8.66 (m, 32 H), 9.15 ppm (t, J = 1.5 Hz, 2 H); elemental analysis calcd (%) for $C_{130}H_{186}I_2N_2O_{24}Pt$: C 59.83, H 7.18, N 1.07; found: C 60.33, H 7.11, N 1.19.

[PtI$_2$(CN-G^2)$_2$]: Yellow waxy solid (0.33 g, 73 %); IR (KBr): $\tilde{\nu}$ = 2195 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): δ = 0.79–1.80 (m, 64 H), 4.29 (t, J = 6.8 Hz, 32 H), 8.05 (d, J = 1.4 Hz, 16 H), 8.35 (d, J = 1.6 Hz, 8 H), 8.57 (t, J = 1.4 Hz, 8 H), 8.64 (d, J = 1.5 Hz, 4 H), 8.96 (t, J = 1.6 Hz, 4 H), 9.15 (t, J = 1.5 Hz, 2 H); elemental analysis calcd (%) for $C_{274}H_{378}I_2N_2O_{56}Pt$: C 65.23, H 7.55, N 0.56; found: C 65.40, H 7.62, N 0.73.

The Supporting Information contains general procedures and instrumentation, representative DSC traces, and small angle X-ray patterns of the mesophases of the metallodendrimers.

Acknowledgements

This work was sponsored by the D.G.I. (Project CTQ2005-08729/BQU) and the Junta de Castilla y León (Project VA099 A05). C.C. thanks the MEC for a grant.

---

[1] a) *Dendrimers and Other Dendritic Polymers* (Eds.: J. M. J. Fréchet, D. A. Tomalia), Wiley, New York, **2001**; b) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Synthesis and Applications*, Wiley-VCH, Weinheim, **2001**; c) F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681–1712.

[2] a) C. Gorman, *Adv. Mater.* **1998**, *10*, 295–309; b) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689–1746; c) I. Cuadrado, M. Morán, C. M. Casado, B. Alonso, J. Losada, *Coord. Chem. Rev.* **1999**, *193–195*, 395–445; d) D. K. Smith, A. R. Hirst, C. S. Love, J. G. Hardy, S. V. Brignell, B. Huang, *Prog. Polym. Sci.* **2005**, *30*, 220–293; e) D. Méry, D. Astruc, *Coord. Chem. Rev.* **2006**, *250*, 1965–1979.

[3] a) J. N. H. Reek, S. Arévalo, R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Adv. Catal.* **2006**, *49*, 71–151; b) *Dendrimer Catalysis* (Ed.: L. H. Gade), Springer, Berlin, **2006**.

[4] a) *Metallomesogens* (Ed.: J. L. Serrano), VCH, Weinheim, **1996**; b) "Metal-Containing Liquid Crystals: D. W. Bruce in *Inorganic Materials*, 2nd ed. (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, **1996**, Chapter 8, pp. 429–522.

[5] a) S. Hecht, J. M. J. Fréchet, *Angew. Chem.* **2001**, *113*, 76–94; *Angew. Chem. Int. Ed.* **2001**, *40*, 74–91; b) L. J. Twyman, A. S. H. King, I. K. Martin, *Chem. Soc. Rev.* **2002**, *31*, 69–82.

[6] R. Van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717–3756.

[7] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serón, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26–34.

[8] S. Achar, J. J. Vittal, R. Puddephatt, *Organometallics.* **1996**, *15*, 43–50.

[9] a) M. Kawa, J. M. Fréchet, *J. Chem. Mater*, **1998**, *10*, 286–296; b) F. Vogtle, M. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. DeCola, V. Demarcáis, M. Ventura, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 6290–6298; c) C. M. Cardona, A. E. Kaifer, *J. Am. Chem. Soc.* **1998**, *120*, 4023–4024.

[10] a) K. Takada, D. J. Diaz, H. D. Abruña, I. Cuadrado, C. Casado, B. Alonso, M. Moran, J. Losada, *J. Am. Chem. Soc.* **1997**, *119*, 10763–10773; b) J. L. Fillaut, J. Linares, D. Astruc, *Angew. Chem.* **1994**, *106*, 2540–2542; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2460–2462.

[11] a) J. W. Goodby, G. H. Mehl, I. M. Saez, R. P. Tuffin, G. Mackenzie, R. Auzély-Velty, T. Benvegnu, D. Plusquellec, *Chem. Commun.* **1998**, 2057–2070; b) S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, *Polym. Sci. Ser. C* **2001**, *43*, 1–45; c) I. M. Sáez, J. Goodby, *J. Mater. Chem.* **2005**, *15*, 26–40; d) V. Percec, *Philos. Trans. R. Soc. A* **2006**, *364*, 2709–2719; e) B. Donnio, D. Guillon, *Adv. Polym. Sci.* **2006**, *201*, 45–155; f) B. Donnio, S. Buathong, I. Bury, D. Guillon, *Chem. Soc. Rev.* **2007**, *36*, 1495–1513; g) V. Percec, M. Peterca, J. G. Rudick, E. Aqad, M. R. Imam, P. A. Heiney, *Chem. Eur. J.* **2007**, *13*, 9572–9581 and refernces there in.

[12] R. Deschenaux, Bertrand Donnio, D. Guillon, *New J. Chem.* **2007**, *31*, 1064–1073.

[13] a) A. G. Serrette, T. M. Swager, *J. Am. Chem. Soc.* **1993**, *115*, 8879–8890; b) C. K. Lai, M. Y. Lu, F. J. Lin, *Liq. Cryst.* **1997**, *23*, 313–315; c) U. Stebani, G. Lattermann, M. Wittenberg, J. H. Wendorff, *Angew. Chem.* **1996**, *108*, 1941–1943; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1858–1861; d) U. Stebani, G. Lattermann, *Adv. Mater.* **1995**, *7*, 578–581; e) J. Barberá, M. Marcos, A. Omenat, J. L. Serrano, J. I. Martínez, P. J. Alonso, *Liq. Cryst.* **2000**, *27*, 255–262; f) E. Terazzi, B. Bocquet, S. Campidelli, B. Donnio, D. Guillon, R. Deschenaux, C. Piguet, *Chem. Commun.* **2006**, 2922–2924.

[14] a) L. Malatesta, F. Bonati, *Isocyanide Complexes of Metals*, Wiley, Chichester, **1969**; b) D. Lentz, *Angew. Chem.* **1994**, *106*, 1377–1393; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1315–1331; c) M. Tamm, F. E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175–209.

[15] M. Tanabiki, K. Tsuchiya, Y. Kumanomido, K. Matsubara, Y. Motoyama, H. Nagashima, *Organometallics* **2004**, *23*, 3976–3981.

[16] Y. Ito, M. Suginome, T. Matsuura, M. Murakami, *J. Am. Chem. Soc.* **1991**, *113*, 8899–8908.

[17] Y. Sun, K. Ye, H. Zhang, J. Zhang, L. Zhao, B. Li, G. Yang, B. Yang, Y. Wang, S.-W. Lai, C.-M. Che, *Angew. Chem.* **2006**, *118*, 5738–5741; *Angew. Chem. Int. Ed.* **2006**, *45*, 5610–5613.

[18] a) P. Espinet, M. A. Esteruelas, L. Oro, J. L. Serrano, E. Sola, *Coord. Chem. Rev.* **1992**, *117*, 215–274; b) B. Donnio, D. W. Bruce, *Struct. Bonding* **1999**, *95*, 193–247; c) P. Espinet, *Gold Bull.* **1999**, *32*, 127–134; d) P. J. Collings, *Liquid Crystals (Nature's Delicate Phase of Matter)*, Princeton University Press, Priceton, NJ, **1990**; e) *Handbook of Liquid Crystals* (Eds.: D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, D. V. Vill), Wiley-VCH, Weinheim, **1998**; f) B. Donnio, D. Guillon, D. W. Bruce, R. Deschenaux, *Metallomesogens, Comprehensive Organometallic Chemistry III: From Fundamentals to Applications, Vol. 12*(Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2006**; g) *Applications III: Functional Materials, Environmental and Biological Applications* (Ed.: D. O'Hare), Chapter 12.05, pp. 195–294.

[19] a) S Coco, E. Espinet, P. Espinet, I. Palape, *Dalton Trans.* **2007**, 3267–3272; b) S. Coco, C. Cordovilla, P. Espinet, J. Martín-Álvarez, P. Muñoz, *Inorg. Chem.* **2006**, *45*, 10180–10187.

[20] S. Coco, F. Díez-Expósito, P. Espinet, C. Fernández-Mayordomo, J. M. Martín-Álvarez, A. M. Levelut, *Chem. Mater.* **1998**, *10*, 3666–3671.

[21] R. Bayón, S. Coco, P. Espinet, *Chem. Eur. J.* **2005**, *11*, 1079–1085.

[22] M. Benouazzane, S. Coco, P. Espinet, J. Barberá, *Inorg. Chem.* **2002**, *41*, 5754–5759.

[23] C. Hammond, *The Basics of Crystallography and Diffraction*, 2nd ed., IUCr, Oxford Science Publications, Oxford, **2001**; $I(\vec{k}^*) = I(-\vec{k}^*)$.

[24] *International Tables for Crystallography, Vol. A*, 4th ed (Ed.: T. Hahn), The International Union of Crystallography, Kluwer Academic, Dordrecht, **1995**.

[25] E. Terazzi, S. Torelli, G. Bernardinelli, J-P. Rivera, J.-M. Bénech, C. Bourgogne, B. Donnio, D. Guillon, D. Imbert, J.-C. G. Bünzli, A. Pinto, D. Jeannerat, C. Piguet, *J. Am. Chem. Soc.* **2005**, *127*, 888–903.

[26] a) G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, *Science* **2003**, *299*, 1208–1211; b) V. Percec, C. M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2004**, *126*, 6078–6094; c) V. Percec, M. N. Holerca, S. Nummelin, J. J. Morrison, M. Glodde, J. Smidrkal, M. Peterca, B. M. Rosen, S. Uchida, V. S. K. Balagurusamy, M. J. Sienkowska, P. A. Heiney, *Chem. Eur. J.* **2006**, *12*, 6216–6241; d) V. Percec, M. Peterca, M. J. Sienkowska, M. A. Ilies, E. Aqad, J. Smidrkal, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 3324–3334.

[27] A. M. Levelut, M. Clerc, *Liq. Cryst.* **1998**, *24*, 105–115.

[28] X. B. Zeng, G. Ungar, M. Imperor-Clerc, *Nat. Mater.* **2005**, *4*, 562–567.

[29] E. Terazzi, C. Bourgogne, R. Welter, J.-L. Gallani, D. Guillon, G. Rogez, B. Donnio, *Angew. Chem.* **2008**, *119*, 500–505; *Angew. Chem. Int. Ed.* **2008**, *47*, 490–495.

[30] M. Impéror-Clerc, *Curr. Opin. Chem. Biol.* **2005**, *9*, 370–376.

[31] a) S. Diele, P. Göring in Handbook of Liquid Crystals, *Vol. 2B* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**, pp. 887–900; b) S. Diele, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 333–342; c) S. Kutsumizu, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 537–543.

[32] G. Ungar, X. Zeng, *Soft Matter* **2005**, *1*, 95–106.

[33] A. Laguna, M. Laguna, R. Usón, *Inorg. Synth.* **1989**, *26*, 85–87.

[34] F. R. Hartley, C. A. McAuliffe, S. G. Murray, *Inorg. Chem.* **1979**, *18*, 1394–1397.

[35] R. N. Keller, H. D. Wycoff, *Inorg. Synth.* **1946**, *2*, 1–4.

Received: January 22, 2008