J|A|C|S
ARTICLES

Published on Web 01/07/2010

Liquid-Crystalline Self-Organization of Isocyanide-Containing Dendrimers Induced by Coordination to Gold(I) Fragments

Carlos Cordovilla,[†,‡] Silverio Coco,[†] Pablo Espinet,[†] and Bertrand Donnio*[,‡]

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Castilla y León, Spain, and IPCMS, CNRS-Université de Strasbourg (UMR 7504), 23 rue du Loess, BP43, 67034, Strasbourg Cedex 2, France

Received November 6, 2009; E-mail: bdonnio@ipcms.u-strasbg.fr

---

Abstract: Dendritic polyisocyanides can be considered as promising polytopic ligands to generate a great diversity of metallodendrimers due to the ability of the isocyanide moiety to bind to various transition metals. Here, new isocyanide-containing dendrimers and their corresponding polynuclear gold complexes have been prepared, [G^i(NC)$_Z$] and [G^i(NCAuR)$_Z$], respectively, where G^i is a poly(phenyl ether) dendrimer, i is the generation number (i = 0, 1, or 2), Z is the number of peripheral groups ($Z = 3 \times 2^i$), and AuR are the surface groups ([R = Cl, C≡C-C_6H_4−$OC_{12}H_{25}$, C≡$CC_6H_2(OC_{12}H_{25})_3$]. The compounds are derived from a highly flexible phenyl ether-based dendritic core, G^i, having the general formula $G^0 = C_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_3$, $G^1 = C_6H_3[OC_{11}H_{22}OC_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_2]_3$, $G^2 = C_6H_3[OC_{11}H_{22}OC_6H_3\{OC_{11}H_{22}OC_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_2\}_2]_3$), growing from the trivalent phloroglucinol and with undecylene aliphatic spacers between each branching benzene ring and end-functionalized by isocyanide groups. As in their monomeric model counterparts, stable liquid-crystalline phases are induced upon complexation of the AuR gold moieties at the branch termini. The nature of the anionic ligand R promotes the appearance of smectic or columnar mesophases, the formation of which are governed by steric and dipolar interactions. Based on X-ray diffraction experiments, models describing the supramolecular organization of these metallodendrimers into smectic and columnar mesophases are proposed: columnar phases result from the one-dimensional stacking of molecular disks made of self-assembled supermolecules in oblate cylindrical conformation, while the smectic phases form by the lateral two-dimensional registry of the supermolecules in antiparallel head-to-head prolate conformation.

Introduction

Research in the field of dendrimers, as monodisperse macromolecules with perfectly controlled cascadelike architectures, has substantially developed and matured from the early pioneering works focused mainly on synthetic methodologies and architectural challenges.[1] Today, interests in dendrimers are mostly driven by the molecular design of novel arborescent functional structures and the subsequent control of weak interactions to subtly modulate physical and chemical properties toward the realization of function-specific nanomaterials and the discovery of novel applications. Due to specific intrinsic features, such as conformational flexibility, leading to proteanlike molecular forms, multivalency, and hyperfunctionality, responsible for the so-called dendritic effect, dendrimers have since been successfully designed and developed for applications in the fields of medicine, biology, and biotechnology[1–3] and are expected to have a huge impact in materials science.[1,4] These aesthetically appealing macromolecules, when adequately functionalized, can be further considered as intricate and versatile multicomponent building blocks for self-assembly and, under particular conditions, can generate various types of periodically ordered networks.[4,5] Both dendrimers[6] and dendrons (the elementary dendritic branches)[7] are particularly versatile candidates as original

---

[†] Universidad de Valladolid.

[‡] IPCMS, CNRS-Université de Strasbourg.

(1) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. In *Dendrimers and Dendrons: Concepts, Synthesis and Applications*; Wiley & Sons: Weinheim, Germany, 2001. (b) Fréchet, J. M. J., Tomalia, D. A., Eds. *Dendrimers and Other Dendritic Polymers*; Wiley Series in Polymer Science; Wiley & Sons: Chichester, U.K., 2001. (c) Majoral, J.-P.; Caminade, A.-M.; Maraval, V. *Chem. Commun.* **2002**, 2929–2942.

(2) (a) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875–909. (b) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681–1712. (c) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884–905. (d) Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845–880. (e) Lee, C. C.; MacKay, J. A.; Fréchet, J. M. J.; Szoka, F. C. *Nat. Biotechnol.* **2005**, *23*, 1517–1526. (f) Caminade, A.-M.; Padié, C.; Laurent, R.; Maraval, A.; Majoral, J.-P. *Sensors* **2006**, *6*, 901–914. (g) Niederhafner, P.; Sebestik, J.; Jezek, J. *J. Pept. Sci.* **2008**, *14*, 2–43. (h) Niederhafner, P.; Sebestik, J.; Jezek, J. *J. Pept. Sci.* **2008**, *14*, 44–65. (i) Tekade, R. K.; Kumar, P. V.; Jain, N. K. *Chem. Rev.* **2009**, *109*, 49–87. (j) Medina, S. H.; El-Sayed, M. E. H. *Chem. Rev.* **2009**, *109*, 3141–3157. (k) Kim, J.; Piao, Y.; Hyeon, T. *Chem. Soc. Rev.* **2009**, *38*, 372–390. (l) Rolland, O.; Turrin, C.-O.; Caminade, A.-M.; Majoral, J.-P. *New J. Chem.* **2009**, *33*, 1809–1824.

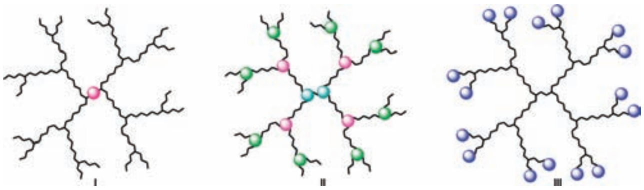
(3) Boas, U.; Christensen, J. B.; Heegaard, P. M. H. In *Dendrimers in Medicine and Biotechnology:New Molecular Tools*; RSC Publishing: Cambridge, U.K., 2006.

(4) (a) Chow, H. F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* **1998**, *54*, 8543–8660. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688. (c) Vögtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987–1041. (d) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867. (e) Caminade, A.-M.; Majoral, J.-P. *Acc. Chem. Res.* **2004**, *34*, 341–348.

(5) Tully, D. C.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1229–1239.

10.1021/ja909435e

Chart 1. Schematic Structures of Metallodendrimers[a]



[a] With emphasis on the different locations of metal fragments within the dendritic frame: at the center (**I**), at the branching points (**II**), and at the periphery (**III**).

scaffoldings for the elaboration of new liquid-crystalline (LC) multifunctional materials. Furthermore, as multicomponent systems, they possess a high density of active groups per unit volume, and it is anticipated that some of the incorporated functions can additionally be amplified within the induced low-dimensional LC mesophases ordering by cooperative and synergistic effects.[8]

While the majority of dendrimers reported so far are purely organic in nature, there is a rising interest in dendrimers containing transition metal ions.[1,9] These so-called *metallodendrimers* are particularly attractive as the metallic moieties can be easily integrated into different parts of the dendritic scaffold, including the nodal core, branching points, and periphery (Chart 1),[9] and their specific properties (e.g., redox, electronic, optic, magnetic, etc.) can be modulated accordingly by collective effects through the hierarchization (generations) and compartmentalization (alternated or segmented constitutive lobes) of the dendrimeric structure and toplology. As a matter of fact, concomitant with judicious molecular designs, metallodendrimers have been found to be particularly efficient materials in catalysis,[10] as molecular devices,[11] or as environmental tools for site isolation and/or recyclability.[12]

In this study, we report on the design of novel metal-containing dendrimers endowed with mesomorphic properties. The overall core architecture of the dendrimers consists of a highly flexible polyaryl ether-based core, with the trivalent phloroglucinol as central node, and the branching benzene rings at each generation are connected by undecylene aliphatic spacers. The dendrimers are end-functionalized by isocyanide groups, versatile moieties owing to their outstanding coordination ability to give very stable complexes with many transition metals. Mesomorphism is induced in these systems upon complexion of gold-containing fragments, and the type of mesophases depends strongly on the molecular shape of the gold complex connected at the dendritic extremities. Thus, smectic phases are obtained after bonding of rodlike gold chloride and gold acetylide fragments, whereas columnar hexagonal phases are formed upon complexion with tapered shape gold-acetylide fragments.

Results and Discussion

Design and Synthesis. LC dendrimers have now reached a high degree of sophistication, and the type and nature of the mesophases can be predicted and controlled through dedicated structural engineering at the molecular level by manipulating the intrinsic dendritic connectivity or by modulating the core flexibility and the nature and type of peripheral substitution.[6,7] Surprisingly, however, very few dendritic metallomesogens[13] (i.e., mesomorphic metallodendrimers) have been yet reported. A simple and well-known synthetic route to prepare metallodendrimers is to use metallic species as nodal linking groups and coordinate protomesomorphic dendritic fragments that can act as ligands (Chart 1, structure **I**). This is the most commonly applied strategy for obtaining metallodendrimer-containing LCs.[14] In this case, the metallic fragment is shielded by the dense organic dendritic shell, and mesomorphism is solely governed by the structure and conformation of the dendritic branches. Alternatively, functionalization of the dendritic pe-

---

(6) (a) Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P. *Polym. Sci. C* **2001**, *43*, 1–45. (b) Donnio, B.; Guillon, D. *Adv. Polym. Sci.* **2006**, *201*, 45–155. (c) Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. *Chem. Soc. Rev.* **2007**, *36*, 1495–1513. (d) Deschenaux, R.; Donnio, B.; Guillon, D. *New J. Chem.* **2007**, *31*, 1064–1073.

(7) (a) Percec, V.; Glodde, M.; Johansson, G.; Balagurusamy, V. S. K.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4338–4342. (b) Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, G.; Zeng, X.; Liu, Y.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2004**, *126*, 6078–6094. (c) Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujiie, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1969–1972. (d) Percec, V.; Imam, M. R.; Bera, T. K.; Balagurusamy, V. S. K.; Peterca, M.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4739–4745. (e) Percec, V.; Glodde, M.; Peterca, M.; Rapp, A.; Schnell, I.; Speiss, H. W.; Bera, T. K.; Miura, Y.; Balagurusamy, V. S. K.; Aqad, E.; Heiney, P. A. *Chem.—Eur. J.* **2006**, *12*, 6298–6314. (f) Kamikawa, Y.; Kato, T. *Org. Lett.* **2006**, *8*, 2463–2466. (g) Percec, V.; Holerca, M. N.; Nummelin, S.; Morrison, J. J.; Glode, M.; Smidrkal, J.; Peterca, M.; Rosen, B. M.; Uchida, S.; Balagurusamy, V. S. K.; Sienkowska, M. J.; Heiney, P. A. *Chem.—Eur. J.* **2006**, *12*, 6216–6241. (h) Percec, V.; Peterca, M.; Sienkowska, M. J.; Ilies, M. A.; Aqad, E.; Smidrkal, J.; Heiney, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 3324–3334. (i) Percec, V.; Won, B. C.; Peterca, M.; Heiney, P. A. *J. Am. Chem. Soc.* **2007**, *129*, 11265–11278. (j) Percec, V.; Smidrkal, J.; Peterca, M.; Mitchell, C. M.; Nummelin, S.; Dulcey, A. E.; Sienkowska, M. J.; Heiney, P. A. *Chem.—Eur. J.* **2007**, *13*, 3989–4007. (k) Percec, V.; Imam, M. R.; Peterca, M.; Wilson, D. A.; Heiney, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 1294–1304. (l) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275–6540.

(8) (a) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68. (b) Kato, T.; Yasuda, T.; Kamikawa, Y.; Yoshio, M. *Chem. Commun.* **2009**, 729–739.

(9) (a) Constable, E. C. *Chem. Commun.* **1997**, 1073–1080. (b) Gorman, C. *Adv. Mater.* **1998**, *10*, 295–309. (c) Hearshaw, M. A.; Moss, J. R. *Chem. Commun.* **1999**, 1–8. (d) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (e) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *193–195*, 395–445. (f) Serroni, S.; Campagna, S.; Puntoriero, F.; Di Pietro, C.; McClenaghan, N. D.; Loiseau, F. *Chem. Soc. Rev.* **2001**, *30*, 367–375. (g) Peris, E. *Coord. Chem. Rev.* **2004**, *248*, 279–297. (h) Méry, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, *250*, 1965–1979.

(10) (a) Kreiter, R.; Kleij, A. W.; Klein-Gebbink, R. J. M.; van Koten, G. *Top. Curr. Chem.* **2001**, *217*, 163–199. (b) Chase, P. A.; Klein-Gebbink, R. J. M.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016–4054. (c) Reek, J. N. H.; Arévalo, S.; van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Adv. Catal.* **2006**, *49*, 71–151. (d) Gade, L. H., Ed. *Dendrimer Catalysis*; Springer: Berlin, 2006.

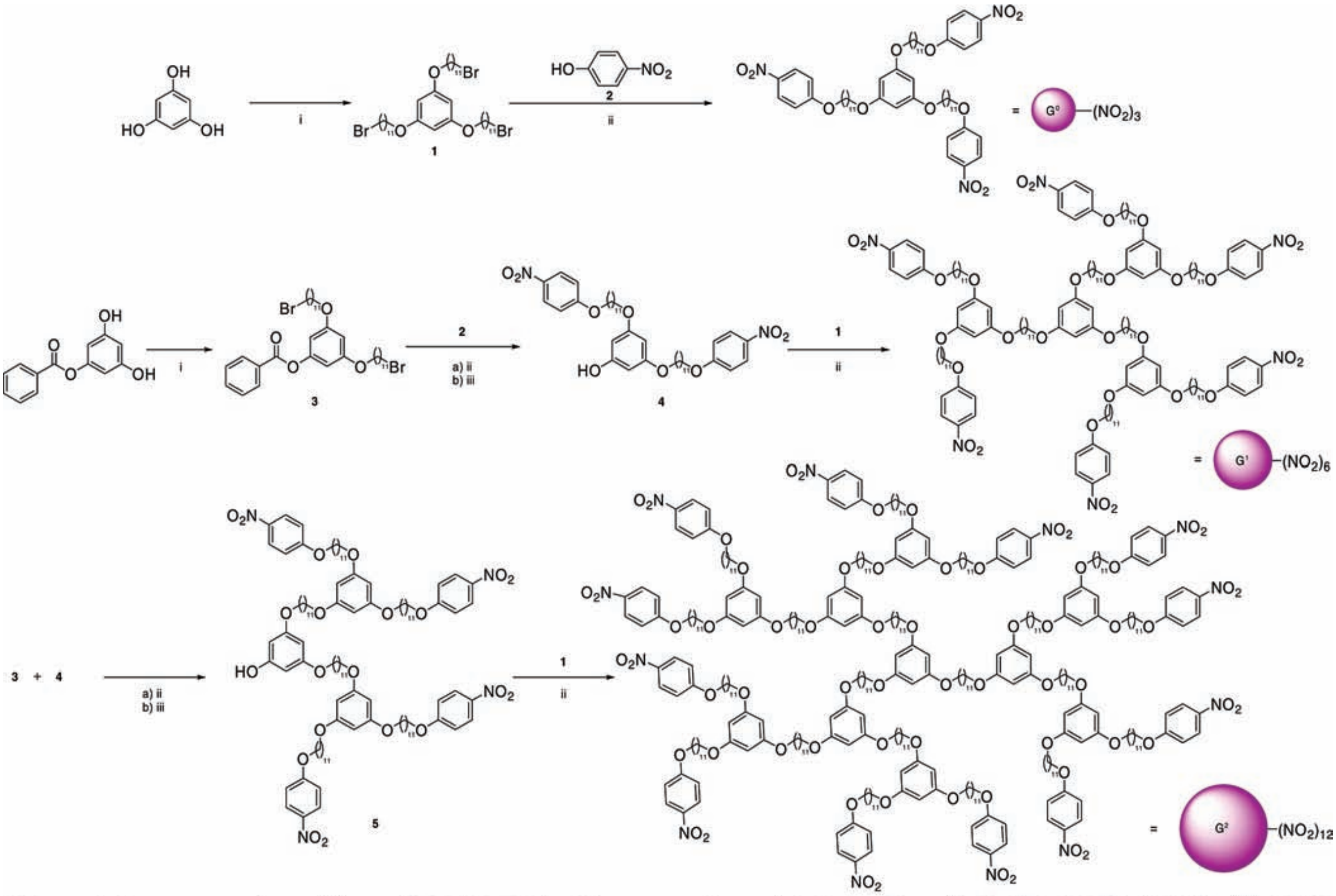
(11) Hwang, S.-H.; Moorefield, C. N.; Newkome, G. R. *Chem. Soc. Rev.* **2008**, *37*, 2543–2557.

(12) (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74–91. (b) Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69–82. (c) Van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717–3756.

(13) Donnio, B.; Guillon, D.; Bruce, D. W.; Deschenaux, R. In *Metallomesogens*; McCleverty, J. A.; Meyer, T. J. Eds; Comprehensive Coordination Chemistry II: From Biology to Nanotechnology; Elsevier: Oxford, U.K., 2003; Vol. 7, Chapt. 7.9, pp 357−627.

(14) (a) Stebani, U.; Lattermann, G. *Adv. Mater.* **1995**, *7*, 578–581. (b) Terazzi, E.; Bocquet, B.; Campidelli, S.; Donnio, B.; Guillon, D.; Deschenaux, R.; Piguet, C. *Chem. Commun.* **2006**, 2922–2924. (c) Terazzi, E.; Bourgogne, C.; Welter, R.; Gallani, J.-L.; Guillon, D.; Rogez, G.; Donnio, B. *Angew. Chem., Int. Ed.* **2007**, *47*, 490–495. (d) Frein, S.; Auzias, M.; Sondenecker, A.; Vieille-Petit, L.; Guintchin, B.; Maringa, N.; Süss-Fink, G.; Barberá, J.; Deschenaux, R. *Chem. Mater.* **2008**, *20*, 1340–1343. (e) Coco, S.; Cordovilla, C.; Donnio, B.; Espinet, P.; Garcia-Casas, M. J.; Guillon, D. *Chem.—Eur. J.* **2008**, *14*, 3544–3552.

Scheme 1[a]



[a] Reagents and conditions: (i) DIAD, PPh_3, 1-bromoundecanol, THF, reflux; (ii) K_2CO_3, DMF, 110 °C; (iii) KOH, THF/H_2O (1:1).

riphery with appropriate metal-biding sites represents a versatile way to modulate the topology of the dendrimer, and thus their self-assembly abilities, and to access to multivalent ligands ("metals' glue") able to bind various metallic entities (Chart 1, structure **III**); only a few such end-functionalized dendritic metallomesogens have been reported.[15,16] As far as we are aware, and despite their potential topological and functional diversity, mesomorphic systems with intermediate structures of type **II** have not yet been considered.[9]

For this purpose, isocyanides are versatile functionalities in organic synthesis and interesting ligands in organometallic chemistry, owing to their outstanding coordination ability with many transition metals.[17] Isocyanide−metal complexes also form stable liquid-crystalline materials,[18] and on these grounds, dendritic polyisocyanides can be used as promising polytopic ligands to construct novel liquid-crystalline metallodendrimers. Therefore, a new end-functionalized polyisocyanide dendritic system and several corresponding polynuclear gold complexes (series **I**−**III**), hereafter abbreviated as $[G^i(NC)_Z]$ and $[G^i(NCAuR)_Z]$, where $i = 0$, 1, or 2 is the generation number, $Z = 3 \times 2^i$ is the number of peripheral groups, and G^i are the highly flexible poly(phenyl ether) dendrimers of generation 0, 1, and 2, that is, $G^0 = C_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_3$, $G^1 = C_6H_3[OC_{11}H_{22}OC_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_2]_3$, and $G^2 = C_6H_3[OC_{11}H_{22}OC_6H_3\{OC_{11}H_{22}OC_6H_3(OC_{11}H_{22}OC_6H_4\text{-})_2\}_2]_3$, have been designed and synthesized. Three types of gold fragments AuR have been considered, namely, [AuCl], $[AuC{\equiv}C\text{-}C_6H_4{-}OC_{12}H_{25}]$, and $[AuC{\equiv}CC_6H_2(OC_{12}H_{25})_3]$, to modulate the structures of the formed mesophases. Moreover, for a complete evaluation of the impact of the dendritic effect (i.e., generation) and the dendrimerization (i.e., monomer → dendrimer) on the mesomorphic properties, the monomers and several dendritic generation compounds were synthesized.

Synthesis and Characterization. The synthesis of the dendritic ligands bearing nitro end groups $[G^i(NO_2)_Z]$ was carried out according to the divergent procedure represented in Scheme 1, starting from the etherification of benzene-1,3,5-triol (phloroglucinol) or benzoic acid 3,5-dihydroxyphenyl ester by 1-bromoundecanol via the Mitsunobu method.[19] The subsequent Williamson etherification of the bromide derivatives (**1**, **3**) with 4-nitrophenol (**2**) led directly to $[G^0(NO_2)_3]$ or, after hydrolysis, to the precursory branch of $[G^1(NO_2)_6]$, **4**, respectively. The

---

(15) (a) Deschenaux, R.; Serrano, E.; Levelut, A.-M. *Chem. Commun.* **1997**, 1577–1578. (b) Dardel, B.; Deschenaux, R.; Even, M.; Serrano, E. *Macromolecules* **1999**, *32*, 5193–5198.

(16) Barbera, J.; Marcos, M.; Omenat, A.; Serrano, J. L.; Martinez, J. I.; Alonso, P. J. *Liq. Cryst.* **2000**, *27*, 255–262.

(17) (a) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Wiley: Chichester, U.K., 1969. (b) Lentz, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1315–1331. (c) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175–209.

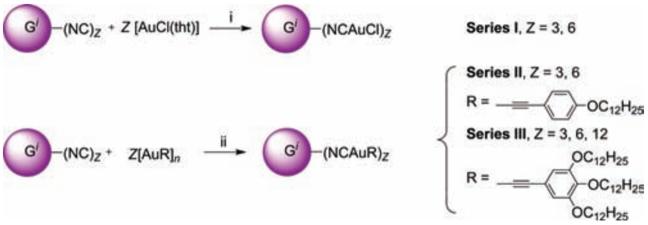
(18) (a) Espinet, P. *Gold Bull.* **1999**, *32*, 127–134. (b) Donnio, B.; Guillon, D.; Bruce, D. W.; Deschenaux, R. In *Metallomesogens*; Crabtree, R. H., Mingos, D. M. P., Eds.; Comprehensive Organometallic Chemistry III: From Fundamentals to Applications; Elsevier: Oxford, U.K., 2007; Vol. 12, Chapt. 12.05, pp 196−293.

(19) Mitsunobu, O. *Synthesis* **1981**, 1–28.

Scheme 2[a]

[a] Reagents and conditions: (i) hydrazine monohydrate, graphite, EtOH, reflux; (ii) formic acid, toluene, reflux; (iii) triphosgene[bis(trichloromethyl)carbonate], NEt_3, CH_2Cl_2, reflux.

Scheme 3[a]



[a] Reagents and conditions: (i) CH_2Cl_2 ($i = 0, 1$; $Z = 3, 6$); (ii) THF, R $= p\text{-}C_6H_4\text{-}OC_{12}H_{25}$, ($i = 0, 1$; $Z = 3, 6$); R $= p\text{-}C_6H_2\text{-}3,4,5\text{-}(OC_{12}H_{25})_3$ ($i = 0, 1, 2$; $Z = 3, 6, 12$).

dendrimer of the first generation, [$G^1(NO_2)_6$], was immediately obtained after ether coupling of 3 equiv of **4** with **1**. Etherification of **4** with **3**, followed by hydrolysis and then a subsequent etherification with **1**, yielded the dendrimer of the second generation, [$G^2(NO_2)_{12}$].

Conventional procedures were also used to transform the nitro groups into the isocyanide functionality (Scheme 2). The synthesis involved the reduction with hydrazine of the nitro-containing dendrimers, [$G^i(NO_2)_Z$], into the corresponding anilines, [$G^i(NH_2)_Z$], which were further treated with formic acid to give the formamides, [$G^i(NHC(O)H)_Z$]. Finally, in the last step, dehydration of the formamides with triphosgene[bis(trichloromethyl)carbonate] yielded the desired isocyanides [$G^i(NC)_Z$].

Depending on the final metallodendrimers, two methods were used for the gold complexation. Reaction of the dendrimers [$G^i(NC)_Z$] with the appropriate amount of [AuCl(tht)] afforded the chloro−gold complexes [$G^i(NCAuCl)_Z$], ($i = 0, 1$) by displacement of the ligand tetrahydrothiophene (tht) for the isocyanide groups (Scheme 3). The gold−acetylide complexes [$G^i(NCAuR)_Z$] were obtained by reaction of the isocyanide dendrimers with $[AuR]_n$ following procedures previously reported for related compounds (Scheme 3).[20]

In order to evaluate the dendrimerization effects on the mesomorphic properties, the two monomeric acetylide complexes, not previously described, were synthesized according to the procedures given in the Experimental Section (see Supporting Information). The purity of all the complexes was confirmed by C, H, and N elemental analysis. IR and ^{1}H NMR spectra of the complexes, very similar to each other due to the high symmetry of the molecules and due to the fact that the aromatic rings are almost isolated electronically, confirmed their structures. The IR spectra showed one $\nu(C{\equiv}N)$ absorption at 2120 cm^{-1} for the free isocyanides and at 2227 cm^{-1} for the chloro complexes and at 2212 cm^{-1} for alkynyl derivatives, confirming complete complexation. The ^{1}H NMR spectra displayed one singlet at 6.06 ppm for the protons of the 1,3,5-trialkoxybenzenic central and internal rings and two resonances for the H_{ortho} and H_{meta} of the C_6H_4NC groups (AA′XX′ spin system). In the case of the alkynylcomplexes the typical resonances for the R groups were also observed (see Supporting Information).

Mesomorphic Properties. The free isocyanide-containing dendrimers are not liquid-crystalline and were obtained as room-temperature oils, while induction of mesomorphism was detected for all the dendritic gold complexes but one, that is, the alkynyl complex [$G^0(NCAuC{\equiv}C\text{-}C_6H_4\text{-}OC_{12}H_{25})_3$]. The morphology of the mesophases is clearly governed by the nature of the end-group mesogen. Thus, the two chloro−gold dendrocomplexes ($i = 0$ or 1, series **I**), [$G^0(NCAuCl)_3$] and [$G^1(NCAuCl)_6$], show a smectic phase, in agreement with the behavior of the monomeric model compound (the monomeric compound was reported to display a smectic A phase).[21] As for the three generations of dendritic gold complexes ($i = 0$, 1, or 2, series **III**), [$G^i\{NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3\}_Z$], they all display a room-temperature columnar mesophase; the model monomer, $H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3$ (vide infra) also exhibits such a two-dimensional (2D) mesophase. The thermal behavior of the first-generation dendrimer bearing the one-chain alkynyl derivative, series **II** [$G^1(NCAuC{\equiv}CC_6H_4OC_{12}H_{25})_6$], is less obvious, as it decomposed rapidly in the mesophase, thus precluding unequivocal analysis; the model compound and the zeroth generation are, however, not mesomorphic and decomposed in the crystalline phase, in contrast to the behavior of some related alkynyl derivatives with alkyl groups.[20] Thermal and thermodynamic data of the metallodendrimers are collected in Table 1, along with the thermal behavior of the precursor monomeric gold complexes.

Most of the mesophases could be recognized by optical microscopy. The smectic C mesophase of the chloro−gold dendrimers was identified by a fluid and homogeneous texture and the absence of homeotropic regions or Brownian flashes under mechanical stress. Moreover, grayish textures could be observed by mechanical displacement. No birefringent texture could be observed for [$G^1(NCAuC{\equiv}CC_6H_4OC_{12}H_{25})_6$] in the explored temperature range (110−130 °C) but only the formation of large and black (homeotropic texture) areas on increasing temperature. However, upon mechanical shear, weakly birefringent, transient dendritic patterns with homeotropic contours were observed under microscope, which disappeared when the pressure was released. These indications suggest the formation of the orthogonal smectic A phase, although complete phase assignment could not be carried out further. The last series of complexes, [$G^i\{NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3\}_Z$], displayed a fan-like texture when viewed with a polarizing microscope on cooling from the isotropic melt down to room temperature, suggesting the formation of a columnar mesophase. The data of the monomeric gold complexes [$H_{25}C_{12}OC_6H_4NCAuCl$],[21] [$H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_4OC_{12}H_{25}$], and [$H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3$] are also included here for comparison.

A net decrease of the transition temperatures (melting and clearing) as well as an overall increase of the mesophase stability (corresponding to an increase of the mesophase temperature range) were observed upon dendrimerization of the mononuclear compounds [$H_{25}C_{12}OC_6H_4NCAuR$] [R = Cl, $C{\equiv}CC_6H_4OC_{12}H_{25}$, and $C{\equiv}CC_6H_2(OC_{12}H_{25})_3$]. In addition, melting and clearing temperatures were found to decrease steadily with increasing generations. Note that for the hairy alkynyl derivatives, [$G^i\{NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3\}_Z$], an important supercooling effect is observed with the generation. No phase formation was detected above 25 °C upon cooling at 10

---

(20) Alejos, P.; Coco, S.; Espinet, P. *New J. Chem.* **1995**, *19*, 799–805.

(21) Coco, S.; Espinet, P.; Falagán, S.; Martín-Alvarez, J. M. *New. J. Chem* **1995**, *19*, 959–964.

Table 1. Thermal Transitions and Corresponding Enthalpy Changes for the Three Series of Compounds[a]

compound	transition temperatures, °C (ΔH, kJ · mol^{-1})
	Series I
$H_{25}C_{12}OC_6H_4NCAuCl$[b]	Cr 123.9 (33.2) SmA 172.0 (8.2) I
	I 171.0 (−15.6) SmA 117.7 (−33.2) Cr
	Cr[c] 124.0 (32.4) SmA 171.7 (7.8) I
$[G^0(NCAuCl)_3]$	Cr 86.4 (9.0) Cr′ 97.2 (11.6) SmC 178.0 (13.9) I
	I 172.6 (−26.7) SmC 67.7 (−23.1) Cr
	Cr[c] 80.8 (30.9) Cr′ 105.3 (12.2) SmC 172.1 (13.9) I
$[G^1(NCAuCl)_6]$	Cr 35.7 (4.3) SmC 132.1 (45.5) I
	I 130.0 (−45.2) SmC
	Cr[c] 35.0 (4.2) SmC 132.6 (45.6) I
	Series II
$H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_4OC_{12}H_{25}$	Cr 47.4 (6.2) Cr′ 58.8 (12.8) Cr″ 94.1 (9.8) Cr‴ 150.6 (24.3) dec
$[G^0(NCAuC{\equiv}CC_6H_4OC_{12}H_{25})_3]$	Cr[d] 150 (−) dec
$[G^1(NCAuC{\equiv}CC_6H_4OC_{12}H_{25})_6]$	Cr 112.2 (121.3) Sm 127.5 (4.2) I
	I 123.2 (−5.3) Sm 48.5 (−1.5) Cr
	Cr[c] 109.5 (7.2) Sm 121.2 (13.4) I
	Series III
$H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3$	Cr 47.2 (80.1) Col$_h$ 125.2 (4.7) I
	I 120.5 (−3.4) Col$_h$ 0 (−26.5) Cr
	Cr[c] 5.9 (25.6) Col$_h$ 114.5 (4.3) I
$[G^0\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_3]$	Col$_h$ 115.9 (13.8) I
	I 112.6 (−11.6) Col$_h$
	Col$_h$[c] 111.6 (13.8) I
$[G^1\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_6]$	Col$_h$ 72.7 (13.9) I
	I 59.6 (−13.5) Col$_h$
	Col$_h$[c] 73.3 (15.9) I
$[G^2\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_{12}]$	Col$_h$ 35.6 (13.1) I

[a] Abbreviations: Cr−Cr‴, crystalline phases; SmA, smectic A phase; SmC, smectic C phase; Sm, unidentified smectic phase; Col$_h$, columnar hexagonal phase; I, isotropic liquid; dec, decomposition. [b] From ref 21. [c] Second heating. [d] Measured by thermogravimetric and thermodifferential analysis (TGA−TDA).

°C/min from isotropic liquid for the second-generation compound. Nevertheless, the same differential scanning calorimetry (DSC) traces on heating can be achieved if the sample is kept at room temperature for several hours. This fact suggests that the I−Col transition is slow, due to the high viscosity of the compounds, but nevertheless is reversible.

The mesogenic behavior of the one-chain alkynyl derivatives is clearly limited by the thermal instability of the Au−C(alkynyl) bond. Related mixed isonitrile−acetylyde complexes, with alkyl groups instead of alkoxy ones, consistently exhibited a SmA phase between 100 and 200 °C and also showed a strong tendency to decompose in the mesophase.[20] It can be speculated thus that the absence of mesomorphic properties in $[G^0(NCAuC{\equiv}CC_6H_4OC_{12}H_{25})_3]$ and in the monomeric compound is due to decomposition starting before melting, since the next generation exhibits a smectic phase.

Temperature-dependent, small-angle X-ray diffraction experiments were systematically carried out in order to identify unequivocally the nature of the mesophase. Their structural data and the mesophases' characteristics are collected in Table 2. All the mesophases can be considered as disordered, as they show only one broad and diffuse signal in the wide-angle region of the X-ray diffraction (XRD) patterns, centered at around 4.5−4.6 Å, distance reflecting the liquidlike state of the molten alkyl chains. In the low-angle region, sharp signals reflecting the 1D lamellar structures $[G^i(NCAuCl)_Z]$ or the 2D arrangement of the columns $[G^i\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_Z]$ series were detected.

The chloro−gold dendrimers (series **I**) showed up to three sharp and intense small-angle diffraction peaks in the 1:2:3 ratio that were indexed as $(00l) = (001), (002), (003)$ of a lamellar structure. In addition to their optical texture, the smectic phase can therefore be safely assigned as a SmC phase. The lamellar periodicity measured for the SmA phase of the monomer is about twice its estimated molecular length in agreement with a head-to-head disposition in dimers stabilized by strong dipolar interactions associated with the Au−Cl bond, as already proposed.[18a] The lamellar periodicity of the phase of dendrimer G^0 has the same magnitude, suggesting that the organization is driven by such an antiparallel disposition of the mesogenic end groups. To have a more precise description of the molecular arrangement in the smectic layers, a quantitative discussion based on the measured periodicities and calculated partial molecular volumes is now proposed. Determination of the molecular cross-section area is usually obtained from the ratio of the molecular volume and the layer periodicity. Given the proposed alternated arrangement of the polar mesogenic units, it is therefore necessary to consider two molecules to calculate the area occupied by the mesogenic units at the interface between the smectic layers, that is, $A_{mol} = 2V_{mol}/d$; a density of 1.2[22] was considered for all these gold-enriched dendrimers. The A_{mol} value found for the model compound (ca. 37 Å^2, Table 2) is compatible with a SmA phase. In this case, either the sublayers containing the supramolecular dimers are partially interdigitated, as in the case of the SmA$_d$ phase,[23] or the mesogenic groups are randomly tilted (without any correlation in the tilt direction, as in the SmA phase of the de Vries type) within the layer to produce an average "zero" tilt. In such a phase, the molecules are assumed to be tilted as in the SmC phase resulting from either tilted layers being stacked in a

---

(22) (a) Lee, K. M.; Lee, C. K.; Lin, I. J. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1850–1852. (b) Barbera, J.; Elduque, A.; Gimenez, R.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Serrano, J. L. *Inorg. Chem.* **1998**, *37*, 2960–2967. (c) Benouazzane, M.; Coco, S.; Espinet, P.; Martýn-Alvarez, J. M.; Barbera, J. *J. Mater. Chem.* **2002**, *12*, 691–696.

Table 2. Mesophases Structural Parameters Extracted from X-ray Diffraction Experiments

	indexation[a]			
compound	d_{meas}, Å	00*l*, *hk*	d_{calc}, Å	parameters[b]
	Series I			
$H_{25}C_{12}OC_6H_4NCAuCl$, SmA	39.0 (VS, sh)	001	38.95	$T = 140$ °C
	19.45 (S, sh)	002	19.47	$d = 38.95$ Å
	4.6 (VS, br)		h_{ch}	$V_{mol} = 720$ Å^3
				$A_{mol} = 36.9$ Å^2
[$G^0(NCAuCl)_3$], SmC	37.95 (VS, sh)	001	37.71	$T = 135$ °C
	18.88 (S, sh)	002	18.85	$d = 37.71$ Å
	12.47 (M, sh)	003	12.57	$V_{mol} = 2260$ Å^3
	4.6 (VS, br)		h_{ch}	$A_{mol} = 120.0$ Å^2
				$A_{mu} = 40.0$ Å^2
[$G^1(NCAuCl)_6$], SmC	58.30 (VS, sh)	001	58.14	$T = 115$ °C
	29.29 (S, sh)	002	29.07	$d = 58.14$ Å
	19.18 (M, sh)	003	19.38	$V_{mol} = 5510$ Å^3
	4.6 (VS, br)		h_{ch}	$A_{mol} = 189.5$ Å^2
				$A_{mu} = 31.6$ Å^2
	Series III			
$H_{25}C_{12}OC_6H_4NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3$, Col_h	30.21 (VS, sh)	10	30.24	$T = 60$ °C
	17.46 (S, sh)	11	17.46	$a = 34.92$ Å
	15.11 (S, sh)	20	15.12	$S = 1056$ Å^2
	11.4 (M, sh)	21	11.43	$V_{mol} = 1575$ Å^3
	10.1 (W, sh)	30	10.08	$\langle N \rangle = 3.0$
	8.77 (VW, sh)	22	8.73	
	8.38 (VW, sh)	31	8.39	
	4.5 (S, br)		h_{ch}	
[$G^0\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_3$], Col_h	30.09 (VS, sh)	10	30.11	$T = 75$ °C
	17.31 (S, sh)	11	17.38	$a = 35$ Å
	15.14 (S, sh)	20	15.06	$S = 1047$ Å^2
	11.39 (W, sh)	21	11.38	$V_{mol} = 4835$ Å^3
	4.6 (S, br)		h_{ch}	$\langle N \rangle = 1.0$
[$G^1\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_6$], Col_h	30.32 (VS, sh)	10	30.43	$T = 50$ °C
	17.63 (S, sh)	11	17.57	$a = 35.1$ Å
	15.25 (S, sh)	20	15.22	$S = 1069$ Å^2
	11.48 (W, sh)	21	11.50	$V_{mol} = 10\,650$ Å^3
	4.7 (VS, br)		h_{ch}	$\langle N \rangle = 0.5$
[$G^2\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_{12}$], Col_h	31.8 (VS, sh)	10	31.84	$T = 20$ °C
	18.41 (M, sh)	11	18.38	$a = 35$ Å
	15.92 (M, sh)	20	15.92	$S = 1171$ Å^2
	4.7 (S, br)		h_{ch}	$V_{mol} = 22\,280$ Å^3
				$\langle N \rangle = 0.25$

[a] d_{meas} and d_{calc} are the measured and calculated diffraction spacings, and distances are given in angstroms. VS (very strong), S (strong), M (medium), W (weak), and VW (very weak) stand for the peak intensity, while br (broad) and sh (sharp) denote peak line shape. 00*l* and *hk* are the Miller indices for the reflections (lamellar and columnar systems, respectively). [b] Molecular volume $V_{mol} = M_W/(N_A\rho)$; where N_A is Avogadro's number and density $\rho = 1.2$ g·mL^{-1}. For smectic phases: *d* is the smectic periodicity, $d = 1/N_{hk}(\Sigma l d_{00l})$, where N_{hk} is the number of reflections; molecular cross-section area $A_{mol} = 2V_{mol}/d$; cross-section area per mesogenic unit $A_{mu} = A_{mol}/Z$. For columnar hexagonal phases: *a* is the columnar phase lattice parameter, $a = \Sigma d_{hk}\sqrt{(h^2 + k^2 + hk)}]/\sqrt{3}N_{hk}$, where N_{hk} is number of reflections; columnar cross-section area $S = a^2\sqrt{3}/2;\cdot NV_{mol} = Sh$, where *N* is the number of molecules (or molecular equivalent) per columnar elementary repeat unit of height *h* ($h = h_{ch} = 4.5-4.7$ Å).

random fashion[24] or the molecules being tilted without long-range order in the direction of tilt within the layer.[24,25] For the supermolecules, if it is reasonably assumed, as in other related systems, that they adopt a cylindrical conformation in the smectic phase,[26] resulting from the antiparallel pairing of neighbored dendrimers, then these calculation performed for the G^0 and G^1 dendrimers lead to molecular and mesogenic unit cross-section values compatible with a SmC phase ($A_{mu} = A_{mol}/3 = 40$ Å^2 for G^0 and $A_{mu} = A_{mol}/6 = 31.6$ Å^2 for G^1, Table 2). The decrease of these values concomitant with the increasing lamellar periodicity between G^0 and G^1 is due to the increasing size of the dendritic core but also to a reduction of the average tilt of the mesogens, consequent to a tighter packing of both species (mesogens and dendrimer). These results validate the above hypothesis: the dendrimers, having three sets of arms, adopt an elongated prolate conformation and associate into supramolecular cylinders required for the formation of the lamellar mesophases, where the rigid parts are quasi-collinear to the layer normal and distributed homogeneously on either side of the molecular center (Figure 1). To achieve such a homogeneous distribution, the dendrimers are arranged in an alternating antiparallel manner within the layers in order to compensate the uneven number of mesogens (G^0) or pairs of mesogens (G^1). A representation of this arrangement into layers is shown below (Figure 1).

As for the acetylene dendrocomplexes of series **III**, up to four sharp reflections (and seven for the monomer, Figure 2)

---

(23) (a) Seurin, P.; Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 37–49. (b) Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 341–352. (c) Hardouin, F.; Levelut, A. M.; Achard, M. F.; Sigaud, G. *J. Chim. Phys.* **1983**, *80*, 53–64. (d) Hardouin, F. *Physica A* **1986**, *140*, 359–367.

(24) De Vries, A. *Mol. Cryst. Liq. Cryst.* **1977**, *41*, 27–31.

(25) De Vries, A. *J. Chem. Phys.* **1979**, *71*, 25–31.

(26) (a) Donnio, B.; Barberá, J.; Giménez, R.; Guillon, D.; Marcos, M.; Serrano, J.-L. *Macromolecules* **2002**, *35*, 370–381. (b) Lenoble, J.; Campidelli, S.; Maringa, N.; Donnio, B.; Guillon, D.; Yevlampieva, N.; Deschenaux, R. *J. Am. Chem. Soc.* **2007**, *129*, 9941–9952. (c) Wolska, J.; Mieczkowski, J.; Pociecha, D.; Buathong, S.; Donnio, B.; Guillon, D.; Gorecka, E. *Macromolecules* **2009**, *42*, 6375–6384.

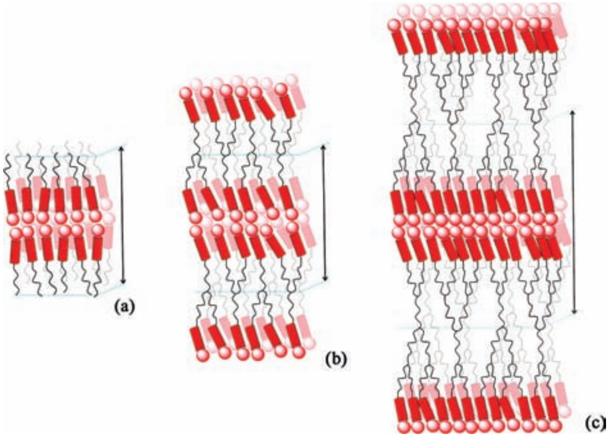


Figure 1. Schematic representation of the self-organization of the chloro−gold mesogens and dendrocomplexes in smectic phases: (a) monomer, (b) G^0, and (c) G^1.

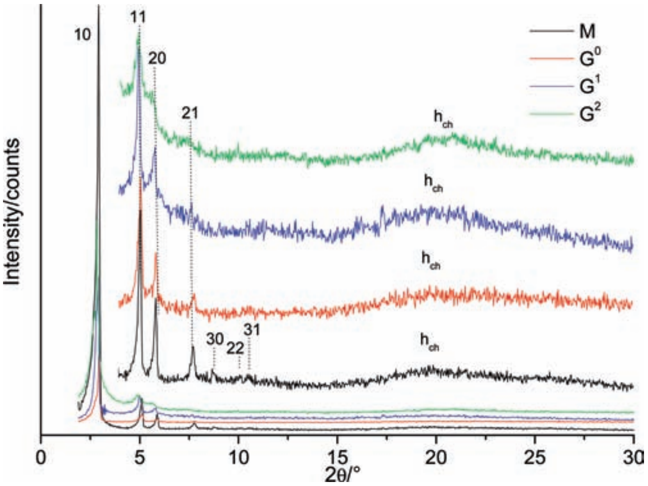


Figure 2. X-ray patterns of the monomeric and dendritic generations in the Col_h phase at 60, 75, 50, and 20 °C for $H_{25}C_{12}OC_6H_4$-$NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3$ and $[G^i\{NCAuC{\equiv}CC_6H_4(OC_{12}H_{25})_3\}_Z]$, respectively.

were observed, with reciprocal *d*-spacings in the ratio $1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}$ ($\sqrt{9}{:}\sqrt{12}{:}\sqrt{13}$), and most readily assigned to the (10), (11), (20) and (21) [(30), (22), and (31)] of a 2D hexagonal lattice with *p*6*mm* planar group (Col_h phase).[27] One can notice a substantial widening and intensity decrease of the small-angle diffraction peaks upon generation increase, which is associated with less sharp interfaces and an increasing difficulty toward ordering, a common behavior for liquid-crystalline macromolecules. A remarkable feature within this series of compounds is the quasi-invariance of the lattice parameter starting from the monomer and up to the second generation (Figure 2, Table 2), suggesting a similar mode of packing within the column for all the members of the series. Such a generation-independent behavior has previously been observed in other mesomorphic dendritic systems[28] and is explained by the great flexibility of the dendritic arborescence, which can easily be deformed because of the steric constraints and confined due to unidirectional stretching along the columnar axis. If a density[22] of 1.1−1.2 $g{\cdot}cm^{-3}$ is assumed and a thickness for the repeating columnar slice along the column $h \sim 4.5{-}4.7$ Å is chosen, corresponding to the average separation between molten alkyl chains and thus to the short-range stacking distance between consecutive layers of aryl ether dendrons,[7,14−16,26] then the average number of dendrimers (or dendritic equivalents), *N*, that associate per such an elementary columnar unit can be estimated according to $N = Sh/V_{mol}$ (V_{mol} = molecular volume). For this series, it was found that 1 G^0, $^1/_2$ G^1, and $^1/_4$ G^2 supermolecule is required to fulfill the available volume of such a defined columnar slice. To do so, the overall supermolecules ought to adopt an oblate conformation (flat cylinder) resulting from the uniaxial stretching of the dendritic skeleton over several repeat units (two for G^1 and four for G^2) and from the radial arrangement of the end mesogens (3 per slice for $G^0 \rightarrow G^2$). As for the monomeric model compound, three complexes, also in such a radial arrangement, are needed to fulfill the geometrical and volume requirements to stabilize the columnar mesophase. In all cases, the perfect paving of the 2D lattice is achieved. Thus, the total number of peripheral alkyl chains radiating from the columnar interface per repeat unit remains constant throughout (ca. nine chains), independent of the generation number.

Despite the huge increase of the molecular volume with generation, the surface area of the hexagonal cell for all of these dendrimers and the monomer is quite similar regardless of the generation number, suggesting that the packing is governed by the tapered molecular shape[7] of the sole mesogenic unit. A plausible model to explain the self-assembling into columns is thus to consider that one, two, and four of these elemental discs are necessary to accommodate the metallodendrimer of the zeroth, first, and second generation, respectively, as schematically shown in the graphical representation below (Figure 3).

Thus, many properties of the materials described here are consistent with those observed previously for other dendrimeric mesogens.[6] The change in the shape of the end groups, monitored by the number of terminal chains per mesogen, modifies the relationships between the hard and the soft parts, and consequently the molecules adopt either a cylindrical (prolate, series **I**) or a disklike (oblate, series **III**) conformation, and smectic and/or columnar mesophases are induced, respectively. Compounds with no terminal chain per end group (series **I**), for which the compatibility of spatial requirement between the aliphatic dendritic matrix and mesogenic cores is immediately satisfied, self-organize into noncurved smectic layers resulting from the lateral two-dimensional registry of cylindrical antiparallel molecular pairs. In contrast, the grafting of hemipolycatenar mesogens[29] at the extremity of the dendrimer prevents such a parallel disposition of the promesogenic groups, since the cross-sectional area of the terminal chains is larger than the area occupied by the mesogenic units (the mismatch between the surface areas of the aromatic cores and the cross-section of the aliphatic chains results in the curvature of the interface); therefore, the metallodendrimers adopt a cylindrical confor-

---

(27) (a) *International Tables for Crystallography, Vol. A*, 4th ed.; Hahn, T., Ed.; International Union of Crystallography; Kluwer Academic: Dordrecht, The Netherlands, 1995. (b) Hammond, C. In *The Basics of Crystallography and Diffraction*, 2nd ed.; International Union of Crystallography; Oxford Science Publications: Oxford, U.K., 2001.

(28) Marcos, M.; Giménez, R.; Serrano, J. L.; Donnio, B.; Heinrich, B.; Guillon, D. *Chem.−Eur. J.* **2001**, *7*, 1006–1013.

(29) Nguyen, H.-T.; Destrade, C.; Malthête, J. *Adv. Mater.* **1997**, *9*, 375–388.

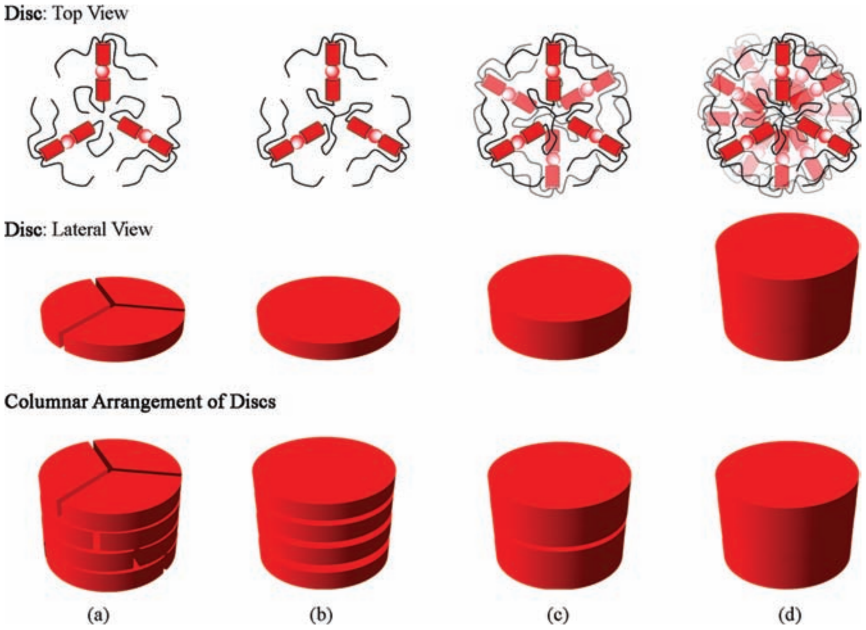


Figure 3. Schematic model representing the supramolecular arrangement in columnar hexagonal mesophase of monomeric compound (a) and dendrimers [$G^i\{NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3\}_Z$] as a function of the generation, G^0 (b) → G^1 (c) → G^2 (d).

mation, allowed by virtue of their great flexibility, and the end mesogens are radially arranged around the dendritic moiety; the columnar phase results from the one-dimensional periodic stacking of these supramolecular discs made of molecules or portions of molecules.

Conclusions

New liquid-crystalline metallodendrimers have been synthesized. Their mesomorphic properties are largely influenced by the nature of the peripheral gold fragments, while the increase of the dendritic generation contributes to a strong stabilization of the mesophases. The chloro−gold complexes (series **I**), [$G^0(NCAuCl)_3$] and [$G^1(NCAuCl)_6$], show a smectic C phase, in agreement with the behavior of the monomeric model compound. As for the three generations of dendritic gold complexes bearing hemipolycatenars (series **III**), [$G^i\{NCAuC{\equiv}CC_6H_2(OC_{12}H_{25})_3\}_Z$], they all display a columnar mesophase, directly from room temperature, as does the model monomer.

Acknowledgment. The work was supported by ESF/2007/03 grant. We thank the CNRS and the Université de Strasbourg for support and funding. P.E. and S.C. thank the DGI (Project CTQ2008-03954/BQU) and INTECAT Consolider Ingenio-2010 (CSD2006-0003) and the Junta de Castilla y León (Projects VA012A08 and GR169).

Note Added after ASAP Publication. In the version published ASAP on January 7, 2010, Scheme 3 and the paragraph describing it contained errors; the corrected version reposted on January 11, 2010.

Supporting Information Available: Complete experimental section and synthesis and characterization of the precursors and final dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

JA909435E