Liquid-Crystalline Mono- and Dinuclear (Perhalophenyl)gold(I) Isocyanide Complexes

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Rodlike gold(I) and gold(III) complexes [AuR(C≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$-*p*)] (*m* = 1, *n* = 10, R = C$_6$F$_5$; *m* = 2, *n* = 4, 6, 8, 10, 12, R = C$_6$F$_5$, C$_6$F$_4$Br-*o*, C$_6$F$_4$Br-*p*), [(*μ*-4,4′-C$_6$F$_4$C$_6$F$_4$){AuC≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$}$_2$] (*m* = 1, 2; *n* = 4, 6, 8, 10, 12), [AuRI$_2$(C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$-*p*)] (R = C$_6$F$_5$, *n* = 8; R = C$_6$F$_4$Br-*o*, *n* = 10), and [(*μ*-4,4′-C$_6$F$_4$C$_6$F$_4$){AuX$_2$C≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$}$_2$] (*m* = 1, 2; *n* = 4, 6, 8, 10, 12) have been prepared and their liquid crystal behavior has been studied. The gold(III) compounds are not mesomorphic, but all the perhalo−gold(I) derivatives described are liquid crystals except the phenyl isocyanide gold(I) derivative [Au(C$_6$F$_5$)(C≡NC$_6$H$_4$-OC$_{10}$H$_{21}$-*p*)]. The mononuclear derivatives show only a nematic (N) phase when the isocyanides have a short tail (*n* = 4), N and smectic A phases (S$_A$) when the isocyanides have an intermediate tail (*n* = 6, 8), and only S$_A$ phases for longer chains. Their thermal stability is high, even in the isotropic state. The variation in transition temperatures is as follows: C$_6$F$_4$Br-*p* ≥ C$_6$F$_5$ > C$_6$F$_4$Br-*o* when *n* ≤ 6 and C$_6$F$_4$Br-*p* > C$_6$F$_4$Br-*o* > C$_6$F$_5$ for *n* ≥ 8. This behavior is understood on the basis of electronic and steric factors. The dinuclear compounds [(*μ*-4,4′-C$_6$F$_4$C$_6$F$_4$){AuC≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$}$_2$] display only N mesophases and all the biphenylisocyanide derivatives and phenyl isocyanide compounds with *n* ≤ 6 undergo some decomposition upon reaching the clearing point to the isotropic state.

Introduction

The continued development of liquid-crystal-based technologies requires mesomorphic materials with adequate physical properties, and much research has been carried out in order to design and prepare new liquid-crystalline materials. In the last years metal-containing liquid crystals with transition or post-transition metals (so-called metallomesogens) have seen systematic research and development.[1−5] Most metallomesogens are based on d^8−d^{10} coordination compounds with planar or linear geometries, but only a few examples of gold mesogens have been reported. Moreover, the kinds of organometallic liquid crystals known are rather limited: A vast family of orthometalated derivatives of Pd[6−16] and a few of Pt,[17] Mn-(I),[18] and Re(I);[19] some ferrocene[20−24] and ruthenocene[25] deriva-

tives; a few olefin complexes of Pt[26,27] and Fe;[28,29] a number of alkynyl complexes of Ni, Pd, and Pt;[30,31] some isocyanide complexes of Au,[32−37] Pd, and Pt;[38,39] and recently a few (carbene)gold derivatives.[40]

In summary the reviews show the absence of metallome-sogens based on molecules with metal−aryl bonds not involved in a metallacycle, with the exception of bis(aryl)mercury derivatives, which were the first metallomesogens described,[41] and arylgermanium, -tin, and -lead derivatives.[42]

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On the other hand, there has been an increasing interest in liquid crystals containing fluorine atoms in the backbone structure,[43−47] due to the fact that fluorination of conventional organic liquid crystals produces important changes on the melting temperatures, viscosity, birefringence, dielectric anisotropy, and mesophase stability.[48,49] However only a limited number of metal complexes with fluorinated ligands have been reported.[50−53]
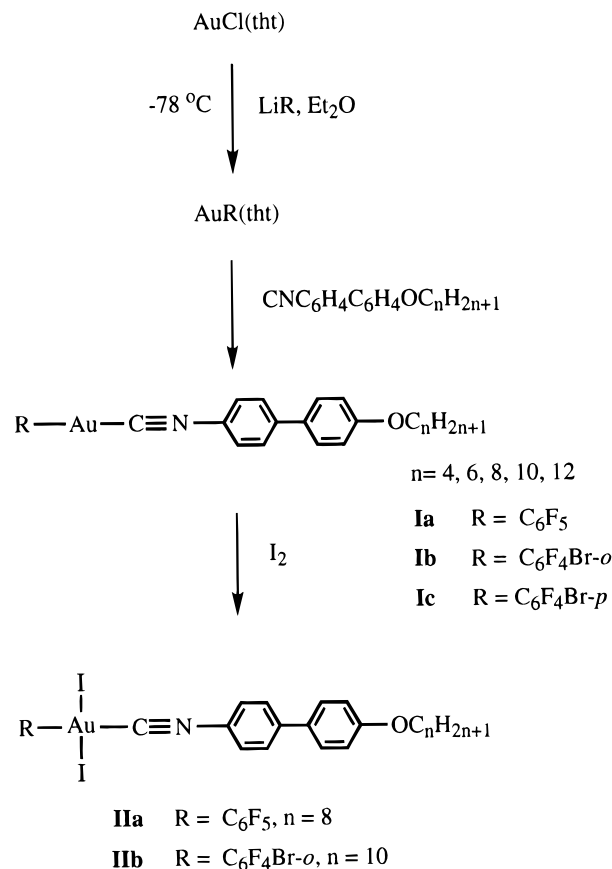
We have reported previously a family of gold complexes $[AuX(C \equiv NC_6H_4OC_nH_{2n+1}\text{-}p)]$ (X = halogen) which show smectic A phases in spite of the fact that their isocyanide ligands are not mesogenic and contain only one aryl ring. These complexes show the induction of mesogenic behavior by the presence of a metal atom that increases the polarizability of the molecule.[34] On this simple mesogenic system, we have studied the effect of modifications in the isocyanide group on the mesogenic properties. Thus, similar gold(I) biphenyl, 2-fluorophenyl, and 3-fluorophenyl isocyanide complexes show mostly S_A mesophases, and gold(I) 3,4,5-trialkoxyphenyl isocyanide derivatives show hexagonal columnar mesophases.[36,37]

In this paper we report the preparation and thermal behavior of uncommon mesogens containing only M−C σ-bonds, based on mono- and dinuclear (perhalophenyl)gold(I) isocyanide compounds of type $[AuR(C \equiv NC_6H_4C_6H_4OC_nH_{2n+1}\text{-}p)]$ (R = C_6F_5, $C_6F_4Br\text{-}o$, $C_6F_4Br\text{-}p$) and $[(\mu\text{-}4,4'\text{-}C_6F_4C_6F_4)\{AuC \equiv N\text{-}(C_6H_4)_mOC_nH_{2n+1}\}_2]$ (m = 1, 2).

Results and Discussion

Synthesis and Characterization. The gold(I) isocyanide complexes and their corresponding gold(III) derivatives have been prepared as described in the literature for similar (pentafluorophenyl)gold(I) and -gold(III) isocyanide derivatives and (4,4′-octafluorobiphenyl)gold(I) complexes, respectively,[54,55] as represented in Schemes 1 and 2 (tht = tetrahydrothiophene). $[AuR(C \equiv N(C_6H_4)_mOC_nH_{2n+1}\text{-}p)]$ (series I: m = 1, n = 10, R = C_6F_5; m = 2, n = 4, 6, 8, 10, 12, R = C_6F_5, $C_6F_4Br\text{-}o$, C_6F_4-Br-p) and $[(\mu\text{-}4,4'\text{-}C_6F_4C_6F_4)\{AuC \equiv N(C_6H_4)_mOC_nH_{2n+1}\}_2]$ (se-

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Scheme 1

ries III: m = 1, 2) are obtained in two steps by arylation of [AuCl(tht)] followed by ligand exchange with the appropriate isocyanide. Oxidative addition of halogen yields the corresponding gold(III) derivatives (series II and IV).

The C, H, N analyses for the complexes, yields, and relevant IR data are given in the Experimental Section. The IR spectra are all similar and show one $\nu(C \equiv N)$ absorption for the isocyanide group at higher wavenumbers (ca. 90 cm^{-1}) than for the free isocyanide, as has been reported for other gold(I) isocyanide compounds.[34−36,54]
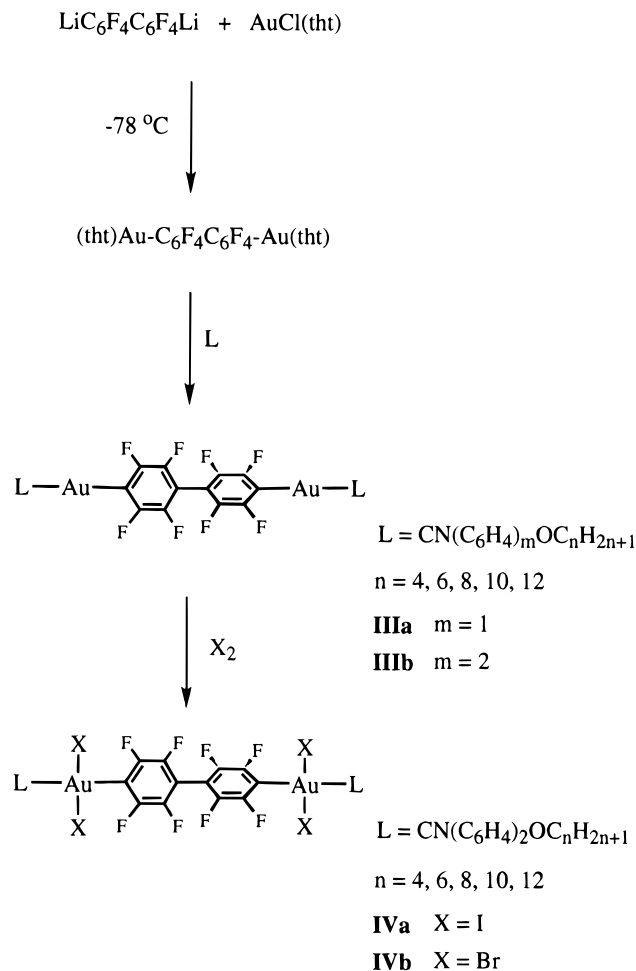
The ^{1}H NMR spectra of gold(I) and gold(III) isocyanide complexes prepared are all very similar, showing at 300 MHz respectively four or two somewhat distorted "doublets" for the biphenyl (strictly two AA′XX′ spin systems) or the phenyl group (one AA′XX′ spin system), as we have reported for similar halogold(I) isocyanide complexes.[34,36]

The ^{19}F NMR spectra of these complexes show the typical patterns of the corresponding perhalophenyl group. Thus, the C_6F_5 derivatives show the three resonances expected from an AA′MXX′ spin system.[56] The $C_6F_4Br\text{-}o$ complexes show four signals (first order, AKRX spin system). The two low-field signals (doublets of doublets) appear at ca. −116 ppm and ca. −127 ppm (reference CFCl$_3$) and are assigned to F(*ortho*) and F(*ortho* to Br), respectively. The two high-field signals appear at ca. −156 and −157 ppm and are assigned to F(*para*) and F(*meta*), respectively. Note that in the precursors [AuR(tht)] (R = C_6F_5, $C_6F_4Br\text{-}o$, tht = tetrahydrothiophene), the signal of F(*para*) appears at lower field than for CNR derivatives. This suggest that, upon substitution of tht for isocyanide, which is a good π acceptor ligand, the R group becomes more electron donating producing a deshielding mainly in the *para* position.

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Scheme 2

$$LiC_6F_4C_6F_4Li \; + \; AuCl(tht)$$

$$\downarrow \text{-78 °C}$$

$$(tht)Au\text{-}C_6F_4C_6F_4\text{-}Au(tht)$$

$$\downarrow L$$

L—Au—[biphenyl core]—Au—L

L = CN(C₆H₄)ₘOCₙH₂ₙ₊₁

$L = CN(C_6H_4)_mOC_nH_{2n+1}$

n = 4, 6, 8, 10, 12

IIIa m = 1
IIIb m = 2

$$\downarrow X_2$$

[diiodo/dibromo biphenyl gold complex]

$L = CN(C_6H_4)_2OC_nH_{2n+1}$

n = 4, 6, 8, 10, 12

IVa X = I
IVb X = Br

The ^{19}F NMR spectra of the C_6F_4Br-p compounds show two somewhat distorted "doublets" flanked by two pseudotriplets (strictly an AA'XX' spin system with $J_{AA'} \approx J_{XX'}$).

The ^{19}F NMR spectra of the 4,4′-octafluorobiphenyl compounds show two complex multiplets at ca. −117 and −140 ppm, corresponding to the *ortho* and the *meta* fluorine atoms as reported for similar tetrahydrothiophene complexes.[55]

Mesogenic Behavior. Mononuclear Compounds. The complex $[Au(C_6F_5)(C\equiv NC_6H_4OC_{10}H_{21}$-$p)]$ does not display liquid crystal behavior, but all the gold biphenyl isocyanide compounds $[AuR(C\equiv NC_6H_4C_6H_4OC_nH_{2n+1}$-$p)]$ (R = C_6F_5, C_6F_4Br-o, C_6F_4Br-p) are mesomorphic and their optical, thermal, and thermodynamic data are presented in Table 1. The free biphenyl isocyanides display nematic (N) and/or smectic A (S_A) phases in the range 40–85 °C.[38] Their (perhalophenyl)gold(I) complexes behave as liquid crystals showing a N phase when the isocyanide has a short tail ($n = 4$), N and S_A phases when the isocyanide has an intermediate tail ($n = 6, 8$), and only a S_A phase for longer chains. The S_A mesophases present the typical mielinic and homeotropic textures reorganizing to the fan-shaped texture at temperatures close to the clearing point and the focal-conic fan texture on cooling from the nematic or isotropic phases. The nematic phases show the *schlieren* texture. Some of the compounds show crystal-to-crystal transitions before melting.

The variation in thermal properties is quite regular and can be summarized for each family as follows: The melting and clearing temperatures decrease with increasing length of the alkoxy chain to reach a roughly constant value beyond $n = 8$. The range of S_A phase increases, and that of N phase decreases as the length of the chain increases.

Table 1. Optical, Thermal, and Thermodynamic Data for the Complexes $[AuR(C\equiv NC_6H_4C_6H_4OC_nH_{2n+1}$-$p)]$

R	n	transition[a]	temp[b] (°C)	ΔH^b (kJ/mol)
C_6F_5	4	C- - -C′	98.5	0.2
		C′- - -N	138.7	31.6
		N- - -I	186.5	0.7
C_6F_5	6	C- - -C′	86.8	2.0
		C′- - -S_A	99.3	33.7
		S_A- - -N	122.6	0.1
		N- - -I	166.8	1.0
C_6F_5	8	C- - -S_A	70.0	37.0
		S_{A---N}	148.8	0.3
		N- - -I	158.9	1.0
C_6F_5	10	C- - -S_A	75.3	42.9
		S_A- - -I	150.5	2.8
C_6F_5	12	C- - -S_A	70.3	41.7
		S_A- - -I	133.4	2.6
C_6F_4Br-o	4	C- - -C′	106.1	5.5[c]
		C′- - -N	119.7	22.2[c]
		N- - -I	168[d] (dec)	
C_6F_4Br-o	6	C- - -S_A	95.4	25.9
		S_A- - -N	128.9	0.1
		N- - -I	166.1	1.1
C_6F_4Br-o	8	C- - -S_A	74.6	22.6
		S_A- - -N	139.7	0.3
		N- - -I	148.0	0.7
C_6F_4Br-o	10	C- - -S_A	80.8	42.3
		S_A- - -I	150.6	2.6
C_6F_4Br-o	12	C- - -S_A	81.0	35.5
		S_A- - -I	147[d] (dec)	
C_6F_4Br-p	4	C- - -N	136.8	36.6
		N- - -I	219.7	0.9
C_6F_4Br-p	6	C- - -S_A	106.4	25.0
		S_A- - -N	140[c]	
		N- - -I	195.7	0.9
C_6F_4Br-p	8	C- - -S_A	114.1	3.1
		S_A- - -N	187.3	0.4
		N- - -I	196.6	0.9
C_6F_4Br-p	10	C- - -S_A	99.4	32.9
		S_A- - -I	192.6	3.7
C_6F_4Br-p	12	C- - -S_A	100.3	42.8
		S_A- - -I	192.7	4.4

[a] C, crystal; S, smectic; N, nematic; I, isotropic liquid. [b] Data refer to the second DSC cycle starting from the crystal formed on cooling the mesophase. Temperature data as peak onset. [c] Data refer to the first DSC cycle. [d] Optical microscopy data.

The decrease of transition temperatures with increasing length is small for C_6F_4Br-p derivatives, greater for those of C_6F_4Br-o, and more marked for C_6F_5 complexes. As a consequence of this trend, a change is produced in the sequence of melting and clearing temperatures the order being C_6F_4Br-$p \geq C_6F_5 > C_6F_4Br$-o when $n \leq 6$ and C_6F_4Br-$p > C_6F_4Br$-$o > C_6F_5$ for $n \geq 8$.

The mononuclear gold(III) isocyanide compounds are thermally unstable, and heating leads to cleavage of the Au−R bond (R = C_6F_5, C_6F_4Br-o) to give the corresponding halogold(I) isocyanide derivatives.[34,36]

Dinuclear Compounds. The mesogenic behavior of $[(\mu$-4,4′-$C_6F_4C_6F_4)\{AuC\equiv N(C_6H_4)_mOC_nH_{2n+1}\}_2]$ ($m = 1, 2, n = 4, 6, 8, 10, 12$) is presented in Table 2. They all display a N mesophase, identified in optical microscopy by its typical *marbled* texture. Some of the compounds show one crystal-to-crystal transition before melting. All the biphenyl isocyanide derivatives and the phenyl isocyanide compounds with $n \leq 6$ undergo some decomposition upon reaching the clearing point to the isotropic state, possibly due to their very high transition temperatures.

The variation in thermal properties can be summarized as follows: The clearing temperatures decrease with increasing length of the alkoxy chain and in the order biphenyl > phenyl. The same trend is observed for the melting temperatures with

Table 2. Optical, Thermal, and Thermodynamic Data for the Complexes $[(\mu\text{-}4,4'\text{-}C_6F_4C_6F_4)\{AuC\equiv N(C_6H_4)_mOC_nH_{2n+1}\text{-}p\}_2]$

m	n	transition[a]	temp[b] (°C)	ΔH^b (kJ/mol)
1	4	C- - -N	224.4	50.1
		N- - -I	275.0[c] (dec)	
1	6	C- - -C′	115.4	5.1
		C′- - -N	173.3	44.9
		N- - -I	254.0[c] (dec)	
1	8	C- - -N	193.6	56.4
		N- - -I	245.7	4.2
1	10	C- - -N	149.5	51.0
		N- - -I	220.8	3.6
1	12	C- - -C′	112.3	2.3
		C′- - -N	152.2	45.5
		N- - -I	202.9	3.1
2	4	C- - -N	246.4[d]	35.8
		N- - -I	261 (dec)	
2	6	C- - -C′	184.3	2.6
		C′- - -N	211.2	42.9
		N- - -I	278[c] (dec)	
2	8	C- - -N	183.8	39.4
		N- - -I	275[c] (dec)	
2	10	C- - -N	175.2	42.0
		N- - -I	245[c] (dec)	
2	12	C- - -C′	93.4	12.0
		C′- - -N	160.9	35.9
		N- - -I	240[c] (dec)	

[a] C, crystal; S, smectic; N, nematic; I, isotropic liquid. [b] Data referr to the second DSC cycle starting from the crystal formed on cooling the mesophase. Temperature data as peak onset. [c] Optical microscopy data. [d] Data referr to the first DSC cycle.

Figure 1. Comparison of the thermal properties of complexes [AuCl-(C≡NC₆H₄C₆H₄OC_nH_{2n+1}-p)] reported in ref 36 and [Au(C₆F₄Br-p)-(C≡NC₆H₄C₆H₄OC_nH_{2n+1}-p)] (**Ic**).

one exception, the gold(I) (octyloxy)phenyl isocyanide compound whose melting point is higher than that of the hexyloxy derivative.

Similarly to the mononuclear perhalophenyl derivatives discussed above, the thermal treatment of dinuclear (octafluorobiphenyl)gold(III) complexes led to cleavage of the gold–octafluorobiphenyl bonds to give the corresponding halogold(I) isocyanide complexes.

Discussion

The simplest way to look at the rodlike molecules [AuR-(C≡NC₆H₄C₆H₄OC_nH_{2n+1}-p)] (R = C₆F₄Br-o, C₆F₄Br-p) is to consider them as formal derivatives of [Au(C₆F₅)(C≡NC₆H₄C₆H₄-OC_nH_{2n+1})] by substitution of a F by a Br atom in the lateral or terminal position, which will determine the magnitude of intermolecular electrostatic interactions.

Irrespective of its position, the introduction of a Br substituent leads to higher values for the molecular polarizability as Br is more polarizable than F,[57,58] increasing intermolecular interactions and leading to higher transition temperatures. On the other hand, a Br atom in the *para* position produces only a small increase in the total length of the molecule, while in the *ortho* position it causes a noticeable increase in the width of the molecule, reducing the intermolecular attractions and leading to lower transition temperatures. Thus, melting and clearing temperatures for the C₆F₄Br-*p* compounds should be higher than those for the C₆F₅ and for the C₆F₄Br-*o* derivatives, as observed.

Similarly, the polarizability of the C₆F₄Br-*o* group is higher than that of the C₆F₅ group, but the width of the former is higher than that of the later. This helps one to understand the fact that the transition temperatures are greater for C₆F₄Br-*o* than for C₆F₅, except for low lengths of the alkoxy chain, where the width of the perhalophenyl group seems to be the determining
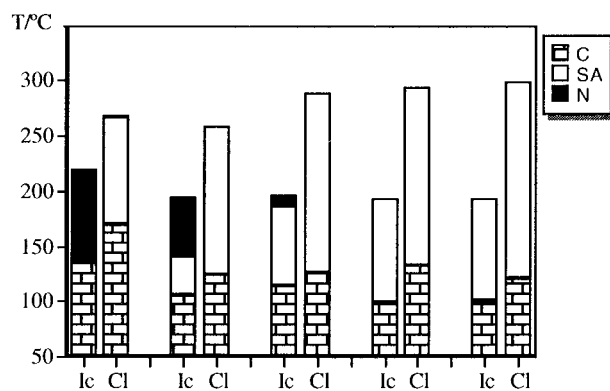
factor. Thus the transition temperatures are in the order C₆F₅ > C₆F₄Br-*o* for n ≤ 6 and the opposite for $n \geq 8$.

It is also interesting to compare the variation of transition temperatures of these complexes [AuR(C≡NC₆H₄C₆H₄OC_nH_{2n+1}-p)] with that of the previously reported compounds [AuX-(C≡NC₆H₄C₆H₄OC_nH_{2n+1}-p)] (X = halogen).[36] The thermal properties of both kinds of complexes are compared in Figure 1 for R = C₆F₄Br-*p* and X = Cl. It can be seen that the perhalophenyl group produces lower transition temperatures, shorter mesogenic ranges, and an enhancement of nematic phases, according to the expected lower lateral intermolecular interactions as consequence of their greater molecular width. Thus it is not unexpected that when the conjugated rigid core is reduced, as in [Au(C₆F₅)(C≡NC₆H₄OC_nH_{2n+1}-p)], the mesogenic properties are lost.

In the complexes $[(\mu\text{-}4,4'\text{-}C_6F_4C_6F_4)\{AuC\equiv N(C_6H_4)_m\text{-}OC_nH_{2n+1}\}_2]$ (m = 1, 2; n = 4, 6, 8, 10, 12) the rather high transition temperatures found suggest good intermolecular interactions. Only the N phase is observed. It is well-known that the steric and electronic repulsions between the fluorine atoms produce large twist angles (about 53°) between the two rings of the octafluorobiphenyl group, as found crystallographically for nickel complexes.[59] This must necessarily reduce the π-conjugation between the two halves of our dinuclear gold complexes to a very small value. In other words, as far as polarizability and other properties associated with π-conjugation are concerned, these gold complexes can be assimilated to two monomeric molecules linked head-to-head, the dimer having no net dipolar moment but possessing a complex multipolar structure. The intermolecular interactions between these large multipolar molecules is strong, as suggested by the high transition temperatures. These high melting temperatures and the nonplanar nature of the octafluorobiphenyl moiety (hindering the adoption of a planar shape for a more efficient stacking of molecules) will both cooperate to create the appearance of the entropically favored nematic phase.

It can be seen that these dinuclear complexes produce nematic phases at temperatures where the monomeric compounds display S_A phases (compare for instance the C₆F₄Br-*p* derivative for n = 12). The accessibility of a N, involving the slip of molecules with mixing of aromatic and aliphatic regions, must depend on the energy difference between that disordered arrangement and the more ordered smectic arrangement with discrimination of aromatic and aliphatic regions. As suggested in Figure 2, for a dipolar molecule the aromatic interactions favor the adoption of smectic arrangements (a), and this interaction must be

(57) Seed, A. J.; Toyne, K. J.; Goodby, J. W. *J. Mater. Chem.* **1995**, *5*, 2201.
(58) *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Ratón, FL, 1992; pp 10−194.

(59) Craig Sturge, K.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D. *Organometallics* **1992**, *11*, 3056.
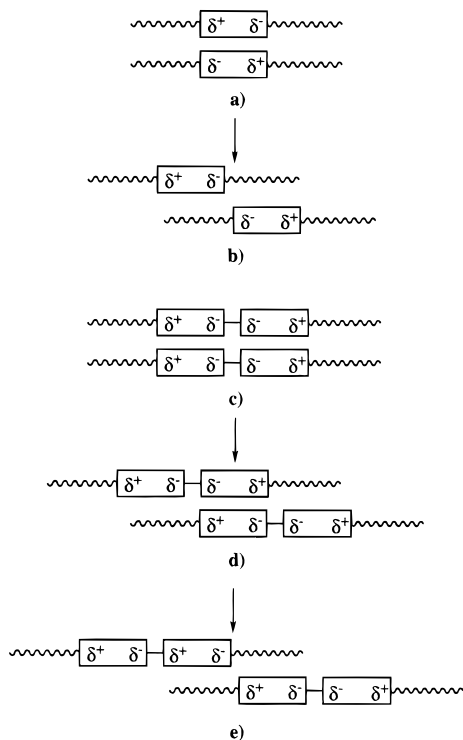
Figure 2. A simple model showing different positions of two molecules as they slip with respect to each other for a molecule with a dipolar rigid core (a, b) or a molecule with a multipolar symmetric rigid core (c, d, e).

overcome to reach the mixing of aromatic and aliphatic regions (b) characteristic of nematic phases. For the symmetric dimers, however, the best multipole−multipole interactions are not those represented in (c), but probably those in (d) which already involve some mixing of aromatic and aliphatic regions. Thus, the slip with mixing of the regions (e) giving rise to a nematic phase must become thermally more easily accessible, and it is the only one observed above the melting point.

Conclusions

The use of perhaloaryl rings, which give quite stable Au−C bonds, allows the synthesis of metal-containing liquid crystals with only M−C σ-bonds. In spite of the bulkiness of some of these groups, large ranges of N or S_A phases are obtained. The mesogenic behavior can be roughly explained using simple arguments of polarization and polarizability of the species involved. The dominance of nematic behavior in symmetric dinuclear complexes is particularly interesting.

Experimental Section

Combustion analyses were completed with a Perkin-Elmer 2400 microanalyzer. IR spectra (cm^{-1}) were recorded on a Perkin-Elmer FT 1720X instrument, and ^{1}H NMR spectra, on a Bruker AC 300 instrument in CDCl$_3$. Microscopy studies were carried out using a Leitz microscope provided with a hot stage and polarizers at a heating rate of approximately 10 °C min^{-1}. For differential scanning calorimetry (DSC) a Perkin-Elmer DSC7 instrument was used, which was calibrated with water and indium; the scanning rate was 10 °C min^{-1}, the samples were sealed in aluminum capsules in the air, and the holder atmosphere was dry nitrogen.

Literature methods were used to prepare [C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$-*p*],[36] [C≡NC$_6$H$_4$OC$_n$H$_{2n+1}$-*p*],[34] and [(μ-4,4'-C$_6$F$_4$C$_6$F$_4$){Au(tht)}$_2$] (tht = tetrahydrothiophene).[55] [Au(R)(tht)] (R = C$_6$F$_4$Br-*o*, C$_6$F$_4$Br-*p*) were prepared similarly to [Au(C$_6$F$_5$)(tht)],[60] using the corresponding bromo derivatives C$_6$F$_4$Br$_2$-*o* and C$_6$F$_4$Br$_2$-*p*. ^{19}F NMR (CDCl$_3$): [Au(C$_6$F$_4$-

(60) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

Br-*o*)(tht)], δ_1 −116.19 (dd, $^3J_{1,2}$ = 30.5 Hz, $^5J_{1,4}$ = 11.9 Hz, F$_{ortho}$), δ_2 −157.08 (ddd, $^3J_{1,2}$ = 30.5 Hz, $^3J_{2,3}$ = 19.5 Hz, $^4J_{2,4}$ = 1.4 Hz, F$_{meta}$), δ_3 −157.80 (dd, $^3J_{2,3}$ = 19.5 Hz, $^3J_{3,4}$ = 21.2 Hz, F$_{para}$), δ_4 −127.10 (ddd, $^3J_{3,4}$ = 21.2 Hz, $^5J_{1,4}$ = 11.9 Hz, $^4J_{2,4}$ = 1.4 Hz, F$_{ortho\ to\ Br}$); [Au(C$_6$F$_4$Br-*p*)(tht)], δ_1 −115.50 (F$_{ortho}$), δ_2 −135.30 (F$_{meta}$), AA'XX' spin system ($^3J_{1,2}$ + $^5J_{1,2'}$ = 18.3 Hz, $^4J_{1,1'}$ + $^4J_{2,2'}$ = 10.0 Hz, $^3J_{1,2}$ − $^5J_{1,2'}$ = 42.5 Hz).

All compounds [AuR(C≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$-*p*)] (*m* = 1, *n* = 10, R = C$_6$F$_5$; *m* = 2, *n* = 4, 6, 8, 10, 12, R = C$_6$F$_5$, C$_6$F$_4$Br-*o*, C$_6$F$_4$Br-*p*), [(μ-4,4'-C$_6$F$_4$C$_6$F$_4$){Au(C≡N(C$_6$H$_4$)$_m$OC$_n$H$_{2n+1}$-*p*)}$_2$] (*m* = 1, 2; *n* = 4, 6, 8, 10, 12), [Au(R)I$_2$(C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$-*p*)] (R = C$_6$F$_4$Br-*o*, *n* = 10; R = C$_6$F$_5$, *n* = 8) and [(μ-4,4'-C$_6$F$_4$C$_6$F$_4$){AuX$_2$(C≡N(C$_6$H$_4$C$_6$H$_4$-OC$_8$H$_{17}$-*p*)}$_2$] (X = I, Br) were prepared as reported for (pentafluorophenyl)gold(I) and -gold(III) isocyanide complexes,[54,55] with some modifications. Only examples are described as the syntheses were similar for the rest of the complexes. Yields, IR, and analytical data are given for all the gold isocyanide complexes.

Preparation of [Au(C$_6$F$_4$Br-*o*)(C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$-*p*)]. *n* = **4.** To a solution of [Au(C$_6$F$_4$Br-*o*)(tht)] (0.100 g, 0.195 mmol) in 40 mL of diethyl ether was added C≡NC$_6$H$_4$C$_6$H$_4$OC$_4$H$_9$-*p* (0.049 g, 0.195 mmol). After the solution was stirred for 1 h, the solvent was removed on a rotary evaporator and the white solid obtained was recrystallized from dichloromethane/hexane (0.095 g, 72% yield). ^{1}H NMR (CDCl$_3$): δ_1 7.58, δ_2 7.68, AA'XX' spin system ($^3J_{1,2}$ + $^5J_{1,2'}$ = 8.6 Hz), δ_3 7.52, δ_4 7.00, AA'XX' spin system ($^3J_{3,4}$ + $^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.5 Hz, O−CH$_2$), 1.86−0.88 (m, 7H, alkyl chain). ^{19}F NMR (CDCl$_3$): δ_1 −116.19 (dd, $^3J_{1,2}$ = 29.3 Hz, $^5J_{1,4}$ = 11.8 Hz, F$_{ortho}$), δ_2 −157.08 (dd, $^3J_{1,2}$ = 29.3 Hz, $^3J_{2,3}$ = 19.9 Hz, F$_{meta}$), δ_3 −156.82 (dd, $^3J_{2,3}$ = 19.9 Hz, $^3J_{3,4}$ = 19.9 Hz, F$_{para}$), δ_4 −127.54 (dd, $^3J_{3,4}$ = 19.9 Hz, $^5J_{1,4}$ = 11.8 Hz, F$_{ortho\ to\ Br}$). IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2214, (KBr) 2214. Anal. Calcd for C$_{23}$H$_{17}$AuBrF$_4$NO: C, 40.88; H, 2.53; N, 2.07. Found: C, 41.12; H, 2.50; N, 2.47.

Yields, IR, and analytical data are as follows:

n = **6.** Yield: 60%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2214, (KBr) 2213. Anal. Calcd for C$_{25}$H$_{21}$AuBrF$_4$NO: C, 42.67; H, 3.01; N, 1.99. Found: C, 43.01; H, 3.01; N, 2.38.

n = **8.** Yield: 70%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2214, (KBr) 2219. Anal. Calcd for C$_{27}$H$_{25}$AuBrF$_4$NO: C, 44.28; H, 3.44; N, 1.91. Found: C, 44.67; H, 3.39; N, 2.18.

n = **10.** Yield: 67%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2214, (KBr) 2218. Anal. Calcd for C$_{29}$H$_{29}$AuBrF$_4$NO: C, 45.80; H, 3.84; N, 1.84. Found: C, 45.46; H, 3.88; N, 1.98.

n = **12.** Yield: 50%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2214, (KBr) 2218. Anal. Calcd for C$_{31}$H$_{33}$AuBrF$_4$NO: C, 47.22; H, 4.21; N, 1.77. Found: C, 47.09; H, 3.82; N, 2.49.

[Au(C$_6$F$_5$)(C≡NC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$-*p*)]. *n* = **4.** Yield: 77%. ^{1}H NMR (CDCl$_3$): δ_1 7.58, δ_2 7.68, AA'XX' spin system ($^3J_{1,2}$ + $^5J_{1,2'}$ = 8.6 Hz), δ_3 7.52, δ_4 7.00, AA'XX' spin system ($^3J_{3,4}$ + $^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.5 Hz, O-CH$_2$), 1.86−0.88 (m, 7H, alkyl chain). ^{19}F NMR (CDCl$_3$): δ_1 −116.47 (m, F$_{ortho}$), δ_2 −162.72 (m, F$_{meta}$), δ_3 −157.84 (t, $J_{2,3}$ = 19.8 Hz, F$_{para}$). IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2216, (KBr) 2210. Anal. Calcd for C$_{23}$H$_{17}$AuF$_5$NO: C, 44.87; H, 2.76; N, 2.28. Found: C, 44.65; H, 2.77; N, 2.34.

Yields, IR, and analytical data are as follows:

n = **6.** Yield: 88%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215, (KBr) 2211. Anal. Calcd for C$_{25}$H$_{21}$AuF$_5$NO: C, 46.66; H, 3.27; N, 2.18. Found: C, 46.30; H, 3.18; N, 2.24.

n = **8.** Yield: 87%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2217, (KBr) 2225. Anal. Calcd for C$_{27}$H$_{25}$AuF$_5$NO: C, 48.29; H, 3.72; N, 2.09. Found: C, 48.16; H, 3.65; N, 2.14.

n = **10.** Yield: 72%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215, (KBr) 2225. Anal. Calcd for C$_{29}$H$_{29}$AuF$_5$NO: C, 49.78; H, 4.15; N, 2.00. Found: C, 49.71; H, 4.03; N, 1.74.

n = **12.** Yield: 79%. IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2215, (KBr) 2225. Anal. Calcd for C$_{31}$H$_{33}$AuF$_5$NO: C, 51.17; H, 4.54; N, 1.93. Found: C, 51.29; H, 4.51; N, 1.91.

[Au(C$_6$F$_5$)(C≡NC$_6$H$_4$OC$_{10}$H$_{21}$-*p*)]. Yield: 79%. ^{1}H NMR (CDCl$_3$): δ_1 7.46, δ_2 6.96, AA'XX' spin system ($^3J_{1,2}$ + $^5J_{1,2'}$ = 8.9 Hz), 4.0 (t, *J* = 6.5 Hz, O−CH$_2$), 1.81−0.88 (m, 19H, alkyl chain). ^{19}F NMR (CDCl$_3$): δ_1 −116.5 (m, F$_{ortho}$), δ_2 −162.84 (m, F$_{meta}$), δ_3 −158.0 (t, $J_{2,3}$ = 20 Hz, F$_{para}$). IR [ν(C≡N)]: (CH$_2$Cl$_2$) 2218, (KBr) 2226. Anal.

Calcd for $C_{23}H_{25}AuF_5NO$: C, 44.35; H, 4.01; N, 2.25. Found: C, 44.21; H, 3.98; N, 2.36. Optical data: C-I, 64 °C.

[Au(C₆F₄Br-*p*)(C≡NC₆H₄C₆H₄OC*ₙ*H₂*ₙ*₊₁-*p*)]. *n* = 4. Yield: 77%. ¹H NMR (CDCl₃): δ_1 7.58, δ_2 7.68, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.6 Hz), δ_3 7.52, δ_4 7.00, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.5 Hz, O–CH₂), 1.86–0.88 (m, 7H, alkyl chain). ¹⁹F NMR (CDCl₃): δ_1 −115.39, δ_2 −135.27, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 17.4 Hz, $^4J_{1,1'} + {}^4J_{2,2'}$ = 9.5 Hz, $^3J_{1,2} - {}^5J_{1,2'}$ = 42.2 Hz). IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2220. Anal. Calcd for $C_{23}H_{17}AuBrF_4NO$: C, 40.88; H, 2.53; N, 2.07. Found: C, 41.22; H, 2.50; N, 2.47.

Yields, IR, and analytical data are as follows:

n = 6. Yield: 74%. IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2207. Anal. Calcd for $C_{25}H_{21}AuBrF_4NO$: C, 42.67; H, 3.01; N, 1.99. Found: C, 42.44; H, 2.91; N, 1.88.

n = 8. Yield: 70%. IR [ν(C≡N)]: (CH₂Cl₂) 2217, (KBr) 2207. Anal. Calcd for $C_{27}H_{25}AuBrF_4NO$: C, 44.28; H, 3.44; N, 1.91. Found: C, 44.05; H, 3.25; N, 2.42.

n = 10. Yield: 74%. IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2224. Anal. Calcd for $C_{29}H_{29}AuBrF_4NO$: C, 45.80; H, 3.84; N, 1.84. Found: C, 45.65; H, 3.70; N, 1.76.

n = 12. Yield: 85%. IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2224. Anal. Calcd for $C_{31}H_{33}AuBrF_4NO$: C, 47.22; H, 4.21; N, 1.77. Found: C, 47.06; H, 3.96; N, 1.72.

Preparation of [(μ-4,4′-C₆F₄C₆F₄){Au(C≡NC₆H₄C₆H₄OC*ₙ*H₂*ₙ*₊₁-*p*)}₂]. *n* = 4. To a solution of [(μ-4,4′-C₆F₄C₆F₄){Au(tht)}₂] (0.100 g, 0.115 mmol) in 40 mL of diethyl ether was added C≡NC₆H₄C₆H₄-OC₄H₉-*p* (0.077 g, 0.26 mmol). After the solution was stirred for 1 h, the solvent was removed on a rotary evaporator and the white solid obtained was recrystallized from dichloromethane/hexane (0.140 g, 89% yield). ¹H NMR (CDCl₃): δ_1 7.59, δ_2 7.68, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.5 Hz), δ_3 7.52, δ_4 7.00, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.3 Hz, O–CH₂), 1.83–0.80 (m, 19H, alkyl chain). ¹⁹F NMR (CDCl₃): −117.70 (F_ortho), −140.50 (F_meta). IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2210. Anal. Calcd for $C_{46}H_{34}Au_2F_8N_2O_2$: C, 46.32; H, 2.87; N, 2.35. Found: C, 45.89; H, 2.92; N, 2.20.

Yields, IR, and analytical data are as follows:

n = 6. Yield: 62%. IR [ν(C≡N)]: (CH₂Cl₂) 2214, (KBr) 2206. Anal. Calcd for $C_{50}H_{42}Au_2F_8N_2O_2$: C, 48.09; H, 3.39; N, 2.56. Found: C, 47.81; H, 3.15; N, 2.36.

n = 8. Yield: 77%. IR [ν(C≡N)]: (CH₂Cl₂) 2214, (KBr) 2219. Anal. Calcd for $C_{54}H_{50}Au_2F_8N_2O_2$: C, 49.70; H, 3.86; N, 2.15. Found: C, 49.59; H, 3.73; N, 2.21.

n = 10. Yield: 76%. IR [ν(C≡N)]: (CH₂Cl₂) 2215, (KBr) 2210. Anal. Calcd for $C_{58}H_{58}Au_2F_8N_2O_2$: C, 51.18; H, 4.29; N, 2.06. Found: C, 51.03; H, 4.23; N, 1.94.

n = 12. Yield: 75%. IR [ν(C≡N)]: (CH₂Cl₂) 2216, (KBr) 2211. Anal. Calcd for $C_{62}H_{66}Au_2F_8N_2O_2$: C, 52.55; H, 4.69; N, 1.98. Found: C, 52.37; H, 4.14; N, 1.41.

Yields, IR, and analytical data for [(μ-4,4′-C₆F₄C₆F₄){Au(C≡NC₆H₄-OC*ₙ*H₂*ₙ*₊₁-*p*)}₂] are as follows:

n = 4. Yield: 72%. IR [ν(C≡N)]: (CH₂Cl₂) 2218, (KBr) 2212. Anal. Calcd for $C_{34}H_{26}Au_2F_8N_2O_2$: C, 39.25; H, 2.52; N, 2.69. Found: C, 39.25; H, 2.56; N, 2.75.

n = 6. Yield: 78%. IR [ν(C≡N)]: (CH₂Cl₂) 2218, (KBr) 2212. Anal. Calcd for $C_{38}H_{34}Au_2F_8N_2O_2$: C, 41.62; H, 3.13; N, 2.56. Found: C, 41.56; H, 3.15; N, 2.53.

n = 8. Yield: 65%. IR [ν(C≡N)]: (CH₂Cl₂) 2218, (KBr) 2211. Anal. Calcd for $C_{42}H_{42}Au_2F_8N_2O_2$: C, 43.76; H, 3.67; N, 2.43. Found: C, 43.80; H, 3.65; N, 2.63.

n = 10. Yield: 81%. IR [ν(C≡N)]: (CH₂Cl₂) 2217, (KBr) 2208. Anal. Calcd for $C_{46}H_{50}Au_2F_8N_2O_2$: C, 45.71; H, 4.17; N, 2.32. Found: C, 45.68; H, 4.18; N, 2.48.

n = 12. Yield: 80%. IR [ν(C≡N)]: (CH₂Cl₂) 2214, (KBr) 2218. Anal. Calcd for $C_{50}H_{58}Au_2F_8N_2O_2$: C, 47.48; H, 4.62; N, 2.22. Found: C, 47.27; H, 4.42; N, 2.15.

Preparation of [Au(C₆F₅)I₂(C≡NC₆H₄C₆H₄OC₈H₁₇-*p*)]. To a solution of [Au(C₆F₅)(C≡NC₆H₄C₆H₄OC₈H₁₇-*p*)] (0.100 g, 0.150 mmol) in 40 mL of diethyl ether was added iodine (0.050 g, 0.200 mmol). After the solution was stirred for 90 min the solvent was removed on a rotary evaporator and the white solid obtained was recrystallized from dichloromethane/hexane (0.027 g, 40% yield). Anal. Calcd for $AuC_{27}F_5H_{25}I_2NO$: C, 35.03; H, 2.70; N, 1.51. Found: C, 35.22; H, 2.62; N, 1.47. IR [ν(C≡N)]: (CH₂Cl₂): 2250 cm⁻¹. ¹H NMR (CDCl₃): δ_1 7.68, δ_2 7.74, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.8 Hz), δ_3 7.53, δ_4 7.00, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.8 Hz), 4.00 (t, *J* = 6.6 Hz, O–CH₂), 1.82–0.88 (m, 15H, alkyl chain). ¹⁹F NMR (CDCl₃): δ_1 −118.59 (m, F_ortho), δ_2 −156.16 (t, *J* = 19.7 Hz, F_para), δ_3 −162.02 (m, F_meta).

[Au(C₆F₄-Br-*o*)I₂(C≡NC₆H₄C₆H₄OC₁₀H₂₁-*p*)] was similarly prepared. Anal. Calcd for $AuBrC_{29}F_4H_{28}I_2NO$: C, 34.34; H, 2.88; N, 1.38. Found: C, 34.31; H, 2.75; N, 1.67. IR [ν(C≡N)]: (CH₂Cl₂): 2245 cm⁻¹. ¹H NMR (CDCl₃): δ_1 7.68, δ_2 7.73, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.7 Hz), δ_3 7.53, δ_4 7.00, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.7 Hz), 4.00 (t, *J* = 6.5 Hz, O-CH₂), 1.83–0.87 (m, 15H, alkyl chain). ¹⁹F NMR (CDCl₃): δ_1 −117.16 (dd, $^3J_{1,2}$ = 24.3 Hz, $^5J_{1,4}$ = 8.2 Hz, F_ortho), δ_2 −155.27 (dd, $^3J_{1,2}$ = 24.3 Hz, $^3J_{2,3}$ = 19.9 Hz, F_meta), δ_3 −155.53 (dd, $^3J_{2,3}$ = 19.9 Hz, $^3J_{3,4}$ = 19.9 Hz, F_para), δ_4 −128.20 (dd, $^3J_{3,4}$ = 19.9 Hz, $^5J_{1,4}$ = 8.2 Hz, F_ortho to Br).

Preparation of [(μ-4,4′-C₆F₄C₆F₄){AuI₂(C≡NC₆H₄C₆H₄OC₈H₁₇-*p*)}₂]. To a solution of [(μ-4,4′-C₆F₄C₆F₄){Au(C≡NC₆H₄C₆H₄OC₈H₁₇-*p*)}₂] (0.080 g, 0.061 mmol) in 50 mL of dichloromethane was added iodine (0.031 g, 0.123 mmol). After the solution was stirred for 90 min, the solvent was removed on a rotary evaporator and the red solid obtained was recrystallized from dichloromethane/hexane (0.033 g, 30% yield). Anal. Calcd for $Au_2C_{54}F_8H_{50}I_4N_2O_2$: C, 35.78; H, 2.78; N, 1.55. Found: C, 35.69; H, 2.74; N, 1.52. IR [ν(C≡N)]: (KBr) 2242 cm⁻¹. ¹H NMR (CDCl₃): δ_1 7.76, δ_2 7.71, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.9 Hz), δ_3 7.55, δ_4 7.02, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.5 Hz, O-CH₂), 1.84–0.87 (m, 15H, alkyl chain). ¹⁹F NMR (CDCl₃): −119.31 (F_ortho), −139.00 (F_meta).

[(μ-4,4′-C₆F₄C₆F₄){AuBr₂(C≡NC₆H₄C₆H₄OC₈H₁₇-*p*)}₂] was similarly prepared. Anal. Calcd for $Au_2Br_4C_{54}F_8H_{50}N_2O_2$: C, 39.92; H, 3.10; N, 1.72. Found: C, 40.52; H, 2.99; N, 3.27. IR [ν(C≡N)]: (KBr) 2251 cm⁻¹. ¹H NMR (CDCl₃): δ_1 7.75, δ_2 7.70, AA′XX′ spin system ($^3J_{1,2} + {}^5J_{1,2'}$ = 8.9 Hz), δ_3 7.55, δ_4 7.01, AA′XX′ spin system ($^3J_{3,4} + {}^5J_{3,4'}$ = 8.8 Hz), 4.01 (t, *J* = 6.5 Hz, O-CH₂), 1.86–0.86 (m, 15H, alkyl chain). ¹⁹F NMR (CDCl₃): −123.27 (F_ortho), −138.38 (F_meta).

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