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Azo Isocyanide Gold(I) Liquid Crystals, Highly Birefringent and Photosensitive in the Mesophase

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Isocyanide ligands bearing an azo group and one alkoxy chain OC_nH_{2n+1} have been synthesized. They are calamitic liquid crystals for $n > 4$ and display nematic (n = 8, 12) and SmA (n = 12) mesophases. Their gold(I) compounds [AuX(CNR)] ($X = Cl, C_6F_5$; $R = C_6H_4N{=}NC_6H_4OC_nH_{2n+1}$, n = 4, 8, 12) have been obtained by displacement of a weakly coordinated ligand. The chloro gold(I) compounds exhibit nematic (n = 4) and SmA mesophases, and decompose at temperatures higher than 200 °C, before reaching the clearing point. The pentafluorophenyl gold(I) compounds show nematic and SmA (n = 12) mesophases. All the derivatives are photosensitive in solution because of trans to cis isomerization of the azo group under UV light, which reverts photochemically or thermally to the trans isomer. Irradiation in the mesophase also induces isomerization with consequent destabilization of the mesophase to an isotropic liquid; the mesophase is recovered as soon as illumination stops. These azo mesogens show high birefringence values, higher for the linear gold complexes than for the free azo ligand.

Introduction

The reversible light induced trans–cis photoisomerization of the azo group has been exploited to modify systems by inducing chemical and physical changes under irradiation. The phenomenon consists of the isomerization of the most stable trans configuration, with an elongated rod-like molecular form, to the bent cis configuration upon UV irradiation at $\lambda \approx 365$ nm (Scheme 1). The reverse transformation can be brought about thermally, or by illuminating with visible light at $\lambda \approx 450$ nm.[1] The application of this phenomenon to compounds or mixtures displaying liquid crystal properties has been envisaged to design optical switching materials based on light-induced isothermal phase transitions,[2-7] as the trans to cis isomerization typically produces the collapse of the mesophase (stable for the rod-like trans isomer) to an isotropic liquid (favored by the bent shape cis isomer).[3,6,8,9] Occasionally more complicated results have been obtained.[10,11]

4,4′-Disubstituted azobenzene compounds with appropriate substituents are liquid crystals that have been used to prepare orthometalated liquid crystals by reaction, mostly with palladium(II).[12] In the cyclometalated mesogens obtained the N═N fragment, being involved in a metallacycle, is obviously blocked in its trans conformation, and the photosensitivity is suppressed.[13] The chemistry of gold with any azo ligand, including orthometalated gold(III) complexes,[14] is

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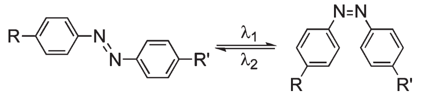
Scheme 1



comparatively scarce, and very little is known about their photoisomerization behavior. To our knowledge, the potential photoisomerization behavior was only studied, in solution, for the interesting case of a tetranuclear macrocyclic gold(I) alkynyl phosphine complex, in which the trans–cis photoisomerization in solution can be locked by addition of silver(I), which π-coordinates to the alkynyl groups and precludes the breadth of the macrocycle associated to the presence of a cis azo group.[15]

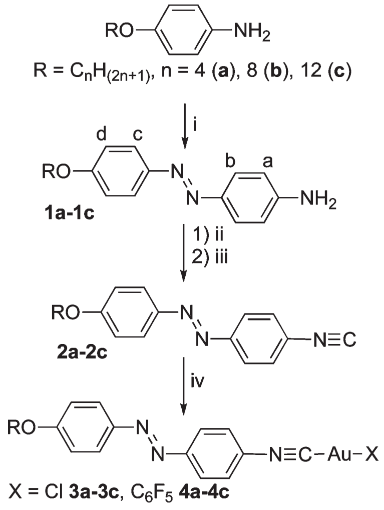
Only a few metallomesogens containing an uncomplexed −N=N− function, and therefore keeping their potential for photoisomerization, have been reported. These are some calix[4]arene W(VI),[16] enamino ketone Cu(II),[17] azopyridine silver(I)[18,19] and salicyl Ni(II), Cu(II), and V(IV) complexes.[20–22] However, very few physical studies have been made: for the salicylidenediaminato nickel complexes,[22] and for the silver derivatives,[18,19] the photoisomerization in solution was studied by UV–vis absorption. Only for the previous silver complexes used as dopant (3% mol) of organic liquid crystals was the photoisomerization verified on LC films formed by this eutectic mixture, at room temperature, by their absorption spectra (reflectance) in the doped mesophase.[18] In summary, there is no previous report of a metallomesogen being tested for photoisomerization in the mesophase produced by the pure compound.

Isocyanide ligands are commonly used to prepare gold mesogens because of the remarkable thermal stability of these complexes.[23–25] Here we report the synthesis of isocyanide ligands containing an azo group (azo isocyanide ligands) and an alkoxy chain, which provide the first gold(I) mesogens bearing an azo group. As the azo group is not involved in coordination, these colored gold-containing liquid crystals are photosensitive, not only in solution but also in the mesophase. This is the first time that the photoisomerization has been demonstrated in a mesophase displayed by a pure metallomesogen.

Results and Discussion

Synthesis and Characterization. The synthesis of the ligands and their gold complexes is summarized in Scheme 2. The amines **1** were readily prepared by diazotization of the corresponding alkoxy amine, coupling with aniline, and isomerization of the diazoamine compound. The corresponding crude formamides, made by reaction with formic acid, were not analytically pure but were used without further purification to obtain the isocyanides **2** by dehydration with triphosgene in the presence of triethylamine. The isocyanides were purified by column chromatography and were used to prepare the gold(I) complexes **3**–**4** by displacement of the weakly coordinating tht (tetrahydrothiophene) ligand from the adequate gold(I) precursor.

Scheme 2. (i) HCl$_{(conc)}$; $T < 5$ °C, NaNO$_2$; NH$_2$Ph; NH$_2$Ph + PhNH$_2$·HCl; (ii) HCOOH, Reflux in Toluene; (iii) OC(OCCl$_3$)$_2$, NEt$_3$; (iv) [AuX(tht)] (X = Cl, C$_6$F$_5$)[a]



[a] Labels for aromatic hydrogen atoms are as shown in the amines.

Compounds **1**–**4** are air-stable red (**1**) or orange (**2**–**4**) solids at room temperature, which were characterized by elemental analysis, and by IR and NMR spectroscopy (see Experimental Section). The IR spectra of **2a-c** in dichloromethane show the characteristic ν(C≡N) absorption at 2127 cm^{-1}, which shift to 2220 cm^{-1} and 2216 cm^{-1}, respectively, for the gold compounds **3a-c** and **4a-c**. In the ^{1}H NMR spectra, the aromatic protons display two pseudodoublets (AA′XX′ systems) at about 7 ppm for H^d (see Scheme 2 for labels), and in the range 7.78–7.95 ppm for H^c; and two pseudodoublets in the range 6.74–7.69 for H^a, and 7.85–8.0 ppm for the H^b. In addition, the resonances corresponding to the aliphatic chain are observed. The ^{19}F NMR spectra of compounds **4** display the three resonances typical of the pentafluorophenyl group, at −116, −158, and −163 ppm.

Mesogenic Behavior. The thermal behavior of all the compounds prepared was studied using polarized light optical microscopy and differential scanning calorimetry. The results are collected in Table 1 and in Figure 1. The mesophases were identified as nematic (N) or smectic A (SmA) by polarized optical microscopy, based on their characteristic textures (Figure 2).

All the azo amine compounds are non-mesogenic. The azo isocyanide ligands are enantiotropic calamitic liquid crystals, except for the shortest aliphatic chain (**2a**). Compound **2b** shows a nematic marbled texture. Compound **2c** exhibits a N mesophase observed as a Schlieren texture; it is observed by optical microscopy in a short-range

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Table 1. Optical, Thermal, and Thermodynamic Data for Compounds **2−4**

comp.	n	transition[a]	T (°C)[b]	ΔH (kJ mol^{-1})
2a	4	Cr−Cr′[c]	70.1	1.1
		Cr′−I	91.7	17.0
		I−Cr	78.1	−12.9
2b	8	Cr−Cr′[c]	72.9	2.0
		Cr′−N	90.7	18.8
		N−I	101.2	0.1
		I−N[d]	97	
		N−Cr	70.7	−19.4
2c	12	Cr−Cr′[c]	70.6	1.9
		Cr′−N[d]−I[e]	87.0	32.2[f]
		(I−N[d]−SmA[e])	(83.3)	(−0.6[f])
		SmA−Cr	71.7	−30.8
3a	4	Cr−SmA	175.5	8.3
		SmA−N(dec.)[d]	207	
3b	8	Cr−SmA	151.0	5.7
		SmA−dec.[d]	220	
3c	12	Cr−SmA	144.5	7.4
		SmA−dec.[d]	250	
4a	4	Cr−Cr′[c]	96.7	0.4
		Cr′−N	153.4	15.8
		N−I[d]	182	
4b	8	Cr−Cr′[c]	33.0	14.8
		Cr′−Cr″[c]	90.0	3.7
		Cr″−N	105.7	14.6
		N−I	152.7	1.3
4c	12	Cr−Cr′[c]	76.2	19.7
		Cr′−SmA	104.2	15.3
		SmA−N[d]	153	
		N−I[d]	167	

[a] Cr, Cr′, Cr″ = crystal; I = isotropic liquid. [b] Data for the first heating scan. [c] Only observed by DSC. [d] Only observed by POM. [e] There are two close consecutive transitions, and the melting point is not sharp. [f] Combined enthalpies.

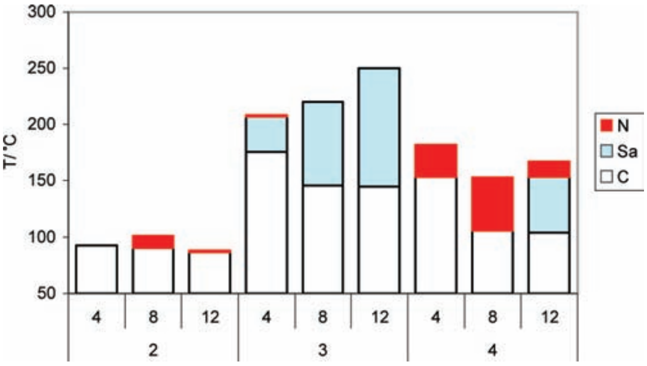

Figure 1. Thermal behavior of compounds CNR (**2**), [AuCl(CNR)] (**3**), and [Au(C_6F_5)(CNR)] (**4**) (upon heating; n = 4, 8, 12).

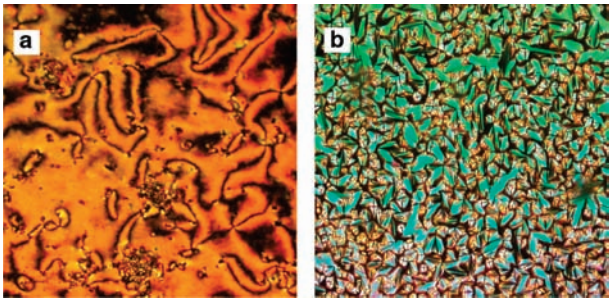

Figure 2. (a) Nematic Schlieren texture (100×) observed for **4b**, obtained on cooling from isotropic liquid at 130 °C. (b) Focal-conic SmA texture (100×) observed for **4c**, obtained on cooling from isotropic liquid at 120 °C.

and mixed with the following transition. Moreover, a monotropic SmA mesophase is observed upon cooling, which appears as the focal-conic fan texture. Therefore, the longer the alkoxy chain, the lower transition temperatures, the wider the LC temperature range, and the more ordered the mesophases obtained. It is worth to remark that analogous ligands CNR are not liquid crystals for R = $C_6H_4OC_nH_{2n+1}$,[26] while for R = $C_6H_4C_6H_4C_nH_{2n+1}$, $C_6H_4{-}C(O)O{-}C_6H_4C_nH_{2n+1}$ the isocyanides are mesogens,[27,28] with transition temperatures lower than for compound **2**, and display N and SmA mesophases.

Coordination to gold(I) leads to compounds with higher transition temperatures, more ordered mesophases and longer mesophase ranges. In fact, all compounds **3** are liquid crystals that exhibit SmA mesophases, identified by a focal-conic fan texture. These chloro complexes have clearing temperatures higher than 200 °C and decompose before reaching the isotropic liquid. In addition, the derivative with the shortest chain, **3a**, displays a nematic mesophase which is observed (Schlieren texture) accompanied by some decomposition. Increasing the alkoxy chain length reduces the melting temperature, which leads to a larger mesophase range: 31.5, 69, and 105.5 °C, for compounds **3a−c** respectively. For the pentafluorophenyl derivatives **4**, the transition temperatures are depressed, and they exhibit shorter mesophase ranges and less ordered mesophases, but the compounds are thermally stable also in the isotropic liquid. All compounds **4** display a nematic mesophase characterized by a Schlieren texture. Previous to the N phase, compound **4c** exhibits a SmA mesophase identified by its focal-conic fan texture. For compounds **4** the longer the alkoxy chain, the lower the melting point, whereas the clearing points follow the order **4a** > **4c** > **4b**. Again, increasing the chain length leads to a more ordered mesophase (for **4c**) and to a wider mesophase range: 28.6, 47, and 62.8 °C, respectively, for **4a−c**. In comparison, analogous chloro and pentafluorophenyl gold(I) compounds with other isocyanides CNR (R = $C_6H_4OC_nH_{2n+1}$,[26] $C_6H_4C_6H_4C_nH_{2n+1}$,[27,29] $C_6H_4{-}C(O)O{-}C_6H_4C_nH_{2n+1}$)[28,30] are mesogens, and they exhibit N and SmA phases, and even SmC mesophases for the latter.

Photosensitivity in Solution. As stated above, the azo functional group can undergo isomerization from the more stable trans isomer to the cis isomer, under UV light illumination. Representative organometallic gold derivatives were studied for this property. The UV−vis spectra of the trans−cis isomers of the chloro gold compound **3b** in CH_2Cl_2 solution are shown in Figure 3. Initially, the trans isomer shows a maximum at 365 nm associated with an azo $\pi\rightarrow\pi^*$ transition. Besides there is a shoulder at 290 nm related to an aromatic $\pi{-}\pi^*$ transition, and an absorption at 460 nm due to an

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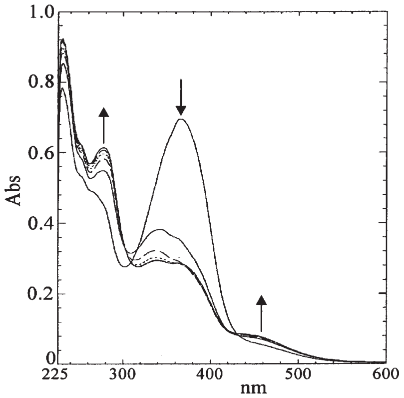

Figure 3. UV−vis absorption spectra of compound **3b** (2.5×10^{-5} M dichloromethane solution). The intense peak at 364 nm corresponds to the trans isomer before irradiation. Arrows indicate how the band intensities change upon irradiation.

$n \rightarrow \pi^*$ transition.[31] After irradiation at 365 nm with an UV lamp, the intensity of the absorptions at 290 and 460 nm rises, whereas that of the band at 365 nm diminishes, because of the formation of the cis isomer. The observation of two isosbestic points in the spectra, located at 302 and 423 nm, confirms the participation of only two compounds, the cis and trans isomers, as expected. The highest photoisomerization is reached in 240 s for illumination intensities of 7 $\text{mW}\cdot\text{cm}^{-2}$. Switching off the irradiation, the thermodynamically less stable cis complex isomerizes to its trans isomer very slowly: it takes around 4 days in the dark to return to the initial point, although this isomerization can be accelerated by using visible light. An analogous result was obtained for the pentafluorophenyl derivative **4b**. These studies show that the photochemical trans−cis and the thermal and photochemical cis−trans isomerizations still occur in our azo gold complexes in solution and take place without any decomposition of the complex.

Photoisomerization experiments in NMR tubes at 295 K and concentrations about 2×10^{-2} M were carried out. The ^{1}H NMR spectra for compounds **2b**−**4b**, after irradiation with 365 nm light for about 1 h show trans/cis ratios of 55/45, 43/67, and 50/50, respectively.

The four resonances corresponding to the cis isomer appear as two pseudodoublets (AA′XX′ systems) at about 6.77 and 6.90 ppm, respectively, for H^d and H^c (see Scheme 2 for labels); and, two pseudodoublets in the range 7.30−7.50 for H^a, and 6.88−6.98 ppm for H^b. Compared to the resonances of the trans isomer, H^b and H^c (ortho to the azo group) are shifted around −1 ppm by the paramagnetic anisotropic shielding of the other phenyl ring, while H^a and H^d (meta to the azo group) are shifted about −0.20 and −0.25 ppm. Besides the methylene alkoxy protons are shifted −0.14 ppm.

Photosensitivity in the Mesophase. Since the gold complexes display photosensitivity in solution, it is interesting to check this behavior in the mesophase. The nematic phase of compound **4b** was chosen for these experiments because it has lower viscosity and appears at lower temperatures (hence it offers higher thermal stability) than other complexes. Planar samples were easily aligned. Upon illumination of a zone of the mesophase at 90 °C (nematic on cooling) with the He−Cd polarized laser, a decrease of the birefringence is observed initially; after a few seconds, the samples undergo an isothermal transition to the isotropic phase (Figure 4). The speed of the effect is maximal when the light polarization is parallel to the nematic director. As soon as the laser light is removed, the illuminated zone recovers the initial aligned nematic mesophase, likely because of the treatment of the surface cell, which facilitates this alignment. As far as kept within the nematic mesophase range, the exact temperature is not very important and the isotropic transition is always observed. The isotropic transition upon laser irradiation is again interpreted as a consequence of the trans−cis photoisomerization of the azo moiety. Under suitable light irradiation, the cis population increases, and the material becomes isotropic. Once the light is switched off, the cis population diminishes as it returns to the more stable (and more suited for mesophase formation) trans configuration. The cis−trans conversion takes place in short times (less than 1 s) at these relatively high temperatures where thermal isomerization is very efficient.[32]

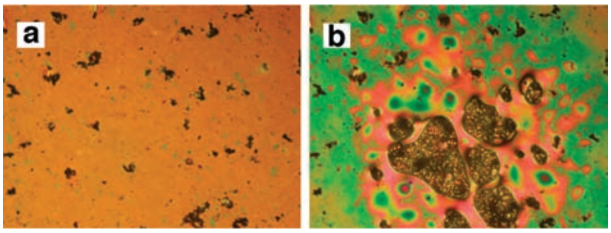

Figure 4. Aligned textures of compound **4b** in the nematic phase (100×) between crossed polarizers before (a) and after (b) 10 s of illumination with light of 442 nm and 1 W cm^{-2}. The different colors in (b) correspond to different degrees of nematic order, the order increasing from black (isotropic phase), to pink and green. The orange color in the original texture (a) indicates even larger birefringence.

Birefringence Studies in the Mesophase. We have also studied the birefringence of compounds **2b**, **3b**, and **4b**, containing the same azo isocyanide ligand (alkoxy chain $n = 8$), to see the effect of coordination. The effect of the metal fragment depends on the structure of the molecule, in fact complexes with birefringence values higher, similar or lower than the free ligands have been described.[33] In our case the three compounds display very high birefringence, which is characteristic of materials based on azo molecules.[34] The measured values of Δn are 0.32 for the free ligand **2b** at 80 °C (N mesophase); 0. 59 for the AuCl complex **3b** at 200 °C (SmA mesophase); and 0.51 for the AuC_6F_5 complex **4b** at 113 °C (N mesophase). At lower temperatures the optical anisotropy is even higher. Although birefringence measurements have been carried out at different reduced temperatures

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($T/T_c = 0.944, 0.959, 0.908$ for **2b**, **3b**, and **4b**, respectively) and even in different phases in some cases (N and SmA), which precludes rigorous comparison, the values are so clearly larger in the gold compounds (**3b** and **4b**) that it seems safe to conclude that the presence of gold plays an important role in increasing the molecular anisotropy.

Conclusions

A new azo isocyanide ligand bearing an alkoxy chain has been prepared. This polyfunctional ligand is suitable for stable coordination to gold(I) fragments through the isocyanide function. These derivatives display liquid crystal behavior and undergo azo trans−cis photoisomerization not only in solution but also in the mesophase. As a consequence of the structural change of the molecular shape associated to azo trans−cis isomerization, the mesophases are destabilized by laser irradiation and lead to an isotropic liquid. This change is reversible, and the initial mesophase is quickly recovered when the laser irradiation is switched off. The gold complexes show noticeably higher birefringence than the free ligands.

Experimental Section

In the photosensitivity studies in solution (on 2.5×10^{-5} M dichloromethane solutions), the UV−vis spectra were measured every 60 s, and the irradiation was carried out with an UV lamp at $\lambda = 365$ nm ($I = 7$ mW$\cdot$cm^{-2}). The same lamp was used for the NMR photoisomerization studies on 2×10^{-2} M $CDCl_3$ solutions. Planar samples were prepared in commercially available cells (Linkam) of nominal thickness of 5 μm. The inner glass surfaces were coated with polyimide and rubbed unidirectionally. The induced alignment was rather good in the nematic phases. Samples were illuminated with polarized laser light, and the textures were simultaneously observed in the polarizing microscope. We employed a He−Cd laser emitting at 442 nm, and the average intensity of irradiation on the samples was about 1 W/cm^2. The birefringence was measured using a Berek compensator. The optical path difference was determined through the rotation angle of a calcite plate cut perpendicular to the polarizing microscope axis.[35] Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin-Elmer DSC-7 (heating rate of 10 K min^{-1}), using aluminum crucibles. The apparatus was calibrated with indium (156.6 °C, 28.45 J g^{-1}) as standard. Other technical details were as previously reported.[36] Literature methods were used to prepare [AuX(tht)] (X = Cl, C_6F_5).[37,38] Only example procedures and IR and NMR data (^{1}H NMR key in Scheme 2) for $n = 8$ are described here, as the syntheses and the IR and NMR data were similar for the rest of the compounds. Yields and analytical data are given for all the compounds.

Synthesis of the Amine R−NH$_2$ (R = C_6H_4−N=N−C_6H_4−OC_nH_{2n+1}), *n* = 4 (1a), 8 (1b), 12 (1c). They were prepared by a standard procedure,[39] but starting with *p*-alkoxyaniline compounds. Yield of **1a**: 348 mg, 67%. Anal. Calcd (%): C, 71.45; H, 7.11; N, 15.60. Found: C, 71.80; H, 6.95; N, 15.43. Yield of **1b**: 63 mg, 26%. Anal. Calcd (%): C, 73.81; H, 8.36; N, 12.91. Found: C, 74.15; H, 7.96; N, 12.81. Yield of **1c**: 783 mg, 17%. Anal. Calcd (%): C, 75.55; H, 9.25; N, 11.01. Found: C, 75.15; H, 8.92; N, 10.65. ^{1}H NMR of **1b**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.84 (m, 12H, CH_3-(CH_2)$_6$-), 4.02 (brm, 4H, O−CH_2-(CH_2)$_n$ and NH_2), 6.74 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^a), 6.98 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^d), 7.78 (d, 2H, H^c), 7.85 (d, 2H, H^b). UV−vis in CH_2Cl_2 (nm; ε/M^{-1} cm^{-1}): 377 (28234), 249 (12481).

Synthesis of the Formamide R−NHCHO and the Isocyanide R−N≡C (R = C_6H_4−N=N−C_6H_4−OC_nH_{2n+1}), *n* = 4 (2a), 8 (2b), 12 (2c). They were prepared by adapting the general method of Ugi.[40] Yield of **2a**: 86 mg, 61%. Anal. Calcd (%): C, 73.10; H, 6.13; N, 15.04. Found: C, 73.43; H, 5.74; N, 15.32. Yield of **2b**: 245 mg, 50%. Anal. Calcd (%): C, 75.19; H, 7.51; N, 13.03. Found: C, 75.52; H, 7.12; N, 13.19. Yield of **2c**: 347 mg, 61%. Anal. Calcd (%): C, 76.69; H, 8.49; N, 10.73. Found: C, 76.85; H, 8.59; N, 11.02. ^{1}H NMR of **2b (trans)**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-(CH_2)$_6$-), 4.06 (t, $^3J_{HH}$ = 6.6 Hz, 2H, O−CH_2-(CH_2)$_n$), 7.02 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^d), 7.51 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H^a), 7.90 (d, 2H, H^b), 7.92 (d, 2H, H^c). IR (CH_2Cl_2): 2127 ν(C≡N) cm^{-1}. IR (KBr): 2118 ν(C≡N) cm^{-1}. IR (Nujol): 2118 ν(C≡N) cm^{-1}. UV−vis in CH_2Cl_2 (nm; ε/M^{-1} cm^{-1}): 356 (19885), 260 (12227), 229 (15429). ^{1}H NMR of **2b (cis)**: δ 0.89 (m, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-(CH_2)$_6$-), 3.92 (t, $^3J_{HH}$ = 6.6 Hz, 2H, O−CH_2-(CH_2)$_n$), 6.76 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^d), 6.88 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H^b), 6.89 (d, 2H, H^c), 7.30 (d, 2H, H^a).

Synthesis of [AuCl(CNR)] R = C_6H_4−N=N−C_6H_4−OC_nH_{2n+1}; *n* = 4 (3a), 8 (3b), 12 (3c). To a dichloromethane solution (20 mL) of [AuCl(tht)] (67 mg, 0.21 mmol) was added the stoichiometric amount of the corresponding isocyanide **2b** (70 mg, 0.21 mmol). The resulting suspension was stirred for 15 min, and compound **3** was obtained as an insoluble orange solid. Yield of **3a**: 85 mg, 79%. Anal. Calcd (%): C, 39.90; H, 3.35; N, 8.21. Found: C, 39.51; H, 2.98; N, 8.08. Yield of **3b**: 95 mg, 80%. Anal. Calcd (%): C, 44.42; H, 4.44; N, 7.40. Found: C, 44.40; H, 4.07; N, 7.43. Yield of **3c**: 113 mg, 86%. Anal. Calcd (%): C, 48.12; H, 5.33; N, 6.73. Found: C, 48.16; H, 5.10; N, 7.06. ^{1}H NMR of **3b (trans)**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-(CH_2)$_6$-), 4.06 (t, $^3J_{HH}$ = 6.6 Hz, 2H, O−CH_2-(CH_2)$_n$), 7.02 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H^d), 7.66 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^a), 7.95 (d, 2H, H^c), 7.98 (d, 2H, H^b). IR (CH_2Cl_2): 2221 ν(C≡N) cm^{-1}. IR (KBr): 2238 ν(C≡N) cm^{-1}. IR (Nujol): 2238 ν(C≡N) cm^{-1}. UV−vis in CH_2Cl_2 (nm; ε/M^{-1} cm^{-1}): 364 (27229), 273 (16915), 227 (19118). ^{1}H NMR of **3b (cis)**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-(CH_2)$_6$-), 3.92 (t, $^3J_{HH}$ = 6.5 Hz, 2H, O−CH_2-(CH_2)$_n$), 6.77 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^d), 6.92 (d, 2H, H^c), 6.98 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H^b), 7.49 (d, 2H, H^a).

Synthesis of [Au(C_6F_5)(CNR)] R = C_6H_4−N=N−C_6H_4−OC_nH_{2n+1}; *n* = 4 (4a), 8 (4b), 12 (4c). To a dichloromethane solution (20 mL) of [Au(C_6F_5)(tht)] (88 mg, 0.19 mmol) was added the stoichiometric amount of the isocyanide **2b** (64 mg, 0.19 mmol). The resulting suspension was stirred for 15 min. Then it was filtered through Kiesselgur (unreacted isocyanide if any) and concentrated to dryness. Compound **4** was obtained as an orange solid. Yield of **4a**: 82 mg, 65%. Anal. Calcd (%): C, 42.94; H, 2.66; N, 6.53. Found: C, 42.58; H, 2.69; N, 6.55. Yield of **4b**: 92 mg, 67%. Anal. Calcd (%): C, 46.36; H, 3.60; N, 6.01. Found: C, 45.97; H, 3.31; N, 5.82. Yield of **4c**: 128 mg, 89%. Anal. Calcd (%): C, 49.28; H, 4.40; N, 5.56. Found: C, 48.91; H, 4.22; N, 5.65. ^{1}H NMR of **4b (trans)**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-(CH_2)$_6$-), 4.06 (t, $^3J_{HH}$ = 6.6 Hz, 2H, O−CH_2-(CH_2)$_n$), 7.03 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H^d), 7.69 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^a), 7.95 (d, 2H, H^c), 8.00 (d, 2H, H^b). ^{19}F NMR: δ −116.41 (m, 2F, F$_o$), −157.73 (m, 1F, F$_p$), −162.73 (m, 2F, F$_m$). IR (CH_2Cl_2): 2216 ν(C≡N) cm^{-1}. IR (KBr): 2221 ν(C≡N) cm^{-1}. IR (Nujol): 2220 ν(C≡N) cm^{-1}.

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UV−vis in CH_2Cl_2 (nm; $\varepsilon/M^{-1}\,cm^{-1}$): 366 (27354), 280 (18952), 254 (20820), 231 (27375). ^{1}H NMR of **4b (cis)**: δ 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.31−1.86 (m, 12H, CH_3-$(CH_2)_6$), 3.93 (t, $^3J_{HH}$ = 6.6 Hz, 2H, O−CH_2-$(CH_2)_n$), 6.78 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H^d), 6.92 (d, 2H, H^c), 6.98 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^b), 7.50 (d, 2H, H^a).

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Supporting Information Available: IR and NMR data for compounds with n = 4, 12. This material is available free of charge via the Internet at http://pubs.acs.org.