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Fluorophobic Effect in Metallomesogens – The Synthesis and Mesomorphism of Ag, Au, Cu, Fe, Pd, and Pt Fluorous Isocyanide Complexes

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The synthesis of $Ag(CNAr)_2BF_4$, $Ag(CNAr)_2NO_3$, AuCl(CNAr), CuCl(CNAr), $[CuCl(CNAr)_2]_2$, $Fe(CO)_4CNAr$, *trans*-$[PdI_2(CNAr)_2]$, and *trans*-$[PtI_2(CNAr)_2]$ complexes containing the fluorous isocyanide ligand CNAr [Ar = $4\text{-}F(CF_2)_8(CH_2)_4OC_6H_4$] and the examination of the mesomorphic properties of these novel fluorous organometallics are reported. The fluorous isocyanide ligand is mesomorphic, as opposed to its hydrocarbon analogue. In general, the fluorophobic effect enhances the microsegregation in the investigated organometallic/isocyanide complexes, as compared to their hydrocarbon analogues. The fluorous mesophases are stable over a wider temperature range and exhibit higher transition temperatures.

Introduction

Compounds containing perfluorocarbon chains (usually called fluorous) attract attention not only due to their synthetic, catalytic, and biomedical applications,[1] but also due to their self-segregation ability that results in the appearance of liquid-crystalline phases. The fluorophobic effect may induce supramolecular organization through the incompatibility of fluorinated and non-fluorinated hydrocarbons.[2–6] This effect results from the differences in the cohesive energy between perfluorocarbon and hydrocarbon groups. Incorporation of perfluorinated alkyl chains into classical organic molecules produces a microsegregation at the molecular level that results in an enhancement of highly ordered lamellar mesophases. An influence on mesomorphic properties by fluorination of classical organic liquid crystals has been investigated.[7–14]

The investigation of metallomesogens (liquid crystals containing transition or post-transition metals) has emerged as an active branch of liquid-crystal research.[15] Studies of structure/property relationships with the purpose of designing new materials, and ultimately predicting the properties, continues to be an important aspect in this area. Isocyanides (CNR) form stable complexes with many transition metals and have been investigated in the pursuit of metallomesogens.[16–21] The earliest mesogenic isocyanide complexes include square-planar palladium(II) and platinum(II) *trans*-$[MI_2(CNR)_2]$ complexes derived from isocyanides with two aromatic rings connected by an ester group.[16a,16b] Other complexes, such as neutral gold(I) complexes [AuCl(CNR)],[17c] ionic silver(I) complexes $[Ag(CNR)_2]Y$ (Y = NO_3^-, BF_4^-),[18] and neutral copper(I) complexes [CuCl(CNR)],[19] all with linear coordination, are also known. More recently, compounds with different coordination at the metal center – tetrahedral copper(I) complexes $[Cu(\mu\text{-}Cl)(CNR)_2]_2$[20] and trigonal-bipyramidal iron(0) complexes $[Fe(CO)_4(CNR)]$ – have been prepared.[21] A recent innovative approach to isocyanide complexes of Au, Pd, and Pt uses *p*-isocyanobenzoic acid, *p*-$CNC_6H_4CO_2H$.[16e] Neither the free isocyanide nor its metal complexes are mesogenic, but the carboxylic group can be used to hydrogen-bond a decyloxystilbazole, and the resulting complexes display enantiotropic smectic A (S_A) or nematic (N) mesophases.

The only calamitic compounds in these series that are mesogenic, while having isocyanide ligands containing only one aromatic ring, are gold and silver complexes. In the rest of the complexes the length/width ratio has to be increased by the inclusion of at least two aromatic rings in order to induce mesogenic properties. As a consequence of such enlargement, the transition temperatures and the viscosity are also raised, disfavoring the potential for practical applications of these materials. Therefore, implementation of the fluorophobic effect into these complexes may result in an improvement of the liquid-crystal properties without increasing transition temperatures and viscosity.

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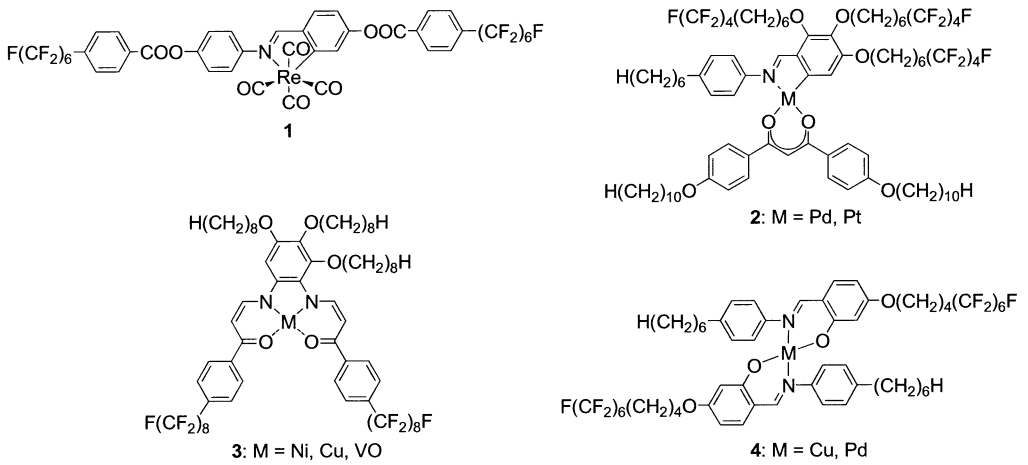


Figure 1. Representative fluorous metallomesogens.

So far, only few examples of fluorocarbon-containing metallomesogens have been described in the literature. Reported by Bruce et al., the *ortho*-metallated imine complex of rhenium(I) containing an octahedral metal center (**1**; Figure 1) exhibits reduced transition temperatures as compared to the free ligands.[22] The coordination of the octahedral metal center widens the molecule in such a way that the mesophase produced is no longer smectic but instead nematic. With the introduction of the perfluorinated segment the corresponding complex is again smectic, which constitutes another example of the strong ordering force associated with the fluorophobic effect.

The examination of fluorinated discotic *ortho*-palladated imine derivatives **2** that were synthesized by Tschierske, Bilgin-Eran et al. shows that the incorporation of the fluorinated chains leads to the replacement of nematic D (N_D) phases by columnar hexagonal (Col_h) phases over a wider temperature range.[23] Again the fluorophobic effect gives more stable and more ordered mesophases. If the *ortho*-metallated palladium(II) and platinum(II) derivatives are near the calamitic-discotic cross point, the fluorophobic effect leads to the disappearance of the cubic and three-dimensional ordered phases found between the lamellar and the columnar organizations of the hydrocarbon analogues.

Other examples of smectic and columnar mesophase stabilization in fluorinated metal complexes are the (enamino ketone)nickel(II), -copper(II) and -vanadium(II) complexes **3** reported by Szydłowska,[24] and the (salicylaldimato)copper(II) and -palladium(II) complexes (such as **4**; Figure 1) investigated by Bilgin-Eran et al.[25]

Incorporation of the fluorinated segments usually does not increase the rotational viscosity of the materials, sought to be low for potential practical applications. However, undesired effects from the presence of long perfluoroalkyl chains may include poor solubility or gelation upon introduction into a nematic host mixture.[26]

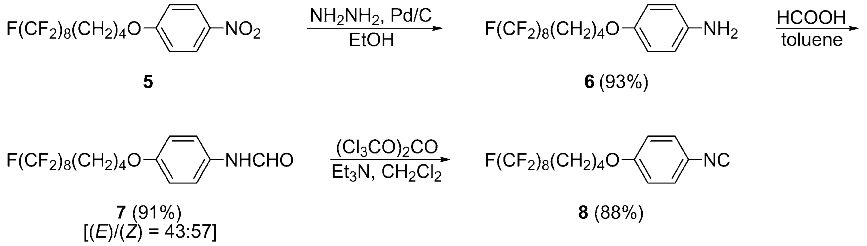
The fluorophobic effect has already been investigated for single aromatic ring-containing organic molecules.[12,13,27,28] In the case of compounds containing a perfluoroalkyl chain, it has been shown that the presence of two aromatic rings in the molecule is not required to induce mesomorphic character in the organic structures.

Results and Discussion

In order to investigate the fluorophobic effect in a variety of metal complexes of isocyanides containing only one aromatic ring, a systematic synthesis and examination of mesomorphic properties of a series of complexes of group-11, and group-10 and -8 metals was pursued. The selection included fluorous analogues of hydrocarbon complexes in which mesomorphic properties are generally not observed, as mentioned in the Introduction.

On the basis of earlier studies on organic rod-like crystals containing a single phenoxy unit,[13a,13b] it can be assumed that four ($m = 4$) will be the optimum number of methylene groups in the hydrogenated part of the molecule's alkoxy chain $O(CH_2)_m(CF_2)_nF$. Analogously, to maintain a sufficient length of the perfluoroalkyl part, the number of CF_2 units was established as eight ($n = 8$; perfluorooctyl).[13] The isocyanide ligand was synthesized starting from 1-nitro-4-[4-(perfluorooctyl)butoxy]benzene (**5**),[13b] by reduction, formylation, and dehydration reactions in sequence. As depicted in Scheme 1, reduction of nitro ether **5** with hydrazine in the presence of 5% Pd/C in ethanol gave the aniline derivative **6** in 93% yield. The aniline **6** was converted by treatment with formic acid in toluene into crude formamide **7** in almost quantitative yield by using a procedure analogous to that for its alkyl analogue.[17g] Compound **7** was subjected, without further purification, to the subsequent reaction with bis(trichloromethyl) carbonate in dichloromethane, by employing conditions similar to those described by Ugi and Meyr,[29] to yield isocyanide $CNC_6H_4[4\text{-}O(CH_2)_4(CF_2)_8F]$ (**8**) in 88% (Scheme 1).[30]

The gold(I) complex **9** was prepared by substitution of the tetrahydrothiophene (tht) in the AuCl(tht) complex with the fluorous isocyanide, as illustrated in Scheme 2. The silver complexes **10** and **11** were obtained by adding silver

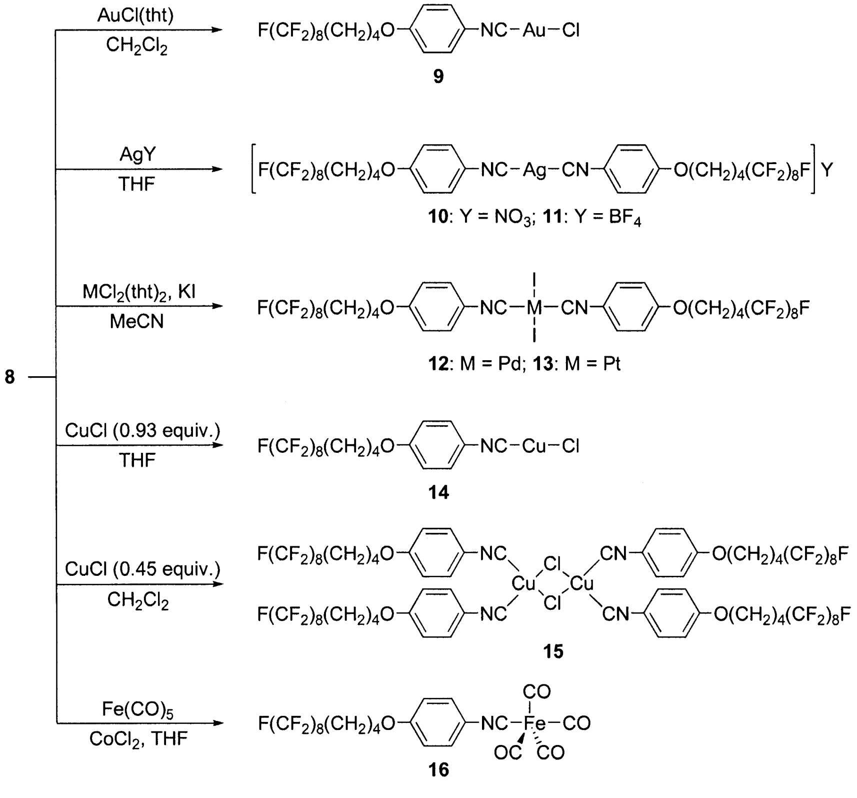


Scheme 1. Synthetic route to fluorous isocyanide **8**.

nitrate or silver tetrafluoroborate, respectively, to a THF solution of the isocyanide. Due to the photosensitivity of the silver salts, the reactions and manipulations were carried out in the dark. The diiodidopalladium(II) and -platinum(II) complexes **12** and **13** were synthesized from the corresponding dichloridobis(tetrahydrothiophene) complexes, the isocyanide **8**, and KI (excess). The appearance of only one ν(N≡C) stretching band in the IR spectrum confirms the *trans* geometry of both complexes.

The synthesis of the copper(I) complexes **14** and **15** was carried out by stirring appropriate stoichiometric amounts of the fluorous isocyanide and copper(I) chloride in dichloromethane. The tetracarbonyliron complex **16** was synthesized from the isocyanide and pentacarbonyliron in the presence of a catalytic amount of cobalt chloride (Scheme 2).

The structures of **8**–**16** were confirmed by NMR[31] and IR spectroscopy and elemental analyses. The IR spectra are all similar and show one ν(N≡C) absorption for the isocyanide group at higher wavenumbers than for the free isocyanide, as has also been reported for the hydrocarbon analogues of the isocyanide complexes. The ^{1}H NMR spectra of the complexes prepared are also alike, showing an AA′XX′ spin system for the phenyl group, again similar to those reported for their hydrocarbon analogues. Although X-ray crystallography characterization of solid complexes was sought, efforts to obtain X-ray quality crystals were only partially successful. To no surprise multiple positions for most of the outer segments of the chains were observed. Figure 2 illustrates a molecular structure of the copper complex **15** based upon poorly refined single-crystal X-ray data. The structure confirmed that the complex is not very polar overall. The packing indicates very little anisotropy as well. It should be noted that although the structure of **15** was assigned and discussed as a dimer (μ-complex) based upon earlier characterization of aryl non-fluorous copper(I)



Scheme 2. Preparation of complexes **9**–**16** (tht = tetrahydrothiophene).

isocyanide complexes, it is known that isocyanide complexes are able to adopt a variety of structural forms.[32] In the acquired crystal structure, the copper atom adopts a trigonal geometry, and the complex is monomeric.

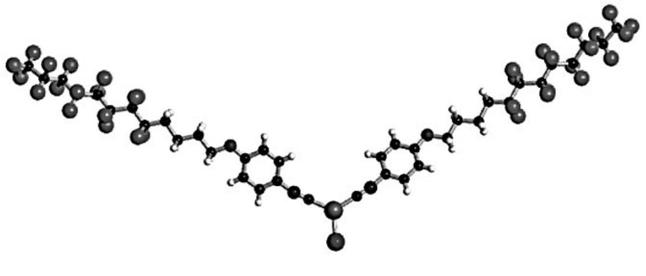


Figure 2. Molecular structure for copper complex **15**. Monoclinic, *C*2/*c*, *a*/*b*/*c* = 20.994(3)/6.1438(9)/35.104(5) Å, *β* = 93.571(2) °, *Z* = 4. Selected interatomic distances [Å]: Cu1–C1 1.895(4), Cu1–Cl1 2.2086(16). Key angles [°]: C1–Cu1–C1′ 125.1(2), C1–Cu1–Cl1 117.46(12), N1–C1–Cu1 176.2(4).

The phase-transition temperatures of the complexes were investigated by DSC and are summarized in Table 1. The ligand, perfluoroalkyl isocyanide **8**, in contrast to its alkyl analogue, exhibits liquid-crystalline properties itself upon both heating and cooling (Figure 3). Upon heating, **8** forms an S_A phase over a 2 °C range,[33] but upon cooling, the mesophase range extends over ca. 25 °C. Thus, the fluorophobic effect has allowed for the mesogenicity of an organic compound (an isocyanide in this case) with a single benzene unit.

Table 1. Optical, thermal, and thermodynamic data for isocyanide **8** and its complexes **9**–**16**.

Compound	Transition[a]	*T*[b] [°C]	Δ*H*[b] [kJ/mol]
8	C···S_A···I[33]	62	39.2[c]
9	C···C′	156	4.8
	C′···C″	173	3.7
	C″···S_A	191	25.2
	S_A···I	274	3.3
10	C···C′	88	14.1
	C′···S_A	120	30.9
	S_A···I	140[d]	
11	C···S_A	92	35.0
	S_A···I	240[d]	
12	C···S_A	56	48.8
	S_A···I	115	7.7
13	C···S_A	60	42.7
	S_A···I	92	5.4
14	C···C′	133	2.0
	C′···S_A	152	23.4
	S_A···I	233	0.8
15	C···C′	128	17.2
	C′···I	142	58.9
16	C···C′	–6	1.4
	C′···I	92	10.2

[a] C: crystal; S: smectic; 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] Combined enthalpies. [d] Optical microscopy data (dec.).

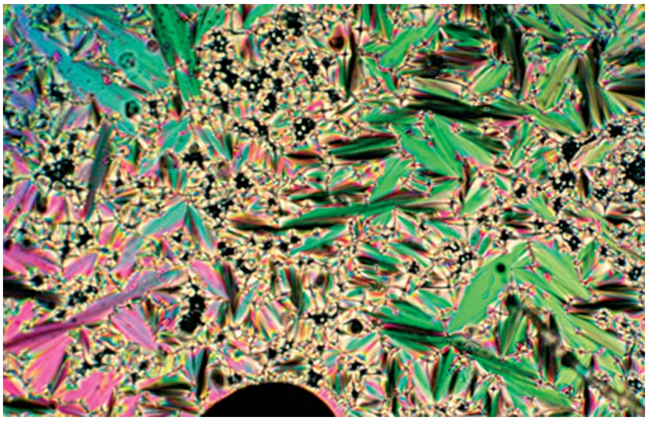


Figure 3. Polarized-light optical photomicrograph of the fan-shaped texture of the smectic A phase on cooling of **8** at 50 °C.

A similar phenomenon is observed with the silver complexes. The nitrate salt **10** forms a smectic A mesophase at 120 °C and undergoes decomposition, completed at 140 °C (observed under the microscope). The tetrafluoroborate salt **11** also forms the smectic A mesophase at 92 °C, and partially decomposes at 240 °C before reaching the clearing point, as observed under the microscope. Decomposition of hydrocarbon analogs has been previously reported;[18] however, the transition temperatures for the silver tetrafluoroborate complex increased upon fluorination, suggesting an increase of the thermal stability due to the fluorophobic effect. Another consequence of this effect is the great stabilization of the smectic A mesophase over the tilted smectic phases. In this way, the smectic C mesophase present in the silver hydrocarbon complexes was not observed for either the nitrate **10** or the tetrafluoroborate **11** fluorinated silver salts.

The planar palladium and platinum complexes **12** and **13** also show mesogenic behavior. The palladium complex melts to a smectic A mesophase at 56 °C, and becomes an isotropic liquid at 115 °C. The analogous platinum complex has a melting point of 60 °C and clearing point of 92 °C. Thus, replacement of palladium by platinum not only does not influence the mesophase type, but also has a mesophase-destabilizing effect, as opposed to observations for phenylpyridine hydrocarbon complexes.[34] The corresponding hydrocarbon analogues show no mesogenic behavior. According to Takahashi et al.,[16a,16b] a more rigid system of two aryl rings in each isocyanide is needed for mesophase formation for palladium(II) and platinum(II) hydrocarbon complexes.

The rod-like mononuclear copper complex **14** shows mesogenic behavior (smectic A phase) in the range between 152 °C (melting point) and 233 °C (clearing point), while the hydrogenated analog is not a liquid crystal. However, complex **15** with different coordination around the copper(I) center is not a mesogen and melts directly into an isotropic liquid at 142 °C. The fluorophobic effect is also not strong enough to introduce mesogenity into the iron complex **16**. Neither the hydrogenated nor the fluorinated iron complexes are liquid crystals. It can be assumed that close packing of the molecules is not achieved by the steri-

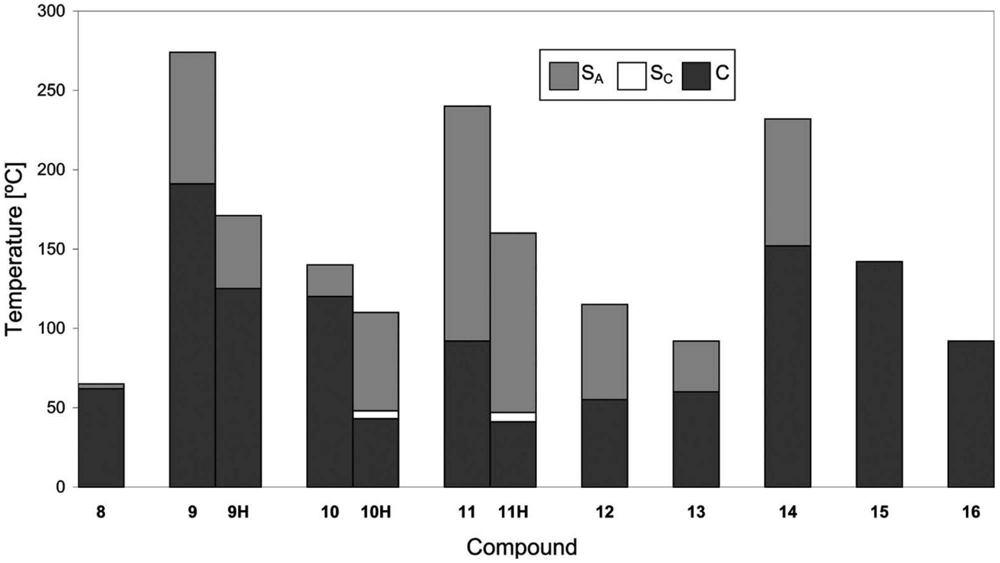


Figure 4. Graphical comparison of phase-transition temperatures for ligand **8**, complexes **9**–**16**, and their hydrocarbon analogues (labeled with suffix **H**).

cally bulky trigonal-bipyramidal carbonyliron group; thus, intermolecular interactions and, accordingly, melting points are reduced.

The mesogenic properties of the complexes, compared with the analogous hydrocarbon compounds, are summarized in Figure 4. The differences between compounds with hydrocarbon and fluorinated chains are clearly apparent when comparing the gold complexes. Both compounds present an S_A mesophase, but the melting and the clearing temperatures are higher in the fluorinated compound. Furthermore, the increase in the clearing point is larger than the increase in the melting point, resulting in a larger mesophase temperature range for the fluorous compound.

Conclusion

In this work we have presented systematic studies of the fluorophobic effect on the liquid-crystalline properties of novel fluorous complexes. We have synthesized a series of fluorous isocyanide organometallics and confirmed that introduction of a fluorous ponytail into non-liquid-crystalline complexes containing a single aromatic ring confers mesomorphic behavior. The fluorous-compound mesophases are stable over a wider temperature range and exhibit higher transition temperatures.

Experimental Section

General: NMR spectra were obtained with Bruker Avance 200 (^{1}H: 200 MHz; ^{13}C: 50 MHz) and ARX 300 (^{1}H: 300 MHz) spectrometers. IR spectra (KBr cell, dichloromethane) were recorded with Bio Rad FTS-175C and Perkin–Elmer FT 1720X spectrometers. Elemental analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Polarized-light microscopy studies were carried out with a Leica DMRB microscope at a heating rate of 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 gas was dry nitrogen. The temperatures correspond to the onset of a transition or to the peak temperatures when the transition is very broad. Dimethylformamide (DMF) and dichloromethane were distilled from calcium hydride, and DMF was degassed (freeze and thaw) three times prior to use; THF was distilled from sodium/benzophenone; toluene was distilled from sodium. Copper(I) chloride (99%; Aldrich), pentacarbonyliron(0) (99%; Strem), silver tetrafluoroborate (99%; Alfa Aesar), silver nitrate (≥ 99.0%; Spectrum), bis(trichloromethyl) carbonate (triphosgene) (TCI), and other materials were used as received. Literature methods were used to prepare 1-bromo-4-(perfluorooctyl)butane,[13a] [AuCl(tht)],[35] [PdCl$_2$(tht)$_2$], and [PtCl$_2$(tht)$_2$][36] (tht = tetrahydrothiophene).

4-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)oxy]-1-nitrobenzene (5):[13b] A round-bottom flask fitted with a reflux condenser was charged with 4-nitrophenol (0.940 g, 6.76 mmol), 1-bromo-4-(perfluorooctyl)butane (3.780 g, 6.810 mmol), K_2CO_3 (2.910 g, 21.05 mmol), and DMF (50 mL). The mixture was refluxed for 8 h and then allowed to reach room temperature. Chilled water (150 mL) was added, and the mixture was acidified with concentrated HCl (5 mL). The brown solid was filtered off. Silica gel column chromatography (dichloromethane) gave a fraction from which the solvent was removed by rotary evaporation to give **5** as a yellow solid (3.360 g, 5.479 mmol, 81%). ^{1}H NMR (CDCl$_3$): δ = 8.22 (d, J = 9.2 Hz, 2 H, *ortho* to NO$_2$), 6.95 (d, J = 9.2 Hz, 2 H, *meta* to NO$_2$), 4.10 (t, J = 5.6 Hz, 2 H, CH_2O), 2.3–2.1 (m, 2 H, CH_2CF$_2$), 2.1–1.8 [m, 4 H, (CH_2)$_2$CH$_2$O] ppm.

4-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)oxy]aniline (6): A round-bottom flask equipped with reflux condenser was charged with **5** (3.506 g, 5.717 mmol), 10% palladium on activated carbon (3.09 g, 2.90 mmol Pd), hydrazine monohydrate (3.8 mL, 74 mmol), and ethanol (120 mL). The mixture was refluxed for 24 h. The mixture was allowed to reach ambient temperature, and the solid was filtered off. The solvent was removed from the filtrate by rotary evaporation (water pump) to give **6** as an off-white solid (3.101 g, 5.479 mmol, 93%). ^{1}H NMR (CDCl$_3$): δ = 6.74 (d, J = 8.8 Hz, 2 H, *meta* to NH$_2$), 6.64 (d, J = 8.8 Hz, 2

H, *ortho* to NH_2), 3.92 (t, J = 5.6 Hz, 2 H, C*H*$_2$O), 3.42 (br. s, 2 H, N*H*$_2$), 2.35–1.95 (m, 2 H, C*H*$_2$CF$_2$), 1.95–1.65 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm.

***N*-{4-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)oxy]phenyl}formamide (7):** A round-bottom flask (100 mL), equipped with Dean–Stark apparatus and reflux condenser, was charged with **6** (0.452 g, 0.775 mmol), formic acid (98%; 3.75 mL), and toluene (25 mL). The solution was refluxed for 2 h and cooled to ambient temperature. The solvent was removed by rotary evaporator (water pump) and the residue recrystallized from hexane/toluene (2:1, v/v; ca. 20 mL) to give **7** (0.428 g, 0.702 mmol, 91%) as a mixture of (*E*)/(*Z*) isomers in a 43:57 ratio.[37] ^{1}H NMR (CDCl$_3$): δ = 8.51 [d, J = 11.5 Hz, 1 H, *H*CONH, (*E*) isomer], 8.35 [d, J = 1.0 Hz, 1 H, *H*CONH, (*Z*) isomer], 7.45 [d, J = 8.8 Hz, 2 H, *ortho* to NHCHO, (*Z*) isomer], 7.39 [s, 1 H, N*H*CHO, (*E*) isomer], 7.33 [s, 1 H, N*H*CHO, (*Z*) isomer], 7.03 [d, J = 9.0 Hz, 2 H, *ortho* to NHCHO, (*E*) isomer], 6.90 [d, J = 9.0 Hz, 2 H, *meta* to NHCHO, (*E*) isomer], 6.86 [d, J = 8.8 Hz, 2 H, *meta* to NHCHO, (*Z*) isomer], 4.00 (t, J = 5.6 Hz, 2 H, C*H*$_2$O), 2.27–2.08 (m, 2 H, C*H*$_2$CF$_2$), 2.08–1.76 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm. ^{13}C NMR: δ = 162.9 [NH*C*HO, (*E*) isomer], 158.9 [NH*C*HO, (*Z*) isomer], 157.1 [*para* to NHCHO, (*E*) isomer], 156.2 [*para* to NHCHO, (*Z*) isomer], 130.1 [*ipso* to NHCHO, (*Z*) isomer], 129.6 [*ipso* to NHCHO, (*E*) isomer], 122.1 [*meta* to NHCHO, (*E*) isomer], 122.0 [*meta* to NHCHO, (*Z*) isomer], 115.7 [*ortho* to NHCHO, (*E*) isomer], 115.1 [*ortho* to NHCHO, (*Z*) isomer], 67.8 [CH$_2$O, (*E*) isomer], 67.7 [CH$_2$O, (*Z*) isomer], 30.9 (t, J = 21.0 Hz, *C*H$_2$CF$_2$, both isomers), 28.9 (*C*H$_2$CH$_2$O, both isomers), 17.5 (*C*H$_2$CH$_2$CF$_2$, both isomers) ppm.[38]

4-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)oxy]phenyl Isocyanide (8): A round-bottom flask was charged with **7** (1.324 g, 2.166 mmol), triethylamine (0.75 mL, 4.5 mmol), and dichloromethane (100 mL). Bis(trichloromethyl) carbonate (0.207 g, 0.782 mmol) was added, followed by an additional portion (0.040 g, 0.15 mmol) after 0.5 h. The stirring was continued under nitrogen for 0.5 h. The solvent was removed by rotary evaporation. Toluene/hexane (1:1, v/v; 50 mL) was added, and the precipitate was filtered off. The filtrate was concentrated by rotary evaporation to give a solid residue. Silica gel column chromatography (dichloromethane/hexanes, 3:2) gave a fraction from which the solvent was removed by rotary evaporation to give **8** as a yellow solid (1.130 g, 1.905 mmol, 88%). $C_{19}H_{12}F_{17}NO$ (593.28): calcd. C 38.46, H 2.04, N 2.36; found C 38.84, H 2.16, N 2.31. IR: $\tilde{\nu}$ = 2127 [ν(N≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.32 (d, J = 8.9 Hz, 2 H, *ortho* to NC), 6.87 (d, J = 8.9 Hz, 2 H, *meta* to NC), 4.01 (t, J = 5.6 Hz, 2 H, C*H*$_2$O), 2.30–2.05 (m, 2 H, C*H*$_2$CF$_2$), 2.05–1.82 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm. ^{13}C NMR: δ = 160.0 (CN), 162.7, 128.3, 119.3, 115.4 (C$_6$H$_4$), 67.9 (CH$_2$O), 30.9 (t, J = 22.3 Hz, *C*H$_2$CF$_2$), 28.7 (*C*H$_2$CH$_2$O), 17.5 (*C*H$_2$CH$_2$CF$_2$) ppm.

AuCl(CNAr) [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (9): A round-bottom flask was charged with [AuCl(tht)] (0.054 g, 0.17 mmol) and dichloromethane (15 mL). A solution of **8** (0.100 g, 0.169 mmol) in dichloromethane (10 mL) was added dropwise, and the solution was stirred for 5 min, during which time a white solid precipitated. Hexane (10 mL) was added to the mixture to complete the precipitation, and the solid was filtered off. Recrystallization (dichloromethane/hexane) gave **9** as white crystals (0.110 g, 0.133 mmol, 79%). $C_{19}H_{12}AuClF_{17}NO$ (825.7): calcd. C 27.64, H 1.46, N 1.70; found C 28.49, H 1.44, N 1.85. IR: $\tilde{\nu}$ = 2227 [ν(N≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.45 (d, J = 9.0 Hz, 2 H, *ortho* to NC), 6.95 (d, J = 9.0 Hz, 2 H, *meta* to NC), 4.09 (t, J = 5.5 Hz, 2 H, C*H*$_2$O), 2.40–2.05 (m, 2 H, C*H*$_2$CF$_2$), 2.0–1.7 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm.

Ag(CNAr)$_2$NO$_3$ [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (10): A round-bottom flask was charged with silver nitrate (0.050 g, 0.29 mmol) and THF (30 mL). A solution of **8** (0.368 g, 0.620 mmol) in THF (10 mL) was added, and the solution was stirred in the absence of light under nitrogen for 4 h. Diethyl ether (10 mL) was added, and the precipitate formed during the reaction was filtered off and dried in vacuo (oil pump) over P$_2$O$_5$ for 16 h to give **10** as a white solid (0.363 g, 0.268 mmol, 91%). $C_{38}H_{24}AgF_{34}N_3O_5$ (1356.43): calcd. C 33.65, H 1.78, N 3.10; found C 33.48, H 1.82, N 3.02. IR: $\tilde{\nu}$ = 2184 [ν(N≡C)] cm^{-1}.[31]

Ag(CNAr)$_2$BF$_4$ [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (11): A round-bottom flask was charged with silver tetrafluoroborate (0.058 g, 0.30 mmol) and THF (30 mL). A solution of **8** (0.365 g, 0.615 mmol) in THF (10 mL) was added, and the solution was stirred in the absence of light under nitrogen for 4 h. Diethyl ether (10 mL) was added. The precipitate (formed in part during the reaction) was filtered off and dried in vacuo (oil pump) over P$_2$O$_5$ for 16 h to give **11** as a white solid (0.260 g, 0.188 mmol, 63%). $C_{38}H_{24}AgBF_{38}N_2O_2$ (1381.23): calcd. C 33.04, H 1.75, N 2.03; found C 33.31, H 1.90, N 1.99. IR: $\tilde{\nu}$ = 2203 [ν(N≡C)] cm^{-1}.[31]

***trans*-[PdI$_2$(CNAr)$_2$] [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (12):** A round-bottom flask was charged with [PdCl$_2$(tht)$_2$] (0.030 g, 0.085 mmol) and acetonitrile (20 mL). A solution of **8** (0.100 g, 0.169 mmol) in acetonitrile (10 mL) was added dropwise and the solution stirred for 2 h. The solvent was removed under vacuum, and the resulting residue was washed with hexane (3 × 10 mL) and dissolved in acetonitrile (20 mL). KI was added (0.060 g, 0.36 mmol), and the mixture was refluxed for 12 h. The mixture was allowed to reach room temperature, and the solvent was removed in vacuo. The residue was extracted with dichloromethane (3 × 30 mL), and the solvent was removed by rotary evaporation to give **12** as a brown solid (0.085 g, 0.050 mmol, 59%). $C_{38}H_{24}F_{34}I_2N_2O_2Pd$ (1546.78): calcd. C 29.51, H 1.56, N 1.81; found C 30.06, H 1.72, N 1.92. IR: $\tilde{\nu}$ = 2211 [ν(N≡C)] cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 8.23 (d, J = 9.0 Hz, 2 H, *ortho* to NC), 7.16 (d, J = 9.0 Hz, 2 H, *meta* to NC), 4.30 (t, J = 5.4 Hz, 2 H, C*H*$_2$O), 2.5–2.2 (m, 2 H, C*H*$_2$CF$_2$), 2.2–1.8 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm.

***trans*-[PtI$_2$(CNAr)$_2$] [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (13):** A round-bottom flask was charged with [PtCl$_2$(tht)$_2$] (0.037 g, 0.084 mmol) and acetonitrile (20 mL). A solution of **8** (0.100 g, 0.169 mmol) in acetonitrile (10 mL) was added dropwise and the solution stirred for 2 h. The solvent was removed under vacuum, and the resulting residue was washed with hexane (3 × 10 mL) and dissolved in acetonitrile (20 mL). KI was added (0.060 g, 0.36 mmol), and the mixture was refluxed for 12 h. The mixture was allowed to reach room temperature, and the solvent was removed in vacuo. The residue was extracted with dichloromethane (3 × 30 mL), and the solvent was removed by rotary evaporation to give **13** as an orange solid (0.057 g, 0.035 mmol, 42%). $C_{38}H_{24}F_{34}I_2N_2O_2Pt$ (1635.44): calcd. C 27.91, H 1.48, N 1.71; found C 28.57, H 1.56, N 1.82. IR: $\tilde{\nu}$ = 2206 [ν(N≡C)] cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 8.21 (d, J = 9.0 Hz, 2 H, *ortho* to NC), 7.10 (d, J = 9.0 Hz, 2 H, *meta* to NC), 4.25 (t, J = 6.1 Hz, 2 H, C*H*$_2$O), 2.5–2.3 (m, 2 H, C*H*$_2$CF$_2$), 2.1–1.8 [m, 4 H, (C*H*$_2$)$_2$CH$_2$O] ppm.

CuCl(CNAr) [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (14): A round-bottom flask was charged with copper(I) chloride (0.050 g, 0.51 mmol) and THF (25 mL). A solution of **8** (0.326 g, 0.549 mmol) in THF (15 mL) was added dropwise over 0.5 h, and the solution was stirred under nitrogen for 1.5 h. Hexane (10 mL) was added to the mixture, and the precipitate formed during the reaction was filtered off and dried in vacuo (oil pump) to give **14** as a white solid (0.293 g, 0.423 mmol, 84%). $C_{19}H_{12}ClCuF_{17}NO$ (692.28): calcd. C

32.96, H 1.75, N 2.02; found C 32.56, H 1.82, N 1.92. IR: $\tilde{\nu}$ = 2156 [ν(N≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.40 (d, J = 9.0 Hz, 2 H, *ortho* to NC), 6.90 (d, J = 9.0 Hz, 2 H, *meta* to NC), 4.03 (t, J = 5.4 Hz, 2 H, CH_2O), 2.35–2.05 (m, 2 H, CH_2CF$_2$), 2.05–1.75 [m, 4 H, (CH_2)$_2$CH$_2$O] ppm. ^{13}C NMR: δ = 159.3 (CN), 128.0, 121.9, 115.2 (C$_6$H$_4$), 67.8 (CH$_2$O), 30.8 (t, J = 22.3 Hz, CH$_2$CF$_2$), 28.7 (CH$_2$CH$_2$O), 17.4 (CH$_2$CH$_2$CF$_2$) ppm.

[CuCl(CNAr)$_2$]$_2$ [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (15): A round-bottom flask was charged with CuCl (0.052 g, 0.53 mmol) and dichloromethane (30 mL). A solution of **8** (0.696 g, 1.17 mmol) in dichloromethane (10 mL) was added, and the suspension was stirred under nitrogen for 6 h. The formed precipitate was filtered off and dried in vacuo (oil pump) for 16 h to give **15** as an off-white solid (0.381 g, 0.148 mmol, 56%). $C_{76}H_{48}Cl_2Cu_2F_{68}N_4O_4$ (2571.11): calcd. C 35.50, H 1.88, N 2.18; found C 34.75, H 1.95, N 2.18. IR: $\tilde{\nu}$ = 2155 [ν(N≡C)] cm^{-1}. ^{1}H NMR ([D$_8$]toluene): δ = 6.77 (d, J = 8.6 Hz, 8 H, *ortho* to NC), 6.38 (d, J = 8.6 Hz, 8 H, *meta* to NC), 3.41 (t, J = 5.6 Hz, 8 H, CH_2O), 2.0–1.6 (m, 8 H, CH_2CF$_2$), 1.6–1.3 [m, 16 H, (CH_2)$_2$CH$_2$O] ppm.

Fe(CO)$_4$CNAr [Ar = 4-F(CF$_2$)$_8$(CH$_2$)$_4$OC$_6$H$_4$] (16): A round-bottom flask was charged with cobalt chloride hexahydrate (0.013 g, 0.055 mmol), THF (20 mL), and pentacarbonyliron (0.10 mL, 0.76 mmol). The mixture was brought to reflux, and a solution of **8** (0.297 g, 0.501 mmol) in THF (3 mL) was added. The solution changed its color from blue to green and gradually to brown over ca. 45 min. The rusty-colored precipitate was filtered off on a silica gel pad; the filtrate was concentrated by rotary evaporator and the residue crystallized from hexanes/dichloromethane (1:1, v/v). The solid was filtered off to give Fe(CO)$_3$(CNAr)$_2$ as a yellowish solid (0.064 g, 0.048 mmol, 10%).[39] The filtrate was concentrated by rotary evaporation and recrystallized from hexane to give **16** as a yellow solid (0.155 g, 0.204 mmol, 41%). $C_{23}H_{12}F_{17}FeNO_5$ (761.16): calcd. C 36.29, H 1.59, N 1.84; found C 36.05, H 1.45, N 1.82. IR: $\tilde{\nu}$ = 2167 [ν(N≡C)]; 2056, 1993, 1965 [ν(C=O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.31 (d, J = 8.8 Hz, 2 H, *ortho* to NC), 6.91 (d, J = 8.8 Hz, 2 H, *meta* to NC), 4.03 (t, J = 5.4 Hz, 2 H, CH_2O), 2.40–2.05 (m, 2 H, CH_2CF$_2$), 2.05–1.85 [m, 4 H, (CH_2)$_2$CH$_2$O] ppm.

Supporting Information (see footnote on the first page of this article): CIF file for compound **15** (thermal and rotational motion at the end of the fluorous ponytail cause that refinement was accomplished with a poor R factor; thus, we did not deposit our crystal structure data with the CCDC since it is of poor quality and contains multiple positions of fluorine atoms in addition to large ellipsoids).

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[38] The assignment of the aromatic signals was based on the spectroscopic data of formamides in ref.[17g]

[39] The formation of bis(isocyanide) complex $\mathrm{Fe(CO)_3(CNAr)_2}$ [$\mathrm{Ar = 4\text{-}F(CF_2)_8(CH_2)_4OC_6H_4}$] as a side product was observed; it was isolated and characterized. $\mathrm{C_{41}H_{24}F_{34}FeN_2O_5}$ (1326.43): calcd. C 37.13, H 1.82, N 2.11; found C 36.65, H 1.94, N 1.83. IR: $\tilde{\nu}$ = 2114 [ν(N≡C)]; 1999, 1932 [ν(C=O)] cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 7.27 (d, *J* = 8.8 Hz, 2 H, *ortho* to NC), 6.87 (d, *J* = 8.8 Hz, 2 H, *meta* to NC), 4.02 (t, *J* = 5.4 Hz, 2 H, $\mathrm{OC}H_2$), 2.40–2.05 (m, 2 H, $\mathrm{C}H_2\mathrm{CF_2}$), 2.05–1.85 [m, 4 H, $(\mathrm{C}H_2)_2\mathrm{CH_2CF_2}$] ppm.

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