Mesogenic Palladium Complexes with Pincer Ligands Derived from Dipicolinic Acid†

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4-Substituted pyridine-2,6-dicarboxylic acids, (E)-dipicH_2, and 4-substituted pyridine-2,6-bis(thiocarboxylic) acids, (E)-pdtcH_2, (E = OC_nH_{2n+1}, SC_nH_{2n+1}) have been synthesized and used as O,N,O- and S,N,S-pincer ligands with palladium. In the fourth coordination site the complexes bear 4-decyloxy-4′-stilbazole (L^1), 4-decyloxy-*N*-(4-pyridylmethylene)anilines (L^2), decyl 4-pyridinecarboxylate (L^3), 4-(4′-decyloxyphenyl)pyridinecarboxylate (L^4), 4-(3′,4′,5′-tridecyloxybenzyl)pyridinecarboxylate (L^5), 4-isocyano-1-decyloxybenzene (L^6), or 4-isocyano-4′-decyloxybiphenyl (L^7). Thermotropic mesomorphism is observed for the (E)-dipic complexes with L^5 and n = 12, which display columnar phases. The complexes with S,N,S-pincers show an important depression in the melting point compared to their O,N,O homologues and this change gives rise to mesomorphic materials (S_C). However, in the case of L^5 the mesomorphic behavior observed for the O,N,O derivative is lost in its S,N,S analogue. The alkylsulfanyl compounds exhibit lower transition temperatures and wider mesophase ranges than their alkoxy analogues.

Introduction

The field of metallomesogens (liquid crystals based on metal-containing molecules) is growing quite fast because of interest in exploring the new structural possibilities that metals offer, and the consequences of their presence on the properties of the material.[1] Some types of ligands, salicylaldimines[2] or imines[1e] for example, have been systematically explored but there are still many other interesting systems and metals that have not been used for liquid crystal systems and that can give new physical properties or permit a better control of the desired properties. Therefore, it is of interest to design and prepare novel structures to add to the still-limited types of metallomesogenic materials.

The use of ligands making strong bonds to the metal helps to produce reasonably inert and thermally robust materials, and chelating ligands are particularly suited for this purpose. Moreover, for calamitic materials it is convenient to look for molecules which are anisotropic in shape but which will pack easily to fill the space efficiently, which possess a high anisotropy of polarizability, and, in most cases, which possess a permanent dipole.

A way to prevent intermolecular interactions that are too strong, which are responsible for the undesired high melting points often found in metal-based molecules, is to incorporate some asymmetry in the molecular shape, together with long alkyl or alkyloxy tails.[3] On the other hand, attempts to produce complexes with a net dipolar moment of the type *trans*-[PdX_2LL′] usually lead to symmetrization to a mixture of *trans*-[PdX_2L_2] and *trans*-[$PdX_2L'_2$] and this is difficult to avoid when using monodentate ligands. With these ideas in mind we have designed a new structural type of metal-containing liquid crystals based on the dipicolinic acid and its derivatives.

Although many different bidentate chelating moieties have been successfully used for the design of metallomesogens, there are only a few examples of tridentate binding units, namely: (a) an example of lyotropic mesophase with Ru(II) coordinated to terminal 4′-substituted terpyridine derivatives;[4] (b) the C,N,N chelating ligand 6′-phenyl-2,2′-bipyridine cyclometalated to Pd(II), which displays a monotropic nematic phase;[5] and (c) some examples exhibiting discotic mesomorphism (dinuclear copper(II) complexes derived from tridentate 1,3,5-triketonate ligands;[6] mononuclear Ni(II), Cr(0), Mo(0), and W(0) with the tridentate ligand 1,4,7-triazacyclononane;[7] and (pyridinediyl-2,6-dimethanolato)dioxomolybdenum complexes).[8]

We have previously reported on palladium complexes containing the dipicolinate anion[9] and its sulfur analogue, 2,6-bis-(thiocarboxylate),[10] on which we explored the coordination

† Dedicated to Professor J. Barluenga on the occasion of his 60th birthday.

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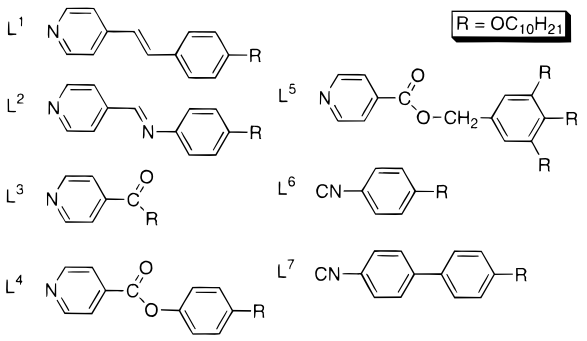
Chart 1



behavior on Pd with regard to their possible functionalization to produce metallomesogens. These compounds showed high thermal stability and usually displayed a rigid tridentate coordination ("pincer" ligands). The coordination of a long-tail ligand in the fourth coordination site was not sufficient to induce mesogenic properties in the material. To obtain liquid crystals based on this chemical system it seemed to us a reasonable strategy to further elaborate the pyridinic ring of the dipic or pdtc ligands, or to incorporate additional benzene rings in the ligands coordinated in the fourth position. In this paper we report the preparation and thermal behavior of uncommon mesogens containing these modified pincer ligands with palladium and 4-decyloxy-4′-stilbazole (L^1), 4-decyloxy-*N*-(4-pyridylmethylene)anilines (L^2), decyl 4-pyridinecarboxylate (L^3), 4-(4′-decyloxyphenyl)pyridinecarboxylate (L^4), 4-(3′,4′,5′-tridecyloxybenzyl)pyridinecarboxylate (L^5), 4-isocyano-1-decyloxybenzene (L^6), or 4-isocyano-4′-decyloxybiphenyl (L^7) occupying the fourth coordination position (see Chart 1).

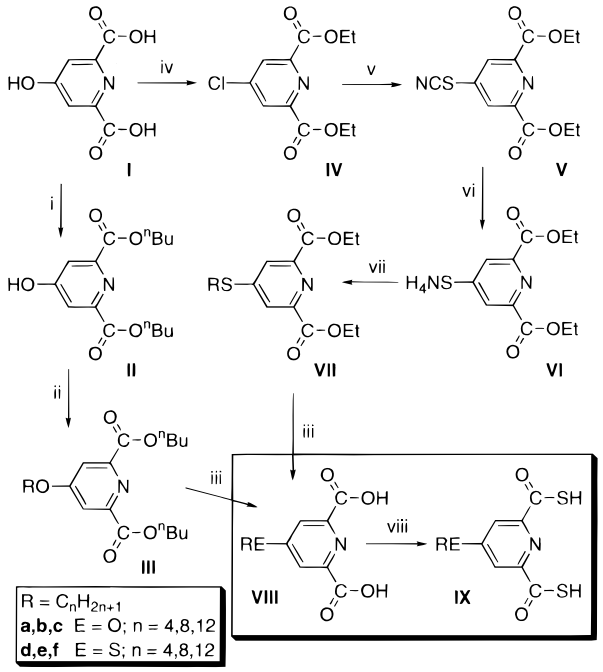
Results and Discussion

Synthesis, Characterization, and Mesogenic Behavior of 4-Alkoxypyridine-2,6-dicarboxylic Acids, 4-Alkylsulfanylpyridine-2,6-dicarboxylic Acids, and Their Metal Complexes. The synthetic steps used to prepare the 4-substituted dipicolinic acids are summarized in Scheme 1. Chelidamic acid (**I**) was esterified with butanol to yield dibutyl 4-hydroxypyridine-2,6-dicarboxylate (**II**). Treatment with $C_nH_{2n+1}Br$ in the presence of K_2CO_3, in anhydrous dimethylformamide (DMF), generated the dibutyl 4-alkoxypyridine-2,6-dicarboxylate (**III**). The sulfur analogues, diethyl 4-alkylsulfanylpyridine-2,6-dicarboxylates (**VII**), were obtained following a procedure described by Markees.[11] Upon hydrolyses of these esters, the corresponding 4-substituted pyridine-2,6-dicarboxylic acids (**VIII**), ((E)-dipicH_2, where E = OC_nH_{2n+1}, SC_nH_{2n+1}), were obtained.

The acids were coordinated to palladium by reaction with $[Pd(AcO)_2]_3$ in acetonitrile to give **1** (Scheme 2), as reported previously by us for [Pd(dipic)($NCCH_3$)].[9] The compounds gave satisfactory C, H, and N analyses and their IR spectra were consistent with the proposed structure. The ^{1}H NMR spectra of the acetonitrile complexes **1** in $CDCl_3$ solution reveal the coexistence in solution of the dimeric and monomeric isomers shown in Scheme 2, in a ratio ca. 45:55, respectively, at 293 K.

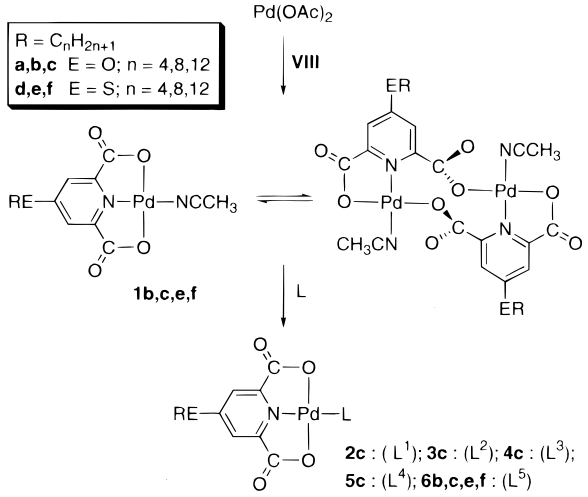
4-Substituted pyridine ligands L (L^1−L^5) easily displace the weakly coordinated acetonitrile (Scheme 2) to give the corresponding monomeric complexes **2**−**6**. Their ^{1}H NMR spectra in $CDCl_3$ show only the resonances expected for the monomolecular structure. However, the reaction with isocyanides (L^6 and L^7) produced mixtures of complexes which could not be isolated. The reason for the instability of the isocyanide complexes is discussed later.

Scheme 1[a]



[a] Reagents and conditions: i, BuOH, sulfuric acid, toluene, reflux; ii, $C_nH_{2n+1}Br$, K_2CO_3, DMF, 65 °C; iii, for derivatives **a**, **b**, **d**, **e**, KOH, EtOH; HCl; for **c**, **f**, HBr, $(Bu_4N)Br$; iv, PCl_5, CCl_4, reflux; EtOH; v, NH_4SCN, acetic acid, H_2O, reflux; vi, $(H_4N)_2S$, EtOH, reflux; vii, $C_nH_{2n+1}Br$, DMF; viii, $SOCl_2$, reflux; H_2S, Py, THF; HCl.

Scheme 2



The mesogenic behavior of **2**−**6** is summarized in Table 1 and in Figure 1. The free acids and their related Pd(II) complexes with acetonitrile (**1**), decyloxystilbazole (**2c**), (pyridylmethylene)aniline (**3c**), decyl pyridinecarboxylate (**4c**), and phenyl pyridinecarboxylate (**5c**) are high-melting solids which, with the exception of **4c**, decompose before melting.

The use of L^5, containing three alkoxy chains, noticeably lowered the melting points of the complexes, but complexes **6b** and **6e** still were not mesomorphic. However, when the length of the alkyl chain in the pyridine ring of the (E)-dipic ligand was increased from $n = 8$ to $n = 12$, the complexes (**6c** and **6f**) displayed mesomorphism. Their fluidity and optical textures determined by polarized optical microscopy, on cooling from the isotropic phase, show birefringent areas in the form

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Table 1. Optical, Thermal, and Thermodynamic Data for Compounds **2**−**14**

compound	transition[a]	temp. (°C)	ΔH (kJ mol^{-1})
2c	C − I[b]	256[c]	
3c	C − I[b]	254[c]	
4c	C − I	181.5	38.4
5c	C − I[b]	192.6	
6b	C − I	117.5	45.6
6c	C − Col_h	89.2	8.9
	Col_h − I	110.1	4.9
6e	C − I	119.2	36.1
6f	C − Col_h	73.2	8.2
	Col_h − I	113.0	5.1
8a	C − S_C	251.7	44.6
	S_C − I[b]	268.2	6.5
8b	C − C′	169.7	9.8
	C′ − S_C	241.5	33.7
	S_C − I[b]	261.4[d]	4.5
8c	C − C′	118.9	34.5
	C′ − S_C	230.7	33.0
	S_C − I[b]	259.5	5.6
8e	C − C′	147.7	10.0
	C′ − S_C	191.4	26.8
	S_C − I	261.2	10.1
9a	C − C′	88.2	15.6
	C′ − C″	183.5	2.6
	C″ − I	219.2	33.3
	I − S_C[e]	208.3	20.4[f]
	S_C − C	207.6	
9b	C − C′	87.8	20.8
	C′ − I	213.9[d]	25.5
	I − S_C[e]	210.7	21.9[f]
	S_C − C	207[c]	
9c	C − C′	71.6	21.9
	C′ − C″	125.9	2.4
	C″ − I	217.5[d]	26.3
	I − S_C[e]	216.1[d]	1.1
	S_C − C	212.4	14.4
9e	C − C′	88.0	18.6
	C′ − C"	111.1	4.9
	C" − S_C	192.2	17.2
	S_C − I	209.5[d]	2.7
10c	C − I	166.0	43.5
11c	C − I	215.9	53.7
12c	C − I	55.8	13.9
13c	C − I	181.4	35.3
14a	C − N	202.2	31.5
	N − I	233.6[d]	2.3
	I − N	232.9	2.6
	N − S_C[e]	202.2	0.9
	S_C − C	198.6	29.7
14b	C − C′	126.7	7.8
	C′ − C″	179.6	21.8
	C″ − S_C	183.8	2.4
	S_C − I	226.4	9.6
14c	C − C′	63.5	13.2
	C′ − S_C	181.9	21.3
	S_C − I	229.3	10.6
14d	C − C′	84.2	4.7
	C′ − S_C	157.2	32.1
	S_C − N	173.6	0.4
	N − I	211.3	1.6
14e	C − S_C	150.2	30.5
	S_C − I	201.8	7.8
14f	C − S_C	139.2	24.3
	S_C − I	208.7	10.6

[a] C, crystal; S_C, smectic C; I, isotropic liquid; N, nematic; Col_h, columnar hexagonal. [b] Transition with decomposition. [c] Observed by means of polarized-light microscopy. [d] Peak temperature. [e] Monotropic transition. [f] Combined enthalpies.

of "petals" coalescing to produce broken-shaped units and dark areas of uniform extinction, characteristic of a columnar phase (apparently hexagonal, Figure 2).[12] This is not unexpected because complexes **6**, bearing four long chains, can no longer be considered rodlike.

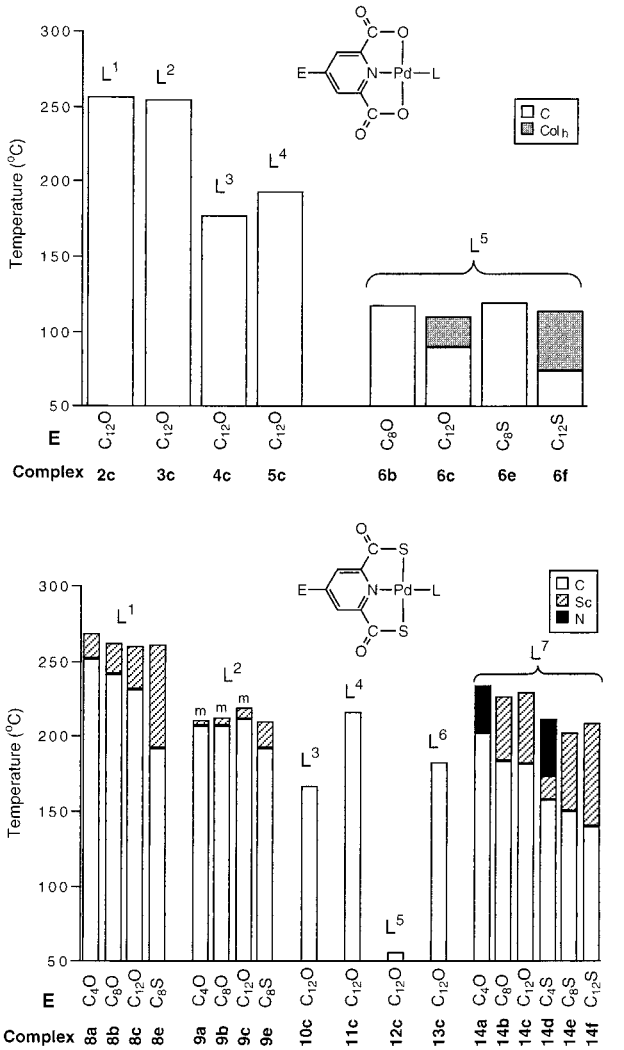

Figure 1. Thermotropic behavior of Pd complexes with O,N,O- and S,N,S-pincers and the ligands L in the fourth coordination site. C, crystal; S_C, smectic C; N, nematic; Col_h, columnar hexagonal; m, monotropic transition.

It is interesting to note that the substitution of E = OC_nH_{2n+1} for E = SC_nH_{2n+1} does not produce a noticeable effect for C_8 (complexes **6b** and **6e**), but induces a clear decrease in the melting temperature and range of mesophase for the longer C_{12} chain (compounds **6c** and **6f**). This is in agreement with the effect noticed for some organic alkoxy- and alkylsulfanyl-substituted biphenyls with terminal isocyanato substituents.[13]

Synthesis, Characterization, and Mesogenic Behavior of the 4-Substituted pyridine-2,6-bis(thiocarboxylic) Acids andTheir Metal Complexes. The new 4-substituted pyridine-2,6-bis(thiocarboxylic) acids, (E)-pdtcH_2 (**IX**) (E = OC_nH_{2n+1}, SC_nH_{2n+1}), were synthesized as shown in Scheme 1. The corresponding acid chlorides, obtained by treatment with thionyl chloride of the (E)-dipicH_2 acids (**VIII**), were reacted with SH_2 in THF, and the resulting precipitate was treated with diluted hydrochloric acid.

These acids were reacted with [Pd(acac)$_2$], giving the binuclear complexes **7** (Scheme 3)**.** The analytical results, the two

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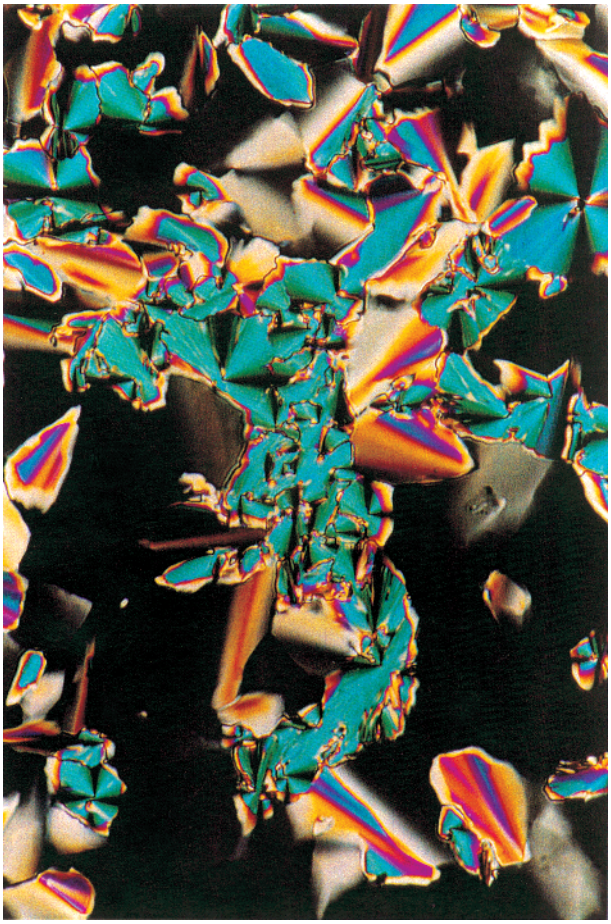
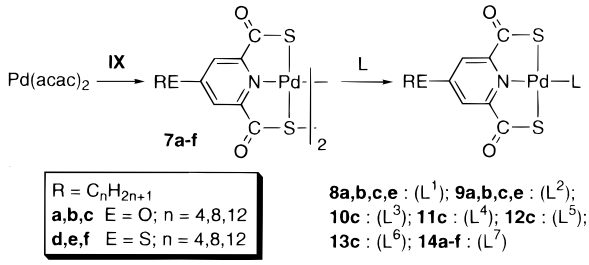


Figure 2. Microphotograph showing the texture of the columnar mesophase of **6f** formed at 105 °C on cooling the isotropic liquid.

Scheme 3



well-separated ν(C═O) bands in their IR spectra in the solid state, and the nonequivalence of the two pyridinic hydrogens observed in their ^{1}H NMR spectra, are consistent with the dimeric structure proposed. Reactions of **7** with 4-substituted pyridines (L^1−L^5) yielded the mononuclear compounds **8**−**12** with acceptable yields. Moreover, in contrast to the (E)-dipic complexes, the reactions with isocyanides (L^6, L^7) gave the stable isocyanide compounds **13** and **14**. It seems that the remarkable difference in stability between the O,N,O- and the S,N,S-pincers, when isocyanide is to be coordinated in the fourth position, is related to the harder nature of the Pd core in the O,N,O-complexes (π-back-donation is important in stabilizing the Pd−isocyanide bond) and to the high trans influence of the isocyanide ligand which induces a long Pd−N bond. This elongation very highly destabilizes the strained situation existing in the O,N,O-complexes involving short C−O distances, whereas it is compatible with the less strained S,N,S-complexes involving longer Pd−S distances.[9,10] The IR spectra of the isocyanide complexes show a ν(C≡N) absorption around 2215 cm^{-1}, at wavenumbers ca. 90 cm^{-1} higher than those for the free isonitriles, as reported for other palladium isocyanide compounds.[10,14] The ^{1}H NMR spectra of **8**−**14** show a singlet corresponding to two equivalent pyridinic hydrogens in a monomeric species, as proposed in Scheme 3.

The dinuclear derivatives **7** are not mesogenic. This is not surprising considering their unfavorable length-to-width ratio. However, they are useful precursors for the synthesis of the mononuclear calamitic molecules **8**−**14**. The mesogenic behavior of the latter is summarized in Table 1 and in Figure 1.

Comparing compounds with the same chain length for L^1−L^5 it can be seen that, with the unexpected exception of L^4,[15] each S,N,S derivative shows an important depression in the melting point relative to its O,N,O homologue. In most cases this change gives rise to mesomorphic behavior (S_C), but in the case of L^5 the mesomorphic behavior observed for the O,N,O compound (Col_h) is lost in the S,N,S homologue. Comparing the Pd(O,N,O) and Pd(S,N,S) fragments it seems reasonable to assume that substitution of O for the less electronegative S can produce a reduction in the polarity of each bond to Pd, and in the polarity of the fragment as a whole. Moreover, the acceptor character of this moiety toward the fourth ligand L^n can be substantially reduced. Both effects can cooperate to reduce the intramolecular interactions and depress the melting points. In the case of the columnar mesophases (L^5), where intense core-to-core interactions seem substantial for LC behavior after melting of the chains, the weakening of these core interactions suppresses the LC behavior, even at lower temperatures.[14] Thus, this is another example of columnar mesophases being suppressed when polar groups are replaced by less polar ones in the center of disklike molecules: the core polarity is decreased and the tendency to give columnar association of the cores diminishes.[16]

The complexes with stilbazole (L^1) undergo some decomposition in the transition to the isotropic liquid, possibly because of the high temperatures (ca. 260 °C) at which the clearing happens. The comparison between the alkylsulfanyl compound **8e** and its oxygen-containing analogue (compound **8b**) shows that, again, substitution of E = OC_nH_{2n+1} for E = SC_nH_{2n+1} causes an important decrease in the melting point while the clearing temperature is maintained, thus producing a broadening of the mesogenic range.

The complexes **9** containing the pyridine-imines L^2 have lower melting points than those of the corresponding derivatives with stilbazole (complexes **8**), but are only monotropic liquid crystals. The alkylsulfanyl derivative **9e** also shows a melting point lower than that of the alkoxy analogue **9b** and displays enantiotropic, instead of monotropic, liquid crystal behavior.

Neither the pyridinecarboxylate derivative **10c**, with just one phenyl ring, nor **11c** is mesogenic. A comparison can be made among **11c**, **8c**, and **9c** (phenyl pyridinecarboxylate, stilbazole, and (pyridylmethylene)aniline derivatives, respectively). The decreased planarity of the pyridinecarboxylate ligand (L^4) compared to the imine (L^2) or stilbazole (L^1) ligands, in concordance with X-ray structures of *trans*-stilbene,[17] benzylideneanilines[18] and phenyl benzoates,[19] might be a further difficulty for **11c** to form mesophases.

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(15) In fact, the temperature given for **5c** is a decomposition temperature whereas the temperature given for **11c** is a real melting point.
(16) Pegenau, A.; Göring, P.; Tschierske, C. *J. Chem. Soc., Chem. Commun.* **1996**, 2563.
(17) Young, W. R.; Aviram, A.; Cox, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3976.

Complex **13c**, with 4-isocyano-1-decyloxybenzene (L^6), is not a mesogen, but all of the biphenyl isocyanide compounds **14a**−**14f** (L^7) display liquid crystal behavior, indicating the necessity of an extended conjugated system. The biphenyl isocyanide complexes form more stable phases and exhibit better liquid crystal properties than the stilbazole or imine compounds. This may be related to the planarity and linearity of the biphenyl isocyanides which exhibit mesomorphism by themselves.[20] The biphenyl isocyanide compounds show both S_C and N phases when the pyridine rings have a short tail ($n = 4$), and only S_C phases when the terminal chain contains 8 or 12 carbon atoms. The S_C mesophases display two microscopic textures, *schlieren* and focal-conic. Both textures are formed directly on cooling from the isotropic liquid, but the *schlieren* texture is more abundant. The nematic phases were identified by the appearance of droplets and the formation of a typical nematic *schlieren* texture.

Again, the alkylsulfanyl derivatives **14d**−**f** exhibit lower transition temperatures and significantly wider mesophase ranges than their alkoxy analogue derivatives **14a**−**c**. Thus, this interesting and favorable influence seems to be quite constant in different types of derivatives.

Conclusions

The use of a series of new ligands, 4-substituted pyridine-2,6-dicarboxylic acids and 4-substituted pyridine-2,6-bis(thiocarboxylic) acids, allows the synthesis of O,N,O- and S,N,S-palladium complexes, respectively, that display liquid crystal properties. These ligands are remarkable as they permit building of a promesogenic core taking three coordination positions on the metal.

The O,N,O-pincers usually give rise to materials with very high melting points and decomposition is often observed. The substitution of O for the less electronegative S produces a reduction of the intramolecular interactions, and lower melting points (often producing the appearance of mesophases) are observed for the S,N,S-pincer complexes. The same effect (lowering of the melting points, often producing a broadening of the mesogenic range) is observed when alkyloxy chains are substituted by alkylsulfanyl.

Experimental Section

Literature methods were used to prepare $[Pd(\mu\text{-}OAc)_2]_3$,[21] $[Pd(acac)_2]$,[22] and the ligands L^1,[23] L^2−L^4,[24] L^6,[25] and L^7.[26] L^5 was synthesized as described for L^4 using 3,4,5-tridecyloxybenzylic alcohol.[27] Chelidamic acid was obtained from commercial sources and was used without further purification. C, H, and N analyses were carried out on a Perkin-Elmer 2400 microanalyzer. All of the new compounds gave satisfactory elemental analyses (Table S1, Supporting Information). IR spectra were recorded on a Perkin-Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. ^{1}H NMR spectra were recorded on Bruker AC-300 or ARX-300 MHz spectrophotometers. The textures of the mesophases were studied with a Leitz microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor and polarizers at a heating rate of approximately 10 °C min^{-1}. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin-Elmer DSC-7 operated at a scanning rate of 10 °C min^{-1} on heating. The apparatus was calibrated with indium (156.6 °C, 28.5 J g^{-1}) as standard, the samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen.

Only representative syntheses are described because they are very similar for the rest of the compounds in each series.

Dibutyl 4-Hydroxypyridine-2,6-dicarboxylate (II). Compound **II** was synthesized as reported for dibutyl pyridine-2,5-dicarboxylate using chelidamic acid (5.00 g, 24.8 mmol) as starting material,[28] except that the final product was chromatographed over SiO_2 using $CHCl_3$/EtOAc (5:1) as eluent. Yield 82%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.33 (s broad, 2H, $H^{3,5}$), 4.37 (t, $J = 6.5$ Hz, 4H, O−CH_2), 1.74 (m, 4H, O−CH_2−CH_2), 1.42 (m, 4H, O−CH_2−CH_2−CH_2−), 0.94 (t, 6H, O−CH_2−CH_2−CH_2−CH_3). IR (Nujol, cm^{-1}) ν(C═O): 1735.

Dibutyl 4-Octyloxypyridine-2,6-dicarboxylate (III). Compound **II** (5.00 g, 16.9 mmol) and K_2CO_3 (7.00 g, 50.6 mmol) were combined in DMF (30 mL) under a N_2 atmosphere. Octylbromide (3.26 g, 16.9 mmol) was added, and the mixture was heated to 65 °C. After 20 h, the reaction was cooled to room temperature and the DMF was distilled off. The residue was diluted with water and extracted into CH_2Cl_2. The combined organic extracts were washed with water, dried ($MgSO_4$), and evaporated. The product was purified on a silica gel column using $CHCl_3$/EtOAc (5:2) as eluent. Yield 87%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.72 (s, 2H, $H^{3,5}$), 4.37 (t, $J = 6.7$ Hz, 4H, O−CH_2), 4.10 (t, $J = 6.4$ Hz, 2H, O−CH_2), 1.80 (m, 4H, O−CH_2−CH_2−), 1.46 (m, 4H, O−CH_2−CH_2−CH_2−), 1.29 (overlapped peaks, 12H, −CH_2−), 0.95 (t, 6H, CH_3−), 0.85 (t, 3H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1751, 1723.

4-Octyloxypyridine-2,6-dicarboxylic Acid (VIIIb). Hydrolysis of dibutyl 4-octyloxypyridine-2,6-dicarboxylate **(IIIb)** (3.44 mmol) was achieved by boiling in aqueous ethanolic KOH for 2 h. After acidification with 5% HCl solution, the precipitate was washed with water and dried under vacuum; mp 156 °C. Yield 87%. Other (E)-dipicH_2 melted in the range 140−170 °C. ^{1}H NMR ($(CD_3)_2CO$, δ, ppm): 7.86 (s, 2H, $H^{3,5}$), 4.35 (t, $J = 6.5$ Hz, 2H, O−CH_2), 1.86 (m, 2H, O−CH_2−CH_2−), 1.52 (m, 2H, −O−CH_2−CH_2−CH_2), 1.35 (overlapped peaks, 8H, −CH_2−), 0.87 (t, 3H, CH_3−). IR (Nujol, cm^{-1}): ν(C═O) 1730.

Diethyl 4-Octylsulfanylpyridine-2,6-dicarboxylate (VIIe). Compound **VIIe** was synthesized as reported for diethyl 4-butylsulfanylpyridine-2,6-dicarboxylate,[11] from ammonium 2,6-dicarbethoxypyridine-4-thiolate (0.50 g, 1.8 mmol) and octylbromide (0.39 g, 2.0 mmol) in DMF (5 mL). The product was purified on a silica gel column using $CHCl_3$/EtOAc (1:1) as eluent. Yield 82%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.02 (s, 2H, $H^{3,5}$), 4.45 (q, $J = 7.2$ Hz, 4H, O−CH_2), 3.05 (t, $J = 7.3$ Hz, 2H, S−CH_2), 1.72 (m, 2H, S−CH_2−CH_2−), 1.43 (t, 6H, −CH_3), 1.27 (overlapped peaks, 10H, −CH_2−), 0.84 (t, 3H, CH_3−). IR (Nujol, cm^{-1}): ν(C═O) 1714.

4-Octylsulfanylpyridine-2,6-dicarboxylic Acid (VIIIe). Compound **VIIIe** was synthesized by hydrolysis of **VIIe** as described for **III**; mp 143 °C. Yield 84%. Other (E)-dipicH_2 melted in the range 120−165 °C. ^{1}H NMR ($(CD_3)_2CO$, δ, ppm): 8.16 (s, 2H, $H^{3,5}$), 3.28 (t, $J = 7.3$ Hz, 2H, S−CH_2), 1.87 (m, 2H, S−CH_2−CH_2−), 1.53 (m, 2H, S−CH_2−CH_2−CH_2−), 1.31 (overlapped peaks, 8H, −CH_2−), 0.86 (t, 3H, CH_3−). IR (Nujol, cm^{-1}): ν(C═O) 1749, 1725, 1703.

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4-Octyloxypyridine-2,6-bis(thiocarboxylic) Acid (IXb). The following is a modification of the procedure reported for pyridine-2,6-bis(thiocarboxilic) acid.[29] A mixture of **VIIIb** (1.00 g, 3.19 mmol) and $SOCl_2$ (30 mL) was refluxed under N_2 atmosphere, until the evolution of HCl gas ceased (ca. 2 h). After the mixture was cooled to room temperature, the excess of thionyl chloride was distilled off and the residue was dissolved in dry THF (30 mL). Pyridine (1.18 g, 14.9 mmol) was added, and SH_2 was bubbled for 4 h. The resulting yellow suspension was filtered, and the precipitate was washed with cold THF (2 × 5 mL), stirred with dilute HCl (20 mL), washed with water, and then vacuum-dried; mp 65 °C. Yield 60%. Other (E)-dptcH_2 melted in the range 70−80 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64 (s, 2H, $H^{3,5}$), 4.12 (t, J = 6.5 Hz, 2H, O−CH_2), 1.82 (m, 2H, O−CH$_2$−CH_2−), 1.42 (m, 2H, O−CH$_2$−CH$_2$−CH_2−), 1.30 (m, 8H, −CH_2−), 0.88 (t, 3H, CH_3−). IR (Nujol, cm^{-1}): ν(C═O) 1669; ν(S−H) 2539, 2511.

4-Octylsulfanylpyridine-2,6-bis(thiocarboxylic) acid (IXe). A mixture of **VIIIe** (0.70 g, 2.13 mmol) and $SOCl_2$ (6 mL) in toluene (30 mL) was refluxed until the evolution of HCl gas ceased (ca. 2 h). The solvent and the excess of thionyl chloride were distilled off, and the resulting diacid chloride was treated with SH_2 as described for **IXb**. Yield 61%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.92 (s, 2H, $H^{3,5}$), 3.06 (t, J = 7.3 Hz, 2H, S−CH_2), 1.80 (m, 2H, S−CH$_2$−CH_2−), 1.46 (m, 2H, O−CH$_2$−CH$_2$−CH_2−), 1.28 (overlapped peaks, 8H, −CH_2−), 0.89 (t, 3H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1681; ν(S−H) 2564, 2530.

Synthesis of 1b and 1e. [Pd(OAc)$_2$]$_3$ (0.72 g, 3.19 mmol) and **VIIIb** (1 g, 3.19 mmol) were stirred in acetonitrile (10 mL) for 24 h. The precipitate **1b** was collected on a frit, washed with acetonitrile (3 × 5 mL), and air-dried; mp 225 °C (dec). Yield 81%. ^{1}H NMR ($CDCl_3$, δ, ppm): dimer (43%), 7.30, 7.22 (s, 4H, H^3, H^5), 4.15 (m, 4H, OCH_2), 2.01 (s, 6H, NCCH_3); monomer (57%), 7.30 (s, 2H, $H^{3,5}$), 4.15 (m, 2H, OCH_2), 2.42 (s, 3H, NCCH_3). IR (Nujol, cm^{-1}): ν(C═O) 1696, 1674; ν(C≡N), δ(CH$_3$) + ν(C−C) 2325, 2297. **1e** was prepared similarly; mp 201 °C (dec). Yield 76%. Other complexes **1** melted in the range 190−230 °C with decomposition. ^{1}H NMR ($CDCl_3$, δ, ppm): dimer (38%), 7.55, 7.40 (s, 4H, H^3, H^5), 3.04 (m, 4H, SCH_2), 2.00 (s, 6H, NCCH_3); monomer (62%), 7.55 (s, 2H, H^{3,5}), 3.04 (m, 2H, SCH_2), 2.42 (s, 3H, NCCH_3). IR (Nujol, cm^{-1}): ν(C═O) 1682; ν(C≡N), δ(CH$_3$) + ν(C−C) 2323, 2295.

Synthesis of 2c. To a suspension of **1c** (0.05 g, 0.10 mmol) in dichoromethane, 4-decyloxy-4′-stilbazole (0.04 g, 0.12 mmol) was added and the mixture was stirred for 1 h. The pale yellow precipitate was collected on a frit, washed with acetonitrile (3 × 3 mL), and dried in a vacuum. Yield 44%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.27, 7.41 (AA′XX′, J = 6.7 Hz, 4H, NC$_5H_4$), 7.37, 6.88 (d, J = 16.3 Hz, 2H, −HC═CH−), 7.50, 6.92 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.35 (s, 2H, $H^{3,5}$), 4.13 (t, J = 6.5 Hz, 2H, OCH_2), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 1.82 (m, 4H, −CH_2), 1.57 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1663.

The following compounds were prepared similarly:

3c: Yield 88%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.47, 7.86 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 8.52 (s, 1H, −HC═N), 7.35, 6.93 (AA′XX′, J = 8.9 Hz, 4H, C$_6H_4$), 7.34 (s, 2H, $H^{3,5}$), 4.13 (t, J = 6.4 Hz, 2H, OCH_2), 3.98 (t, J = 6.5 Hz, 2H, OCH_2), 1.82 (m, 4H, −CH_2), 1.55 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1673.

4c: Yield 49%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.61, 7.99 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.37 (s, 2H, $H^{3,5}$), 4.40 (t, J = 6.8 Hz, 2H, OCH_2), 4.16 (t, J = 6.6 Hz, 2H, OCH_2), 1.83 (m, 4H, −CH_2), 1.56 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1726, 1666.

5c: Yield 91%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.69, 8.15 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.13, 6.95 (AA′XX′, J = 9.0 Hz, 4H, C$_6H_4$), 7.38 (s, 2H, $H^{3,5}$), 4.16 (t, J = 6.4 Hz, 2H, OCH_2), 3.96 (t, J = 6.5 Hz, 2H, OCH_2), 1.83 (m, 4H, −CH_2), 1.55 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1738, 1687.

6b: Yield 60%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.61, 8.00 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.36 (s, 2H, H^{3,5}), 6.62 (s, 2H, $H^{2,6}$ L^5), 5.31 (s, 2H, OCH_2), 4.15 (t, J = 6.5 Hz, 2H, OCH_2), 3.96 (m, 6H, OCH_2), 1.83 (m, 8H, −CH_2), 1.57 (m, 8H, −CH_2), 1.27 (overlapped peaks, 44H, −CH_2), 0.88 (m, 12H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1723, 1669.

6e: Yield 78%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.58, 7.99 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.59 (s, 2H, H^{3,5}), 6.60 (s, 2H, H^{2,6} L^5), 5.29 (s, 2H, OCH_2), 3.94 (m, 6H, OCH_2), 3.06 (t, J = 7.3 Hz, 2H, SCH_2), 1.72 (m, 8H, −CH_2), 1.45 (m, 8H, −CH_2), 1.25 (overlapped peaks, 44H, −CH_2), 0.86 (m, 12H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1733, 1678, 1662.

Synthesis of 7b. [Pd(acac)$_2$] (0.47 g, 1.53 mmol) and the acid **IXb** (0.5 g, 1.53 mmol) were stirred in $CHCl_3$ (30 mL) for 24 h. The orange solution was filtered through Celite and the solvent was removed under reduced pressure. The resulting orange solid was washed with acetone (3 × 5 mL), collected on a frit, and dried in vacuum; mp 219 °C (dec). Yield 66%. Other complexes **7** decomposed above 200 °C except **7a** and **7c** (both with n = 4) which seem thermally stable below 300 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.47, 7.24 (d, J = 2.9 Hz, 4H, H^3, H^5), 4.24 (t, J = 6.5 Hz, 4H, OCH_2), 1.90 (m, 4H, −CH_2), 1.57 (m, 4H, −CH_2), 1.30 (overlapped peaks, 16H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1689, 1636.

7e was prepared similarly. Yield 53%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.72, 7.48 (d, J = 2.3 Hz, 4H, H^3, H^5), 3.14 (t, J = 7.3 Hz, 4H, SCH_2), 1.80 (m, 4H, −CH_2), 1.52 (m, 4H, −CH_2), 1.30 (overlapped peaks, 16H, −CH_2), 0.87 (m, 6H, −CH_3). IR (Nujol, cm^{-1}) ν(C═O): 1689, 1634.

Synthesis of 8b. To a solution of **7b** (0.05 g, 0.06 mmol) in dichloromethane (20 mL) was added 4-decyloxy-4′-stilbazole (0.05 g, 0.16 mmol) and the mixture was stirred for 17 h. The solvent was evaporated off, and the yellow residue was washed with diethyl ether (3 × 5 mL), filtered to collect the product, and dried in a vacuum. Yield 63%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.47, 7.41 (AA′XX′, J = 6.5 Hz, 4H, NC$_5H_4$), 7.35, 6.84 (d, J = 16.4 Hz, 2H, −HC═CH−), 7.49, 6.92 (AA′XX′, J = 8.7 Hz, 4H, C$_6H_4$), 7.27 (s, 2H, $H^{3,5}$), 4.17 (t, J = 6.5 Hz, 2H, OCH_2), 4.00 (t, J = 6.5 Hz, 2H, OCH_2), 1.80 (m, 4H, −CH_2), 1.60 (m, 4H, −CH_2), 1.28 (overlapped peaks, 20H, −CH_2), 0.87 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1627.

The following compounds were prepared similarly:

8e: Yield 88%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.46, 7.41 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.35, 6.84 (d, J = 16.3 Hz, 2H, −HC═CH−), 7.49, 6.92 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.54 (s, 2H, $H^{3,5}$), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 3.07 (t, J = 7.2 Hz, 2H, SCH_2), 1.76 (m, 4H, −CH_2), 1.45 (m, 4H, −CH_2), 1.26 (overlapped peaks, 20H, −CH_2), 0.87 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1620.

9b: Yield 67%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.71, 7.87 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 8.49 (s, 1H, −HC═N−), 7.33, 6.95 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.26 (s, 2H, $H^{3,5}$), 4.16 (t, J = 6.4 Hz, 2H, OCH_2), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 1.81 (m, 4H, −CH_2), 1.58 (m, 4H, −CH_2), 1.27 (overlapped peaks, 20H, −CH_2), 0.87 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1627.

9e: Yield 81%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.70, 7.87 (AA′XX′, J = 6.5 Hz, 4H, NC$_5H_4$), 8.49 (s, 1H, −HC═N−), 7.33, 6.94 (AA′XX′, J = 8.7 Hz, 4H, C$_6H_4$), 7.53 (s, 2H, $H^{3,5}$), 3.98 (t, J = 6.5 Hz, 2H, OCH_2), 3.07 (t, J = 7.3 Hz, 2H, OCH_2), 1.75 (m, 4H, −CH_2), 1.59 (m, 4H, −CH_2), 1.27 (overlapped peaks, 20H, −CH_2), 0.87 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1630, 1622.

10c: Yield 82%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.83, 7.99 (AA′XX′, J = 6.7 Hz, 4H, NC$_5H_4$), 7.26 (s, 2H, $H^{3,5}$), 4.38 (t, J = 6.7 Hz, 2H, OCH_2), 4.16 (t, J = 6.5 Hz, 2H, OCH_2), 1.80 (m, 4H, −CH_2), 1.58 (m, 4H, −CH_2), 1.26 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1719, 1632.

11c: Yield 89%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.90, 8.15 (AA′XX′, J = 6.6 Hz, 4H, NC$_5H_4$), 7.29 (s, 2H, $H^{3,5}$), 7.10, 6.94 (AA′XX′, J = 9.2 Hz, 4H, C$_6H_4$), 4.15 (t, J = 6.4 Hz, 2H, OCH_2), 3.96 (t, J = 6.5 Hz, 2H, OCH_2), 1.80 (m, 4H, −CH_2), 1.57 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1739, 1631, 1615.

12c: Yield 86%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.82, 8.00 (AA′XX′, J = 6.7 Hz, 4H, NC$_5H_4$), 7.25 (s, 2H, $H^{3,5}$), 6.59 (s, 2H, $H^{2,6}$ L^5), 5.28

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(s, 2H, OCH_2), 4.15 (t, J = 6.5 Hz, 2H, OCH_2), 3.96 (m, 6H, OCH_2), 1.80 (m, 8H, −CH_2), 1.45 (m, 8H, −CH_2), 1.26 (overlapped peaks, 52H, −CH_2), 0.87 (m, 12H, −CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1733, 1620.

13c: Yield 44%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.42, 6.92 (AA′XX′, J = 9.0 Hz, 4H, C_6H_4), 7.31 (s, 2H, $H^{3,5}$), 4.18 (t, J = 6.5 Hz, 2H, OCH_2), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 1.82 (m, 4H, −CH_2), 1.57 (m, 4H, −CH_2), 1.27 (overlapped peaks, 28H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2212; ν(C═O) 1632.

14b: Yield 83%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64, 7.53 (AA′XX′, J = 8.4 Hz, 4H, C_6H_4), 7.50, 6.98 (AA′XX′, J = 8.6 Hz, 4H, C_6H_4), 7.31 (s, 2H, $H^{3,5}$), 4.18 (t, J = 6.4 Hz, 2H, OCH_2), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.82 (m, 4H, −CH_2), 1.56 (m, 4H, −CH_2), 1.27 (overlapped peaks, 20H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2213; ν(C═O) 1626.

14e: Yield 41%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.65, 7.54 (AA′XX′, J = 8.5 Hz, 4H, C_6H_4), 7.51, 6.99 (AA′XX′, J = 8.7 Hz, 4H, C_6H_4), 7.59 (s, 2H, $H^{3,5}$), 4.00 (t, J = 6.4 Hz, 2H, OCH_2), 3.10 (t, J = 7.3 Hz, 2H, SCH_2), 1.77 (m, 4H, −CH_2), 1.57 (m, 4H, −CH_2), 1.28 (overlapped peaks, 20H, −CH_2), 0.88 (m, 6H, −CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2218; ν(C═O) 1630.

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Supporting Information Available: Table S1 including the microanalysis and yield of the (E)-dipic and (E)-pdtc complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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